ONONDAGA LAKE BASELINE MONITORING
BOOK 2 WORK PLAN
FISH, INVERTEBRATE, AND LITTORAL WATER MONITORING FOR 2008

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September 2008

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AMP	Ambient monitoring program
C/f	Catch per unit effort
DOH	New York State Department of Health
DUSR	data usability and summary report
JSA	Job Safety Analysis
NYSDEC	New York State Department of Environmental Conservation
OCDWEP	Onondaga County Department of Water Environment Protection
QAPP	Quality Assurance Project Plan
PCB	Polychlorinated Biphenyl
PDI	Pre-Design Investigation
PRG	Preliminary Remediation Goal
RI	Remedial Investigation
ROD	Record of Decision
SMU	Sediment Management Unit
SOP	Standard Operating Procedures
SSP	Subcontractor Safety Plans
SUNY-ESF	State University of New York College of Environmental Science and Forestry
USEPA	United States Environmental Protection Agency

SECTION 1

INTRODUCTION

This work plan describes the samples and data to be collected in 2008 during implementation of the biota (fish and benthic macroinvertebrates) monitoring defined in the draft Baseline Monitoring Scoping Document for the Onondaga Lake Bottom Subsite (Parsons 2008). This work plan describes the objectives, sample locations, sample and data gathering methods, and sample analyses to be performed on Onondaga Lake biota as part of baseline monitoring. A detailed description of the field and analytical methods and quality assurance program supporting the field work is described in the Quality Assurance Project Plan (QAPP), which is provided in Appendix A of this work plan. Baseline monitoring is planned to be conducted annually until the start of remediation. The baseline monitoring work scope beyond 2008 has not yet been determined. Baseline monitoring changes may be made in future years based on results available at that time from completed baseline monitoring efforts. In subsequent years, it is anticipated that any changes to the field or analytical program described in this work plan will be documented by addenda to this work plan.

Various biota monitoring programs have been conducted on Onondaga Lake over the past several years by various entities and these programs are summarized in the Baseline Scoping Document (Parsons 2008). The remedial investigation for the lake included fish and macroinvertebrate tissue sampling and community composition from locations around the lake in 1992 and 2000 (TAMS Consultants 2002). The New York State Department of Environmental Conservation (NYSDEC) analyzes tissue samples annually to evaluate mercury and approximately biannually to evaluate organic contaminants in adult sport fish (primarily largemouth and smallmouth bass) for the New York State Department of Health (DOH) fish consumption advisory. The Onondaga County Department of Water Environment Protection (OCDWEP) has assessed fish community composition annually since 1998 and macroinvertebrate community composition every five years since 2000 as part of its ambient monitoring program (AMP) to assess municipal wastewater discharges to the lake (EcoLogic,2007). Researchers at the State University of New York College of Environmental Science and Forestry (SUNY-ESF) have conducted periodic assessments of fish population size and migration patterns, as well as macrophyte surveys and macroinvertebrate community analysis. The baseline monitoring described in this work plan builds on previous efforts so that a consistent database can be maintained.

1.1 OBJECTIVES

The primary purpose of baseline monitoring is to develop a database of existing conditions for comparison with post-remediation conditions. As described in the Baseline Monitoring

Scoping Document (Parsons 2008), the baseline monitoring for Onondaga Lake has three objectives:

- Establish a comprehensive description of baseline chemical conditions prior to remediation to assess remedy effectiveness and to facilitate remedy design;
- Provide additional data for future understanding of remedy effectiveness in achieving remediation goals for Onondaga Lake ; and
- Provide habitat-related information.

The third general objective, provide habitat related information, is being addressed by the Habitat Technical Working Group. Much of the data needs for habitat are related to design of the habitat layer for a future isolation cap to be placed within portions of the lake to be remediated as part of the lake remedy specified in the 2005 Record of Decision (NYSDEC and USEPA 2005). The habitat-related sampling program is being developed as part of the Phase IV Pre-Design Investigation (PDI) and includes fish nest characterization, macrophyte surveys, and habitat substrate and colonization evaluation to be preformed by the State University of New York College of Environmental Science and Forestry (SUNY-ESF) located in Syracuse, NY.

Specific objectives for the biota baseline monitoring include:

- Provide basis to measure achievement of Preliminary Remediation Goal 2 (PRG 2) from the 2005 Record of Decision which is to achieve CPOI concentrations in fish tissue that are protective of humans and wildlife that consume fish. PRG 2 includes a mercury concentration of 0.2 mg/kg in fish tissue (fillets) for protection of human health based on the reasonable maximum exposure scenario, USEPA's methylmercury National Recommended Water Quality criterion for the protection of human health for the consumption of organisms of 0.3 mg/kg in fish tissue, and a mercury concentration of 0.14 mg/kg in fish (whole body) for protection of ecological receptors; and
- Assess biological factors that may contribute to variability in fish mercury concentrations.

Biota monitoring described herein addresses the need to document contaminant body burdens in Onondaga Lake biota prior to remedial action and to provide the data needed to support development of the remedial action monitoring. Establishing baseline conditions in biota is necessary to evaluate trends over time (e.g., year-to-year variability in fish tissue) as a function of the remedy, as well as other factors that can reasonably be expected to impact achievement of the remedial action objectives and remediation goals (see Parsons 2008). Such factors can be beyond the scope of the lake remedy (e.g., remediation of Honeywell upland sites that contribute mercury to the lake) or even beyond the control of Honeywell (e.g., food web dynamics in the lake), but can have significant impact on the outcome of the remedy. Data

collection efforts to fulfill this program objective involve sampling of sport and prey fish, as well as other aquatic biota.

In addition to mercury concentrations in prey items, food web structure and fish population and community composition are important factors that can influence mercury concentrations in fish. The structure of the fish community and the number of trophic levels represented influence mercury bioaccumulation throughout the food web because mercury concentrations increase with trophic level. Understanding the dynamics of the food web is important to gain an understanding of how mercury is bioaccumulating and resulting in exposure to upper level predators. Thus, baseline monitoring will include analysis of the food web (by analysis of fish gut contents and invertebrate tissue and community composition) and an assessment of fish population and community composition.

SECTION 2

SAMPLING DESIGN AND APPROACH

The biota monitoring objectives described above will be met by performing the following sampling and analysis activities:

- Fish tissue sampling and analysis; and
- Sampling and analysis of other aquatic biota (aquatic macroinvertebrates). Zooplankton sampling and analysis is part of the Book 1 baseline monitoring work plan being conducted by Upstate Freshwater Institute.

This section describes the sampling design and rationale. A summary of the sampling activities is provided in Table 1. A scientific collector's license has been obtained from NYSDEC for this biota collection work scope.

2.1 FISH TISSUE SAMPLING AND ANALYSIS

Based on the results from the remedial investigation (RI), it is not anticipated that chemical concentrations in adult sport fish species will vary significantly within the lake. Many sport fish species will utilize multiple locations within the lake as well. However, the lake remedy includes more sediment remediation in the southern half of the lake than in the northern half; therefore, 2008 baseline monitoring will include adult sport fish samples from both basins to assess the significance of localized variability in fish tissue concentrations. Prey fish samples, on the other hand, will be analyzed by location, since these fish tend to be less mobile and may reflect more localized conditions within the lake. The rationale for selection of station location, frequency, species, and sample numbers is provided below.

Station Locations Fish sampling locations will be dispersed among eight locations around the lake, coinciding with historical tissue sampling locations occupied during the RI, as well as sampling locations occupied by the OCDWEP (see Figure 1). Both adult sport fish and prey fish will be sampled from the eight sampling locations listed below:

- Maple Bay and Willow Bay at the lake outlet (OL-STA-50057);
- The mouth of Ninemile Creek (in Sediment Management Unit 4 referred to as SMU 4) (OL-STA-40212);
- Wastebeds 1 through 8 along the western shoreline (OL-STA-30093);
- The portion of SMU 2 southeast of Tributary 5A and the westernmost portion of SMU 1 (OL-STA-20158);

- The easternmost portion of SMU 1 and SMU 7 (OL-STA-70124);
- SMU 6 south of the mouth of Ley Creek (OL-STA-60225);

Near the railroad bridge south of the Village of Liverpool along the eastern shoreline (OL-STA-50059); and

- Adjacent to the marina along the eastern shoreline in the Village of Liverpool (OL-STA-50058).

Sampling Frequency Fish sampling will take place during late July and August to coincide with previous collections, using standard sampling methods including electroshocking, netting, and angling (see Table 1).

Species Selection Fish collections will consist of four adult sport fish species including smallmouth bass (*Micropterus dolomieu*), brown bullhead (*Ameiurus nebulosus*), walleye (*Sander vitreum*), pumpkinseed sunfish (*Lepomis gibbosus*), and prey fish from the minnow family (Cyprinidae), excluding carp (*Cyprinus carpio*) and goldfish (*Carassius auratus*). Carp and goldfish are not included in prey fish collection due to their large size. Exact species of prey fish will be determined based on availability which may vary from year to year, but will likely include the two most common species currently captured in the lake, banded killifish (*Fundulus diaphanus*) and golden shiner (*Notemigonus crysoleucas*) as well as alewife (*Alosa pseudoharengus*) less than 180 mm total length. Adult sport fish and prey species have been selected to cover a range of trophic levels including top level piscivores (smallmouth bass, walleye), benthic invertivores (bullhead), invertivores (pumpkinseed), and planktivores (golden shiner, banded killifish).

Sample Numbers For adult sport fish, each sample will consist of a single adult sport fish. These fish will be collected from eight locations to yield a maximum of 50 individual fish for each of the four adult sport fish species for a total of 200 adult sport fish (see Table 1). A reasonable effort will be made to capture the targeted number of adult sport fish at each sampling location; determination of the effort will be discussed with NYSDEC while the sampling is being conducted. Although the results from the RI indicated that fish tissue concentrations did not vary significantly within the lake, baseline monitoring in 2008 will include adult sport fish samples from both the northern and southern halves of the lake to assess the significance of localized variability in fish tissue concentrations. If possible, adult sport fish will be evenly distributed among all the eight adult sport fish sampling locations. The target for adult sport fish sampling will be six to seven individual fish from each species and each location.

For prey fish sampling, a maximum of five composite samples will be collected from each of the eight locations, for a total of 40 composites. Reasonable attempts will be made to include at least two alewife composites from each location Composites will be comprised of 10 or 15 prey fish per sample, depending on weight. The number of fish samples is similar to the numbers collected during the remedial investigation, as well as what is currently sampled by

NYSDEC and OCDWEP for New York State Department of Health fish consumption advisories. Sample numbers will be sufficient for statistical comparison while still targeting a reasonable number of fish that can be collected over a two to three week period. Potential statistical tests include comparison of tissue concentrations with length and weight by species, assessment of condition factor (i.e., length-weight factor), population estimates, diversity indices for fish and invertebrate communities, and analysis of variance for comparison of contaminant concentrations between stations as well as between the north and south basins.

Tissue Analysis Individual adult sport fish fillet samples and tissue plugs will be collected from each adult sport fish for analysis of the comparability of mercury concentration in the two tissue types and comparison to site remediation goals. Whole body composite samples will be collected for prey species for comparison to site remediation goals. Tissue plugs will be evaluated in 2008 for use in reducing fish mortality in future years due to continued harvesting while still collecting the required tissue samples for mercury analysis. Collection of fillet samples from all adult sport fish will result in 100 percent mortality. While the use of tissue plugs in place of fillet samples will not result in eliminating mortality, it likely will be reduced significantly. Previous studies have shown limited mortality and sublethal effects in laboratory studies, as well as from field studies (Baker et al. 2004). If results from the comparison of the two methods indicate suitability of tissue plugs, discontinuation of fillet samples will be considered for subsequent years of adult sport fish sampling for mercury. The typical sealant applied to a fish tissue plug wound is an antibiotic salve that should not pose any health concerns to future anglers.

Each of the adult sport fish fillet/tissue plugs and prey fish composite samples will be analyzed for total mercury. In addition, a subset of adult sport fish fillet samples (12 per species for a total of 48 samples) will be analyzed for polychlorinated biphenyls (PCBs), DDT and its metabolites, hexachlorobenzene, and lipids. Dioxins/furans will be analyzed in five samples from each of the species of adult sport fish fillet samples for a total of 20 samples. PCBs, DDT and its metabolites, hexachlorobenzene, and lipids will also be analyzed in a subset of prey fish (10 composite samples) collected during the summer sampling event. Samples selected for analysis of PCBs, DDT and its metabolites, hexachlorobenzene, and lipids will be representative of the various locations in the lake, including Sediment Management Unit (SMU) 2 and SMU 4. PCBs and dioxins/furans are bioaccumulative and are documented in the Record of Decision, along with mercury as the primary sources of human health risk from consumption of lake fish. Soxhlet extraction will be used for organic analysis extractions.

Conversion factors used in the Onondaga Lake baseline ecological risk assessment (BERA; TAMS, 2002; Section 8) to adjust mercury, PCB, and DDT and metabolite concentrations in fillets to whole-body concentrations will be applied for comparison of adult sport fish data to target tissue levels that are protective of ecological receptors. Note that hexachlorobenzene and dioxins/furans were not identified as risk drivers for ecological receptors and do not have target tissue levels for ecological receptors (see Table 7 in the 2005 Record of Decision); therefore

conversion of hexachlorobenzene and dioxin/furan fish fillet results to whole body concentrations is unnecessary.

2.2 SAMPLING AND ANALYSIS OF OTHER AQUATIC BIOTA

Mercury concentrations in fish collected from Onondaga Lake and other systems vary from year to year, from species to species, and even within species as a function of age. Because uptake of methylmercury through the diet accounts for more than 90 percent of total methylmercury uptake in fish (Weiner et al. 2003), sampling and analysis by Honeywell of other aquatic biota will focus on the biological component of variability in fish mercury concentrations. Diet (rather than, for example, direct uptake from water or methylmercury production in the slime layer) accounts for the vast majority of methylmercury uptake in fish. Variability in fish mercury concentrations will be assessed by performing fish tissue sampling as described in Section 2.1. Concentrations of mercury and methylmercury in sediment and water, which clearly impact mercury concentrations in biota, are being assessed through sediment and water sampling activities described in the Baseline Monitoring Scoping Document (Parsons 2008).

The purpose of sampling other aquatic biota in Onondaga Lake is to provide baseline information on mercury in these other organisms in order to understand how they influence mercury concentrations in fish. The primary biological factors that influence mercury concentrations in fish are:

- mercury concentrations in and abundance of fish prey;
- food web structure (e.g., primary prey items for various species, number of trophic levels); and
- fish community composition.

Zooplankton are important fish prey and are a key step in mercury bioaccumulation from water to fish. Collection of zooplankton samples for mercury and community analysis is being conducted by Honeywell as a separate part of the baseline monitoring effort for 2008 (UFI and Syracuse University, 2008).

2.2.1 Macroinvertebrate Tissue Collection, Community Composition, and Abundance

Macroinvertebrates (benthic macroinvertebrates and zebra mussels [*Dreissena polymorpha]*) also are important fish prey organisms and are a key step in mercury bioaccumulation from sediment (and possibly water) to fish. Benthic macroinvertebrates were collected during the remedial investigation in 1992 and 2000 for both community analysis and mercury body burden. They also are being collected every five years (beginning in 2000) for community analysis by

OCDWEP. The purpose of analyzing mercury levels in macroinvertebrates is to provide additional data that will aid in the future in understanding remedy effectiveness.

Zebra mussels, an exotic species native to the Caspian Sea region of Asia, have recently colonized in Onondaga Lake. These mussels have the potential to affect Onondaga Lake water quality and water clarity, particularly within the lake's littoral zones. Zebra mussels also provide a potential food source to benthivorous fish. Both OCDWEP and UFI have been monitoring zebra mussel populations in the lake and the adjacent Seneca River. These organisms filter plankton from the water column to meet their energy needs and represent a potential vector for mercury bioaccumulation.

Phytophilous macroinvertebrates have not been sampled in the past; however, due to the increased macrophyte coverage, these will be collected to assess community composition and the relationship with plant species composition for this program. Mercury analysis of phytophilous invertebrates will be considered in future years for baseline monitoring.

The rationale for macroinvertebrate station locations, frequency, taxa, and sample numbers are provided below.

Station Locations Benthic and phytophilous macroinvertebrates and zebra mussels will be collected from 18 locations around the lake. These locations are distributed around the perimeter of the lake in water depths of 1.0 to 1.5 m to be consistent with previous benthic macroinvertebrate sampling efforts in Onondaga Lake and to represent a range of sediment mercury concentrations while still targeting samples within each nearshore portion of the lake. In addition, benthic macroinvertebrate samples will be collected from two SMU 8 locations adjacent to the littoral zone SMUs – one in the South Basin and one in the North Basin to assess community composition. Plants are not located in SMU 8, so phytophilous invertebrates are not available in SMU 8 to collect.

Sampling Frequency Sampling will take place in 2008 in mid-summer (August), to coincide with previous collections and peak plant biomass (see Table 2). One additional sampling of macroinvertebrates at the littoral locations will be conducted in October-November following fall turnover to assess if methylmercury concentrations increase in benthic invertebrates following release of methylmercury from the hypolimnion.

Taxa Selection Macroinvertebrate sampling for tissue analysis will target three taxa: Amphipoda, Chironomidae, and zebra mussels. These taxa are commonly found in the lake and are preyed upon by fish species. Therefore, they represent an important component of the aquatic food web. While the zebra mussel represents a single filter-feeding species and the amphipods represent a single genus that scavenges on surface matter, Chironomidae represent a family with approximately 30 species represented in the lake. This family also includes several different feeding strategies including detritus feeders, herbivores, and predators that may result in

different exposure to methyl mercury. Currently, the Chironomidae family in Onondaga Lake is dominated by the genus *Chironomus*, which is a detritus feeder.

Sample Number A separate composite sample will be collected from each of the Amphipoda, Chironomidae, and zebra mussels taxa at each of the 18 lake perimeter locations and analyzed for total mercury and methyl mercury. For the benthic and phytophilous community and abundance analyses, five replicates per location will be collected (see Figure 2). The number of samples and target taxa are comparable to sampling conducted as part of the remedial investigation. The number of samples will allow for comparison among locations, while still targeting a reasonable number of organisms that can be collected over a two week period.

2.2.2 Food Web Structure and Fish Community Assessment

In addition to mercury concentrations in prey items, food web structure, fish population, and community composition are important factors that can influence mercury concentrations in fish. As indicated in Section 1.1, understanding the dynamics of the food web is important to gain an understanding of how mercury is bioaccumulating and resulting in exposure to upper level predators. To further assess the food web structure and mercury cycling in Onondaga Lake, the 2008 baseline monitoring will include: 1) sampling and analysis of fish gut contents; and 2) an assessment of fish population and fish community composition..

Fish population estimates will be evaluated for several adult sport fish species including largemouth and smallmouth bass, pumpkinseed and bluegill sunfish, and bullhead; using a mark-recapture technique. While catch per unit effort (C/f) can predict relative abundance of species with less sampling effort, it cannot provide an indication of the absolute abundance of species. Obtaining population estimates of several of the dominant sport fish provides an estimate of abundance, which then can be used to develop a relationship between C/f and population density. Since this is a labor intensive effort, the population estimate will only be completed in the first year of baseline monitoring. The population estimates will be compared to Onondaga County's C/f sampling to obtain a relationship between C/f and absolute abundance. In subsequent years, this relationship can be used to estimate population densities based on the County C/f data.

Fish species that will be analyzed for stomach contents include smallmouth and largemouth bass, bluegill and pumpkinseed sunfish, and brown bullhead. Fifty fish per species will be targeted over the course of the summer for stomach content analysis. The stomach contents of individual fish larger than 150 mm in length will be evaluated on the sampling boat using gastric lavage to assess the various sources of prey consumed. Fish smaller than 150 mm in length will be preserved and brought back to the laboratory for dissection of stomach contents. Prey fish submitted for tissue analysis will not be sampled for stomach contents. This analysis will provide an estimate of the trophic structure within the lake and facilitate understanding of the lake's food web.

Fish community will be assessed from at least eight locations around the lake from the same locations to be sampled for tissue analysis. Fish sampling for community assessment will require use of a variety of methods to fully assess species present in the lake. Depending on the species and the size, fish are susceptible to collection using different types of collection gears. Sampling at all locations will include seining, gill netting, trap netting, pop netting, and electrofishing. The Fish Collection SOP SB-1 in Appendix A describes these procedures. Fish community assessments will be conducted several times from May through October to account for species shifts due to changes in water temperature and dissolved oxygen concentrations, as well as fish immigration and emigration. These data also will be used to assess the reproductive success of several sport fish species.

2.3 LITTORAL WATER SAMPLING

The purpose of littoral water sampling is to understand the movement of mercury/methylmercury generated from the hypolimnion during and following fall turnover into the surface waters of the lake for assessing exposure to biota. Littoral water samples will be collected at six fish sampling locations within the littoral zone: four locations in the south basin and two locations in the north basin. See SOP SB-9 in Appendix A for sampling procedures. The littoral zone water samples will be collected during three events - one event prior to fall turnover (August) and two events following fall turnover (mid-October to early November). Every reasonable effort will be made to collect these littoral water samples on the same day that deep basin water samples are collected by Upstate Freshwater Institute as part of the Book 1 baseline monitoring effort. These samples will be analyzed for total mercury and for methylmercury (unfiltered).

SECTION 3

METHODS

3.1 FISH SAMPLING

Adult sport fish and prey fish sampling and analysis for mercury will be conducted in late July and August. Adult sport fish sampling will target four species and prey sampling will focus on species from the minnow family (Cyprinidae) and alewife.

3.1.1 Tissue Collection

Fish will be collected from each station using a variety of sampling methods. Standard sampling methods including gill and trap netting, seining, electroshocking, and angling will be used to collect target species. The edible portions for humans and wildlife will be monitored; skin-on fillets (or tissue plugs) for smallmouth bass, bullhead, walleye, and pumpkinseed and whole body composites (10 or 15 individuals each) for prey fish species. Collections of adult sport fish will target the legal or edible size; greater than 305, 200, 380, and 130 mm (or greater than 12, 8, 15, and 5 inches in total length, for smallmouth bass, bullhead, walleye, and pumpkinseed, respectively). Fish sampling will be conducted within a targeted size range to reduce variability in concentrations due to size, with maximum total length of 500 mm (20 inches) for bass, 350 mm (14 inches) for bullhead, 575 mm (23 inches) for walleye, and 200 mm (8 inches) for pumpkinseed. Minimum adult sport fish sizes are based on minimum size limits from NYSDEC regulations for bass, bullhead, and walleye; while for pumpkinseed, the minimum size was based on minimum tissue requirements. Maximum sizes are based on OCDWEP data and size ranges generally sampled within the lake, with the largest fish excluded.

Fish will be handled according to standard procedures developed by NYSDEC (NYSDEC 2000) and documented in the Standard Operating Procedures (SOP) for Fish Sampling (Appendix A). Preparation of standard fillets for bullhead will include skinning, while fillets for other fish types will be skin-on fillets. For each specimen, the date of collection, a unique identification number or code, the station identification, genus and species, total length in millimeters (to nearest mm), weight in grams (to nearest gram), sex (if possible), and method of collection will be recorded on a Fish Collection Field Log (see Figure 3). The same information also will be collected for composited fish, as well as the number of individuals within the composite (target 10 or 15, depending on size). Any observed external abnormalities also will be noted on the Field Log. Fish samples will be wrapped in aluminum foil, labeled appropriately, and placed in a resealable plastic bag. Chain-of-custody forms will be maintained and processed samples kept cool (below 4^{o}C) and shipped overnight to the analytical laboratory.

Scale samples will be collected from each adult sport fish from the appropriate region on the body based on Devries and Frie (1996). For brown bullhead, a pectoral spine will be removed for age estimation. Scales or spines will be placed into a coin envelope labeled with species, total length, weight, location, date, and unique identification number. Age estimates will be determined in the laboratory from scale samples based on the procedures in Appendix A.

3.1.2 Gut Analysis

A subset of individuals (50 per species) collected during tissue sampling, as well as community assessment sampling, will be evaluated for gut contents. For samples being collected for adult sport fish tissue analysis, stomach contents will be sampled by gastric lavage prior to processing. Stomach contents will be placed into a labeled vial in 75 percent ethanol for subsequent identification in the laboratory. For smaller individuals (less than 150 mm total length) not collected for tissue analysis, the fish will be sacrificed, placed in a labeled jar with 75 percent ethanol, and stomach contents removed and identified in the laboratory. Detailed procedures for gut analysis are included in the Fish Sampling SOPs (Appendix A). Stomach contents will be identified to lowest taxonomic order reasonably achievable with abundance of each reported. A field log will be maintained for fish gut samples.

3.1.3 Fish Community Assessment

The density and distribution of adult sport fish will be assessed during the spring, summer, and fall using electroshocking and netting to determine overall community structure. Density and distribution of prey fish will be sampled using seine nets and popnets every three weeks from eight locations around the lake from late June to mid October (Figure 1). Seining will be conducted in relatively macrophyte-free areas, while popnet sampling will be conducted within the macrophyte beds. Fish will be identified to species, measured for total length in mm and weighed to the nearest gram prior to being released. A subset of prey fish will be sacrificed and preserved in 75 percent ethanol for stomach content analysis, as described above. Details of the sampling procedures are described in the SOP (Appendix A). For adult sport fish, a maximum of 10 scale samples will be collected within each 25 mm (1 inch) size class (e.g., 200-225 mm; 225-250 mm, 250-275 mm), for each sport fish species for age and growth analysis.

3.1.4 Adult Sport Fish Population Assessment

Adult sport fish will be assessed during a two week period in late June to early July to estimate population densities of several species. Fish will be sampled from locations around the lake and individuals of largemouth and smallmouth bass, pumpkinseed and bluegill sunfish, brown bullhead, and yellow perch will be marked with a fin clip (for smaller individuals) or a uniquely numbered t-bar anchor floy tag (for larger individuals) during sampling. Fish will be measured for total length in mm prior to release. Fish marking will occur during the first week in an intensive sampling effort to mark as many fish possible. During the second week a second

intensive effort will be conducted to assess the number of fish recaptured. Population estimates will be calculated using the Chapman estimate (Seber, GAF, 1982):

$$\hat{N} = ((M+1)(C+1))/(R+1)$$

Where:

N = population estimate

M = number of fish marked and released

C = resample capture size (includes marked and unmarked fish)

R = number of marked fish recaptured

The variance of the Chapman estimate can be approximated by:

$$\hat{V}(N) = [(M+1)(C+1)(M-C)(C-R)/(R+1)^2(R+2)]-1$$

3.1.5 Water Quality Parameters

During fish sampling activities, water quality parameters will be measured on a daily basis with a calibrated YSI or similar meter. Temperature, dissolved oxygen, conductivity, and pH will be recorded in approximately 1 m of water at each station prior to sampling.

3.1.6 Fish Laboratory Analyses

Fish samples collected for tissue analysis (including adult sport fish tissue plugs) will be submitted to the analytical laboratory for total mercury analysis in accordance with the methodologies presented in the QAPP. As indicated in Section 2.1, a subset of the adult sport fish tissue samples (12 per species for a total of 48 samples) from each basin also will be analyzed for total PCBs (Aroclors), DDT and its metabolites, hexachlorobenzene, and lipids. A second subset of five adult sport fish tissue samples from each of the four sport fish species to be sampled will be analyzed for dioxins/furans. A subset of prey fish samples will be analyzed for PCBs, DDT and its metabolites, hexachlorobenzene, and lipids as well. Samples will be processed by experienced personnel at the laboratory and prepared tissues, standard skin-on fillets (except for bullhead), tissue plugs, or whole bodies, will be frozen until analyzed. Dry and wet weight of the laboratory sample (whole body or fillet) will be measured. Each sample (individual or composite) will be identified by a unique sample number. If possible, sex of individual adult sport fish will be determined in the analytical laboratory during processing.

Standard fillets and tissue plugs will be processed according to procedures in the SOP (Appendix A). Sample extracts for mercury analysis and homogenized samples from fish tissue samples will be held (frozen at below -10°C for extracts and below-18°C for tissue) for one year from sample collection.

Fish and invertebrate samples to be analyzed for chemical content will be frozen and grouped at the laboratory into project-specific sample delivery groups prior to being analyzed.

3.2 INVERTEBRATE SAMPLING AND ANALYSIS

Benthic macroinvertebrates will be collected using a petite ponar dredge in water depths between 1.0 m and 1.5 m following the SOP (Appendix A). Samples will be sieved in the field using a U.S. Standard Number 30 Nalgene sieve (mesh size 0.600 um) and sieved material placed into a plastic bucket for picking on shore. A maximum of five ponar dredge samples will be collected at each location. The samples will be sorted using plastic utensils and a composite of each target organism placed into a labeled glass vial until the appropriate mass is obtained for analysis. Zebra mussel shell length will be measured and recorded and a composite sample of 10 to 15 similar-sized individuals will be placed into a sample container (tissue removal to be done in the analytical laboratory following methods in Appendix A). Sample containers will be labeled with the unique identification number, station identification, date, and sampler initials. For each sample container, the date of collection, a unique identification number or code, the station identification, date, type of invertebrate, number of individuals, total biomass weight, method of collection, and sampler's initials will be recorded on a Macroinvertebrate Collection Field Log (Figure 4).

Samples for community composition and abundance will be collected with a petite ponar dredge similar to collection for tissue analysis. Five samples will be collected from each location with a petite ponar dredge and sieved in the field, similar to tissue samples. Following sieving, the sample will be placed in a labeled polyethylene container and preserved with a 10 percent buffered formalin solution following the SOP (Appendix A).

Phytophilous invertebrates will be collected from macrophyte beds during August. Samples will be collected from 18 locations as close to the benthic macroinvertebrate stations as feasible, depending on plant coverage (see Figure 2). Five replicates per location will be collected with a petite ponar dredge. Macrophyte samples will be removed from the sediment and placed in a resealable plastic bag labeled with unique sample code, station location, replicate number, date, and sampler initials, preserved in 10 percent buffered formalin and rose bengal dye, and brought to the laboratory for sorting and processing following the SOP (see Appendix A).

In conjunction with the benthic samples, a surface sediment sample will be collected from the same location for comparison with tissue concentrations. One push core sample will be collected, and the sample split into two sediment depth segments, 0 to 2 cm and 2 to 15 cm.

Each segment will be homogenized and the sediment placed into a labeled glass jar and submitted to the analytical laboratory in accordance with the SOP (Appendix A).

Chain-of-custody forms will be maintained and processed samples kept cool (below $4^{o}C$) and shipped overnight to the analytical laboratory.

Invertebrate samples (benthic macroinvertebrates and zebra mussels) will be submitted to the analytical laboratory for total and methylmercury analysis in accordance with the methodologies presented in the QAPP. Samples will be processed by experienced personnel at the laboratory and then frozen until analyzed. Dry and wet weights of the laboratory sample will be measured. Each sample will be identified by a unique sample number. Sample extracts for mercury analysis and homogenized samples from invertebrate tissue samples will be held (frozen at less than minus $10^{o}C$ for extracts and less than minus $18^{o}C$ for tissue) for one year from sample collection.

Sediment samples will be submitted to the analytical laboratory and analyzed for total mercury, methylmercury, and total organic carbon in accordance with the QAPP (Appendix B). Sediment samples will be analyzed for total mercury and methylmercury to correlate macroinvertebrate concentrations with sediment concentrations.

Samples for benthic community composition and abundance will be sorted and identified in the laboratory following procedures in the SOP (Appendix A). Prior to sorting, samples will be rinsed through a sieve with water and returned the original container with 75 percent ethanol and rose bengal stain to assist with sorting. Zebra mussel abundance will be determined for the entire sample; all other macroinvertebrates will be subsampled following procedures in the SOP (Appendix A) and then identified to the lowest taxonomic level reasonably achievable.

3.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

QA/QC procedures are presented in the QAPP (Appendix B). QA/QC sampling and analytical activities will include the collection of equipment rinse blanks, matrix spike samples, and laboratory duplicate samples. A summary of field QA/QC samples to be collected is presented in the QAPP. Personnel conducting sampling will be either trained fisheries biologists or students studying fisheries biology. A certified fisheries professional from the American Fisheries Society will oversee all field activities through daily communications and periodic field visits (e.g., once or twice per week) for the duration of sampling.

3.4 HEALTH AND SAFETY

Subcontractor Safety Plans will be used for this investigation and will be strictly followed by all field personnel. Any task outside of the previous field efforts will have a new Job Safety Analysis completed before the task begins. Minor modifications to the Subcontractor Safety

Plans have been made to account for the activities identified in this work plan. Copies of the Subcontractor Safety Plans will be maintained at the support zone and on each vessel.

SECTION 4

DATA MANAGEMENT AND REPORTING

4.1 DATA COMPILATION

The data will be organized into a compilation of laboratory and field generated data in electronic file format. Electronic data files will be generated by the analytical laboratory, while pertinent field data will be entered into electronic format during collection. Data will be added to Locus Focus through an input module of the system by the Data Manager Access to the input module will be restricted to the Syracuse Portfolio Data Managers or delegates. Chemical analytical data will be loaded/entered into a database as discussed in the QAPP. The QAPP specifies minimum requirements for sample information that will be entered into the database.

A field database will be developed that will include field observations and measurements. The field database will also clarify how information related to biological components of the program will be reported. Screen shots of the field database are provided in the Fish Collection SOP SB-1. The field database will include a field log for fish gut observations.

4.2. REPORTING

Unvalidated data will be submitted to NYSDEC consistent in content and timing with submissions being provided for other pre-design investigation and baseline monitoring efforts for Onondaga Lake. Analytical data generated during this investigation will be reviewed and validated as described in detail in the QAPP associated with this work plan (Appendix A). All analytes will be subject to Level III validation as described in the PDI QAPP (Parsons 2005). In addition, ten percent of the total mercury, methylmercury, PCB, and dioxin/furan data will be validated based on Level IV protocols. The validated results will be incorporated into the Locus Focus database by Parsons following validation.

Once the data validation has been completed, a data usability and summary report (DUSR) will be prepared and submitted to NYSDEC as an attachment to the Annual Baseline Monitoring Report in June of the year following the field season in accordance with the Consent Decree for the Lake. The DUSR will present the results of data validation and data usability assessment. A data export will be provided in the DUSR on CD/DVD. Data interpretation and trend analysis will be discussed with the Baseline Monitoring Technical Work Group and incorporated into the baseline monitoring report.

As part of the assessment of mercury concentrations in benthic tissue samples, it will be recognized that the results for chironomids may be more variable than for other taxa of

macroinvertebrates. The zebra mussels represent a single filter feeding species and the amphipods represent a single genus that scavenges on surface matter. In contrast, the *Chironomidae* is a family that is represented in the lake by about 30 species, based on 1992 and 2000 data. The *Chironomidae* include several different feeding strategies such as detritus feeders, herbivores, and predators, which may have different exposures to methylmercury. Currently, this family in Onondaga Lake is dominated by *Chironomus* spp., a genus restricted to in-sediment detrital feeders. With improvements in the lake, the composition of this group may change in the future.

SECTION 5

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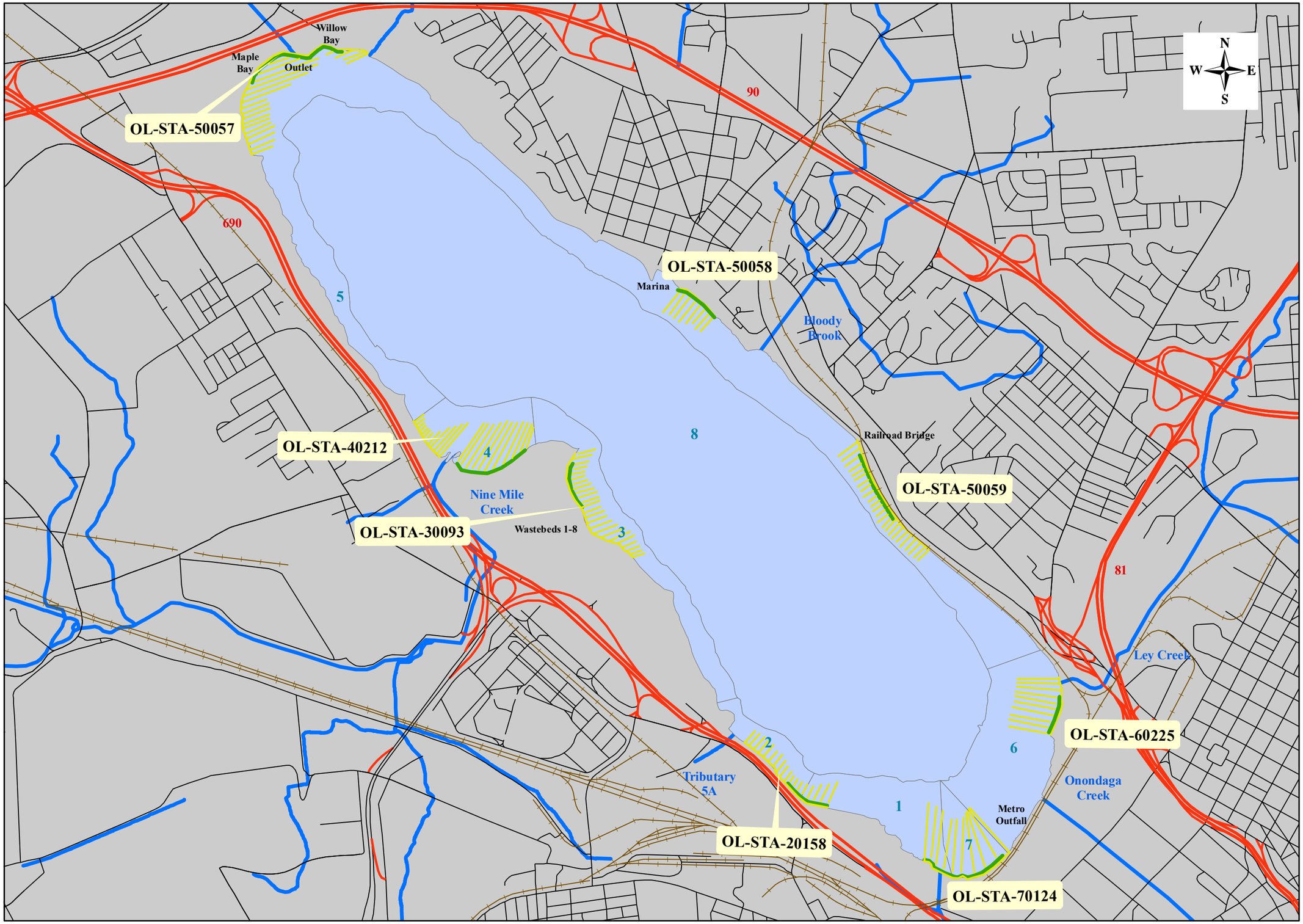

Locator

Scale

Feet

0 1,500 3,000

Legend

Proposed Fish Locations

- Prey Fish
- Adult Sport Fish*

Roads

- Road
- Highway/Interstate
- Railroad
- SMU Boundaries
- Tributaries

**Hatching indicates approximate extent (5m depth) of adult sport fish sampling in the littoral zone.*

Figure 1:
Approximate Fish Sampling Locations.

Honeywell
PARSONS
QEA
Quantitative Environmental Analysis, LLC

PARbas June 2008

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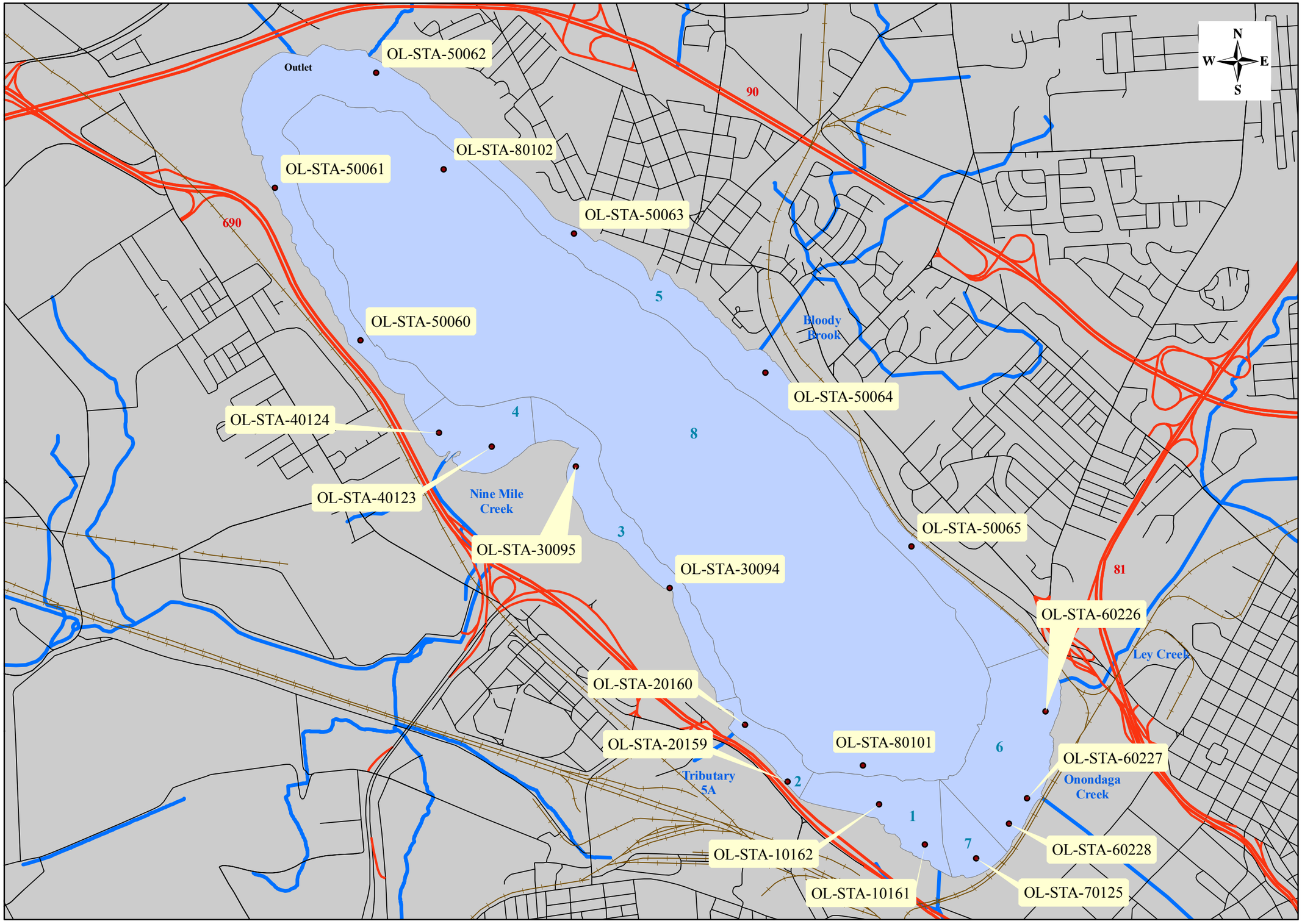

Locator

Scale

Feet

0 1,500 3,000

Legend

Proposed Sampling Locations

- Invertebrates*
- Railroad

Roads

- Road
- Highway/Interstate
- SMU Boundaries
- Tributaries

**Benthic invertebrates will be collected in these locations and phytophilous invertebrates will be collected in the vicinity.*

Figure 2:
Approximate Invertebrate Sampling Locations.

Honeywell
PARSONS
QEA
Quantitative Environmental Analysis, LLC

PARbas June 2008

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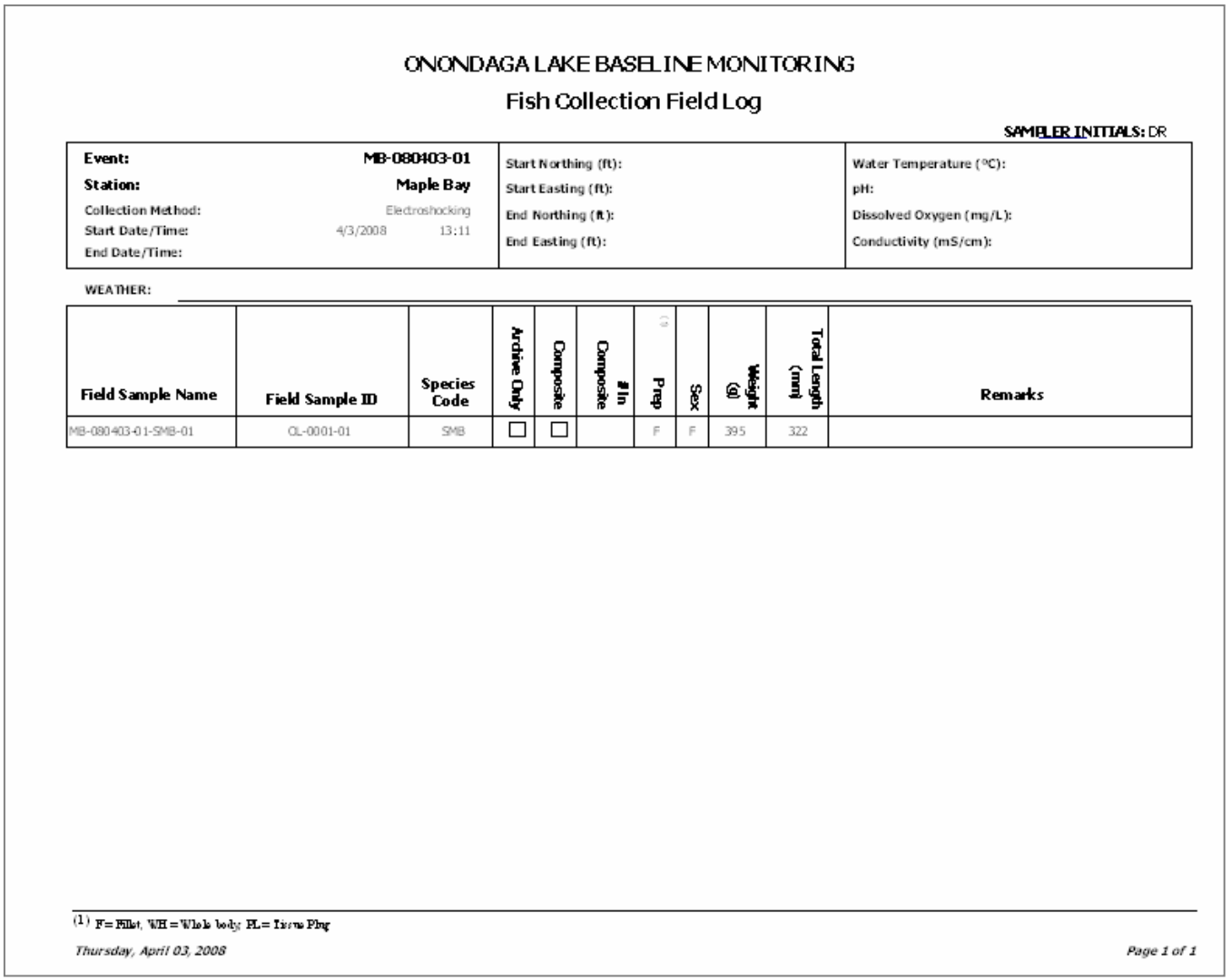


ONONDAGA LAKE BASELINE MONITORING

Fish Collection Field Log

SAMPLER INITIALS: DR

Event:	**MB-080403-01**	Start Northing (ft):		Water Temperature (°C):	
Station:	**Maple Bay**	Start Easting (ft):		pH:	
Collection Method:	Electroshocking	End Northing (ft):		Dissolved Oxygen (mg/L):	
Start Date/Time:	4/3/2008 13:11	End Easting (ft):		Conductivity (mS/cm):	
End Date/Time:					

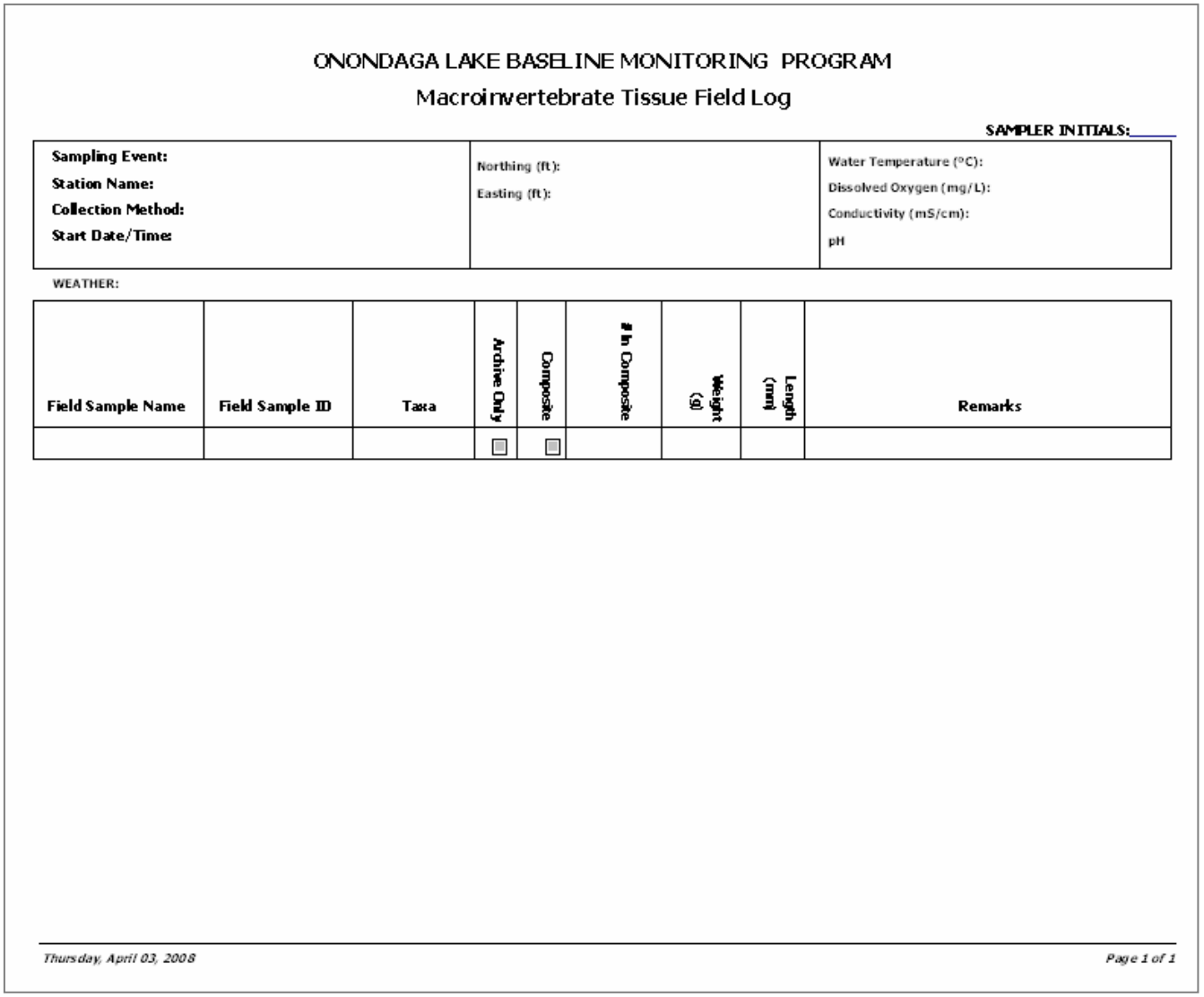
WEATHER:

Field Sample Name	Field Sample ID	Species Code	Archive Only	Composite	# In Composite	Prep [1]	Sex	Weight (g)	Total Length (mm)	Remarks
MB-080403-01-SMB-01	OL-0001-01	SMB	☐	☐		F	F	395	322	

(1) F= Fillet, WH = Whole body, FL= Tissue Plug

Thursday, April 03, 2008 *Page 1 of 1*

Figure 3. Onondaga Lake fish tissue collection field log.



ONONDAGA LAKE BASELINE MONITORING PROGRAM

Macroinvertebrate Tissue Field Log

SAMPLER INITIALS:____

Sampling Event: **Station Name:** **Collection Method:** **Start Date/Time:**	Northing (ft): Easting (ft):	Water Temperature (°C): Dissolved Oxygen (mg/L): Conductivity (mS/cm): pH

WEATHER:

Field Sample Name	Field Sample ID	Taxa	Archive Only	Composite	# In Composite	Weight (g)	Length (mm)	Remarks
			☐	☐				

Thursday, April 03, 2008 *Page 1 of 1*

Figure 4. Onondaga Lake macroinvertebrate tissue collection field log.

TABLE 1

SUMMARY OF PROPOSED BIOTA SAMPLING LOCATIONS, NUMBER OF SAMPLES, SAMPLE PREPARATION, AND DURATION OF SAMPLING

Activity	Number of Locations	Number of field matrix samples per location	Number of species	Sample Preparation	Duration
Adult Sport Fish Tissue Sampling[1]	8	6-7	4	Fillets and Tissue plugs	Approximately 15 days in late July and August
Prey Fish Tissue Sampling (minnow species, alewife)	8	5	Variable (composites of a prey species)	Whole body composite	Approximately five days in August
Sport Fish Population Estimate	Lakewide	NA	4	None	June-July
Fish Community Assessment	8	NA	NA	None	May to October
Fish Diet Assessment	Lakewide	50 per species	5	Dissection for smaller fish	June to September
Benthic Macrovertebrate Tissue Sampling	18	1	3	Whole body composite	Approximately 10 days in August
	18	1	3	Whole body composite	Approximately 10 days in late October/early November[2]
Benthic Macroinvertebrate Community Assessment	18	5	N/A	N/A	Approximately 10 days in August
Phytophilous Macroinvertebrate Community Assessment	18	5	N/A	N/A	Approximately 10 days in August

TABLE 1

SUMMARY OF PROPOSED BIOTA SAMPLING LOCATIONS, NUMBER OF SAMPLES, SAMPLE PREPARATION, AND DURATION OF SAMPLING
(Continued)

Activity	Number of Locations	Number of field matrix samples per location	Number of species	Sample Preparation	Duration
Littoral Water Sampling	6	1	N/A	N/A	August
	6	1	N/A	N/A	Mid – late October[3]
	6	1	N/A	N/A	Late October/early November[2]
Sediment	18	2	N/A	0 to 2 cm 2 to 15 cm	Approximately 10 days in August
	18	2	N/A	0 to 2 cm 2 to 15 cm	Approximately 10 days in late October/early November[2]

[1] Target for adult sampling is 6 to 7 individuals per station. The goal is to evenly distribute these numbers of individuals from each location. However, if species are sparse at one location, additional individuals will be collected from one of the other locations to achieve the target numbers.

[2] Sampling will be conducted two to four weeks after fall turnover.

[3] Sampling will be conducted approximately one week after fall turnover.

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TABLE 2

PROPOSED SAMPLING SCHEDULE FOR BASELINE FISH AND INVERTEBRATE BIOTA

Activity	Month						
	May	**June**	**July**	**Aug**	**Sept**	**Oct**	**Nov**
Adult sport fish tissue			****				
Prey fish tissue				****			
Adult sport fish population assessment		**********					
Fish community assessment	**********						
Fish diet assessment		**********					
Invertebrate tissue and sediment				*****		**********	
Invertebrate community analysis				*****			
Phytophilous invertebrates			*****				
Littoral water sampling			*****			****	**

APPENDIX A

STANDARD OPERATING PROCEDURES (SOP)

APPENDIX A

STANDARD OPERATING PROCEDURES (SOPs)

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization
Sampling SOPs		
SB-1	Fish Collection	QEA
SB-2	Benthic Macroinvertebrate Collection	QEA
SB-3	Biota Tissue Processing	QEA
SB-4	Fish Stomach Sampling	QEA
SB-5	Adult Sport Fish Population Estimate	QEA
SB-6	Fish Community Assessment	QEA
SB-7	Sediment Sample Collection	QEA
SB-8	Phytophilous Invertebrate Sampling	QEA
SB-9	Littoral Zone Surface Water Sampling	QEA
Analytical SOPs		
LB-1	Mercury (Cold Vapor Technique) SW846 Method 7471A, SOP BR-ME-004, Revision 11	TestAmerica Burlington, VT
LB-2	Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Method 8290, 1613B, 23, 0023A, and TO-9A, KNOX-ID-0004, Revision 7	TestAmerica Knoxville, TN
LB-3	Summary of SOP #BR-0011 Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630, Revision 012	Brooks Rand Labs
LB-4	Polychlorinated Biphenyls (PCBs) by Gas Chromatography (SW-846 Method 8082). SOP BR-GC-005, Revision 8	TestAmerica Burlington, VT
LB-5	Total Organic Carbon in Soils and Sediment, (Lloyd-Kahn) SOP BR-WC-008, Revision 11	TestAmerica Burlington, VT
LB-6	Percent Lipid Determination SOP No., BR-EX-016, Revision 6	TestAmerica Burlington, VT

LB-7	Extraction Cleanup Procedure SOP No. BR-EX-002, Revision 7	TestAmerica Burlington, VT
LB-8	SOP No. NC-MT-0001 (Revision No. 5.1) Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7	TestAmerica North Canton, OH
LB-9	Organochlorine Pesticides by Gas Chromatography. SOP No.BR-GC-006, Revision 8 (EPA Method 8081A)	TestAmerica Burlington, VT
LB-10	Homogenization of Biota/Tissue. SOP BR-EX-009, Revision 5	Test America Burlington, VT
LB-11	Determination of Limits of Detection, Limits of Quantification, and Reporting Limits SOP No. BR-QA-005, Revision 7.	Test America Burlington, VT

STANDARD OPERATING PROCEDURE SB-1:

FISH COLLECTION

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for fish collection in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the fish collection. The scope of work including quantities and locations is defined in the Book 2 Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

Several methods may be used to collect fish for the program. This SOP includes procedures to collect fish by popnetting, gillnetting, seining, trap netting, and electrofishing. Use of each method will be dependent on species and life stages being targeted; a combination of methods likely will be necessary to obtain the required species.

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment, stepping in the sight of lines or cables, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

The use of electrofishing equipment involves potential hazards related to the high voltage output. Because water is an excellent conductor of electricity, the operator of the electrofishing equipment (SUNY ESF) must observe certain precautions to avoid injury. For example, the acceptable voltage range for electroshocking is 300 to 400 volts, and the acceptable current range is 19 to 23 amps based on experience from previous investigations.

3.0 EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Since multiple procedures or alternate methods may be employed to achieve the objectives, not all materials and equipment included on the list may be necessary to complete the task.

- Popnet constructed from PVC pipe and mesh net

- Seine net
- Gill net
- Anchors with approximately one meter of rope attached for gill net (2 per net)
- Buoys with rope attached for gill net (3 per net)
- Trap net
- Sampling vessel
- Electroshocking boat
- High voltage gloves
- PFDs
- Waders
- Measuring board
- Weight scale
- Small and large baskets for weighing fish
- Fish holding tub
- Minnow nets
- Large dip nets
- Long handled nets
- Water quality meter
- Digital camera
- Field notebook
- GPS unit
- Cellular phone

4.0 PROCEDURE

4.1 Popnet Sampling

Popnets will quantitatively sample fish densities in areas that are inaccessible to seining techniques (macrophyte beds where water depth is up to 1.2 meters [4 ft]), using a similar design pop net as Connolly (1994). Popnets used in this SOP are constructed with four 3.048 meter [10 ft] pieces of 2.54 cm [1 in] PVC pipe. Each PVC pipe is sealed and the corners are held together by removable flexible connectors. The mesh wall (1.3 meters [4.26 ft] high and 0.635 cm [0.25 in] stretched mesh) is attached to the PVC with heavy duty zip ties. The bottom of the mesh wall is weighted by interlacing a weighted line through the mesh. Below are procedures for sampling with a popnet.

Station selection

1. Proceed to the appropriate station and record in the field log.
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface where net will be located.

Setting the Net:

1. Tie a 10-meter (32.8 ft) rope around each of the four cinderblocks.
2. Pound a stake into the substrate near the outside corners of the PVC enclosure.
3. Position the PVC enclosure over the desired site and arrange the mesh wall underneath the PVC.
4. Two people stand on opposite sides of the net at the corners, push the PVC under the water, and place a cinderblock on top of the PVC to hold it on the bottom. Repeat at the other corners of the net.
5. Extend the 10-meter [32.8 ft] rope tied to each cinderblock and fasten to a stake on either side of the net (Figure 1). This will enable popping the net without disturbing the fish within the study area.
6. Let the net set overnight in the collapsed position and pop the following morning.

Sampling inside the Net:

1. To pop the net, one person goes to each stake, the lines are held taught, and then simultaneously pulled which moves the cinderblocks off the PVC. The PVC rises to the surface within 2 seconds and the mesh wall is held on the bottom by the weighted line.
2. Once the popnet has been released, estimate the percent cover of all of the macrophyte species inside the enclosure and the percent cover of the individual species using the Daubenmire cover class:
   - 0 percent coverage
   - Less than 5 percent coverage
   - 25 to 50 percent coverage
   - 50 to 75 percent coverage
   - 75 to 95 percent coverage
   - Over 95 percent coverage

3. Two people stretch a bag seine (30 m [98.4 ft] long; 0.635 cm [0.25 in] stretched mesh) inside the enclosure. Standing just outside the enclosure, pull the seine along the inside the walls of the enclosure with the brails.

4. Concentrate the fish into the bag, remove the net from the enclosure, and place the fish in a live well for processing.

5. Following processing, repeat steps 3 and 4 two more times for a total of three seining rounds within the enclosure.

Data Collection

1. Fish are processed for assessment of population density and abundance according to the Fish Community Assessment SOP. Fish not required for other analyses will be released.

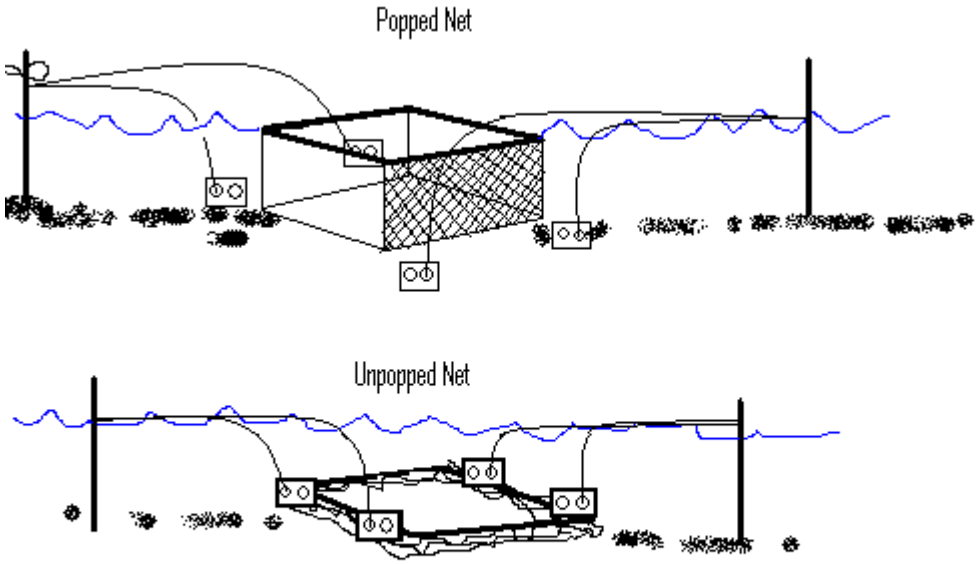

Figure 1 Popnet Diagram

4.2 Sampling with a Seine

For near shore shallow study areas with minimal to no macrophyte coverage, a bag seine (30 m [98.4 ft] length; 0.635 [0.25 in.] cm mesh) will be used to collect juvenile and prey fish for abundance estimates and prey fish tissue samples. The bag seine is typically used in shallow water where the net wall can extend from the surface of the water to the bottom. It is useful in the capture of near-shore species or for species that use the near-shore area seasonally or daily. In addition, the substrate needs to be relatively smooth so that the lead line of the seine drags along the bottom of the river preventing fish escapement. The fish are herded into the net as it is swept through the water. Seining will be conducted by a minimum of two people. The following outlines the procedures for seine netting (based on NYSDEC 1989):

Sampling

1. Proceed to the appropriate station and record in a field log (Figure 2).
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface where the net will be located.
3. Prior to entering the water stretch the bag seine out on shore and remove any material lodged in the mesh. Inspect the net for holes and make repairs, if necessary.
4. One person begins extending the seine perpendicular to the shoreline until the net is straightened out or the water becomes too deep. Be sure bag is fully deployed and not tangled.
5. One person holds the on-shore brail stationary while the off shore person sweeps the brail towards shore. A third persons walks behind the bag to dislodge any snags if the seine becomes stuck. Reject the sample if the lead line is lifted or if the seine is stopped to dislodge a snag.
6. As the person holding the offshore brail approaches shore, the two ends are worked together to beach the seine while maintaining the integrity of the bag section and keeping the lead line on the bottom.
7. Fish are removed from the net and placed into holding buckets for identification. Be sure to pick through any debris captured in the net to retrieve all fish.
8. Stretch out the seine on shore and remove any material lodged in the net.
9. Process fish for assessment of abundance estimates according to the Fish Community Assessment SOP. Fish not required for other analyses will be released.

4.3 Gill net sampling

Fish collection for tissue analysis may be conducted with gill net sets. Fish are captured when they swim into the gill net and become entangled in the mesh of the net. A gill net consists of a net vertically suspended between a float line on top and a weighted lead line at the bottom. The mesh size of the net can consist of different sized panels or one single size for the entire length of net. For this sampling the gill net will be one size mesh (15.24 cm[5.9 in.] stretch), 38.1 m [125 ft] long and 2.44 m [8.0 ft] high. To keep the net in a vertical orientation, anchors

are attached to either end of the lead line and buoys are attached to either end of the float line. The lengths of the anchor and buoy lines are adjusted so that the net is suspended at the target water depth. The following describes the procedure for sampling with gill nets:

Station selection

1. Proceed to the appropriate station and record in field log (Figure 2).
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at one meter vertical intervals from the surface to just off the bottom where net will be located. If water quality conditions are not suitable for fish habitation, do not set net at this depth.

Setting the gill net perpendicular to shore:

1. Attach anchors to both ends of the lead line and attach buoys to both ends of the float line
2. Stack the gillnet in a large storage bucket by placing the end with the larger mesh size in the tub first (if the net has variable mesh sizes), and coiling the rest of the net into the tub. This procedure facilitates setting the net.
3. Beginning close to shore, or in water approximately 2 m deep, remove the outer end of the net from the storage bucket and drop the anchor (attached to the lead line) and buoy (attached to the float line) over the bow of the boat. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
4. Begin slowly backing the boat away from the shore.
5. Carefully, play out the remainder of the net as the boat is moving backwards, shaking out any tangles.
6. Once the inner end of the net is reached, stop the boat and pull on the net until it is taut.
7. Drop the anchor (attached to the lead line) overboard.
8. Pull on the float line to make sure the net is taut.
9. Drop the buoy that is attached to the float line into the water. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
10. Allow the gill net to be in place for the prescribed sampling period (e.g., 1-24 hours).

Retrieving the gill net.

1. Arrive at the end of the net in deeper water and retrieve the buoy and anchor.
2. Begin pulling the net on board the boat and stacking it in coils in the storage bucket.
3. Remove fish from the net as it is brought aboard the boat and place in holding bucket. All fish will be placed in the holding bucket until the entire net is retrieved.

4. Process fish according to procedures in Biota Tissue Processing SOP or the Fish Population Estimation SOP. Fish not required for other analyses will be released.

4.4 Trap Net Sampling

A trap net is used as a passive sampling device to capture fish as they swim along the shoreline. Samples will be collected in the trap net for tissue analysis and population studies. A trap net consists of a leader line (23 m [75.4 ft] length), two wings (11.5 m [37.7 ft] each), and a series of hoops; the entire net consists of 0.635 cm [0.25 in.] stretch mesh. The net is set perpendicular to and facing the shoreline. When fish encounter the leader line, they are directed offshore into the mouth of the net, through the hoops, and into the end of the net. As fish move through the series of hoops, escape becomes increasingly difficult. Fish may be attracted to the net by other fish that are already captured in it.

Station selection

1. Proceed to the appropriate station and record in field log (Figure 2).
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface where net will be located.

Setting the net

1. Anchor the shoreward end of the leader line near the shoreline or attach it to the shoreline by tying it to a fixed object on shore (e.g., tree).
2. Extend the leader line out into the water and perpendicular to shore, until it is taut.
3. Extend each wing at a 45 to 90 degree angle to the leader line. This can be done either by boat or by wading, depending on the water depth and substrate characteristics.
4. Anchor the lower ends of both wings with anchors and attach buoys to the upper ends of the wings. Adjust the buoy lines so that the buoys are floating and the lines are relatively taut.
5. Extend the hoops of the trap away from shore in line with the leader line and pull on the end of the net until all of the hoops are upright.
6. Close the end of the net with a piece of line.
7. Attach an anchor to the end of the net to keep it submerged and attach a buoy to the anchor to mark the location of the end of the net. Record the depth below the water surface of the car end of the net.
8. Allow the net to soak (i.e., fish) for the prescribed sampling period (e.g., 24 to 48 hours).

Sample Collection

1. Arrive at the buoy at the end of the net and pull the buoy and its anchor into the boat.
2. Retrieve the hoops in sequence, while moving toward shore.
3. Starting at the mouth of the net, shake the captured fish into the closed end of the net.
4. Once all captured fish are in the end of the net, remove the piece of line from the end of the net and empty fish into the collection buckets.
5. If sampling will continue at the collection site, reset the trap according to steps 3 through 8 above for setting a trap net.
6. Process fish according to procedures in Biota Tissue Sampling SOP, Fish Community Assessment SOP, or the Fish Population Estimation SOP. Fish not required for other analyses will be released.

4.5 Electrofishing

Electrofishing uses electrical currents to immobilize fish for capture. Electrofishing is less effective in deeper waters, where fish can swim and avoid the current, so this method will be limited to areas that are less than 4 meters [13.2 ft] deep. The following outlines the procedures for electrofishing:

1. Personnel performing the electroshocking will wear appropriate health and safety gear (rubber boots, rubber gloves, PFD).
2. Position the electrofishing boat in the water.
3. Optional use of a “fish finder” may increase efficiency and aid in targeting locations for sampling.
4. Measure the water conductivity and temperature to determine the appropriate operating voltage and amperage.
5. Adjust the output voltage and amperage dials until the desired output setting is obtained without harming fish. Use pulsed output to reduce stress on fish.
6. Maintain the output for a predetermined amount of time or sampling area.
7. Collect the fish with dip nets and place in bucket of water for processing.
8. Release all unselected fish following processing.
9. Process fish retained for analysis according to the procedures described in the Fish Population Estimate SOP, Fish Community Assessment SOP, or Biota Tissue Processing SOP.

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Fish

collection will be conducted by personnel from SUNY-ESF and Onondaga County Department of Water Environment Protection (OCDWEP). Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. A certified fisheries professional will oversee the QA/QC for the various activities.

6.0 REFERENCES

Connolly R.M. 1994. Comparison of Fish Catches From a Buoyant Pop Net and Beach Seine in a Shallow Sea Grass Habitat. Marine Ecology Progress Series. 90:305-309.

New York State Department of Environmental Conservation. 1989. Guidelines for the Collection, Analysis, and Interpretation of Fisheries Data by Units of the NYSDEC Division of Fish and Wildlife.

Zippin, C. 1958. The removal method of population estimation. J. Wildlife Management 22:82-90.

STANDARD OPERATING PROCEDURE SB-2:

BENTHIC MACROINVERTEBRATE COLLECTION

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for benthic macroinvertebrate collection in Onondaga Lake. Benthic invertebrate sampling will be conducted to collect organisms for tissue analysis as well as assessing community composition. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the benthic macroinvertebrate sampling. The scope of work including quantities and locations is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

3.0 EQUIPMENT LIST

- petite ponar with rope
- US Standard No. 30 mesh (600µm opening) Nalgene sieve
- 5 gal buckets (12)
- wash bottle and garden sprayer
- water quality meter
- sampling vessel
- PFDs
- sample containers
- 10 percent buffered formalin
- rose bengal dye

- sample labels
- Digital global positioning system (DGPS)
- resealable plastic bags
- sample containers
- 70 percent ethanol
- sorting tray
- plexiglass divider for subsampling
- forceps
- spatula
- dissecting microscope
- petri dish
- vials
- labels
- alcohol proof marker
- deionized water
- balance for weighing samples
- cellular phone
- digital camera
- field notebook

4.0 PROCEDURES

Sample Collection

1. Upon arrival at a sampling station, position the boat in 1.0 to 1.5 meter [3.3 to 4.9 ft] water depth. Record water depth.
2. Collect water quality data at the water surface and just off the bottom (pH, DO, temperature, conductivity). Log data on the meter to download at the end of the day.
3. Collection at each station will begin with tissue samples, followed by community samples, and then the sediment sample. Decon the ponar sampler prior to collection of the first sample in accordance with previously-implemented decontamination procedures (SOP 3; Parsons, 2005).
4. Tie one end of a rope to the ponar and the other to the boat. Before lowering the ponar into the water, with the line taut, remove the safety pin and replace with the pinch pin. As long as the line is taut the pinch pin will stay in place. The petite ponar is now set,

and will be lowered into the water, and allowed to free-fall for the last 0.5 m [1.6 ft] to the bottom with a slack line. The impact with the bottom activates the closing mechanism, and the dredge is then slowly brought to the surface.

5. Retrieve the sampler. Once at the surface, place the petite ponar over a labeled stainless steel pail (clean pail for tissue samples), check the surface of the sample prior to opening the jaws allowing the contents to drop into the pail. Resample if no overlying water is present (overpenetrated) if sampler is only partially filled with sediment, or if sample is not relatively uniform across. Record the depth of sediment sampled. If a sample is rejected, repeat procedure. Rinse off any remaining material from the ponar with lake water.
6. Repeat procedure to obtain the necessary number of samples (five each for tissue and community composition). Once tissue samples are collected from a station, proceed with collection of samples for community analysis. Transfer the tissue samples from a location to the on-shore tissue processing crew and community samples to the community processing crew.

Tissue Sample Processing

1. Collect the 5 ponar samples from different locations on the boat and place into the same labeled bucket. Use a second clean bucket if needed (be sure to sample at different points on the boat so as not to sample the exact same location twice). Place the contents of the sample into a U.S. Standard No. 30 mesh (0.600 mm opening) Nalgene sieve inside a washtub overhanging on the side of the boat. Gently wash the sample with lake water using a small impeller pump to remove small particles (clays and silts). Transfer the contents remaining in the sieve to a labeled bucket for transfer to the tissue processing team.
2. Transfer the bucket for tissue analysis from one station to the tissue processing team on shore.
3. The processing team will pick through each sample and remove the amphipods, chironomids, and zebra mussels. Transfer a portion of the sample to a labeled clean tray for picking.
4. Place each taxon in a labeled decontaminated Petri dish and continue picking until enough biomass is obtained.
5. Record the shell length of each zebra mussel and total weight of amphipods and chironomids on the field log (Figure 3).
6. Process samples according to the Biota Tissue Processing SOP.
7. Proceed to the next location and repeat procedures for sample collection.

Community Composition Collection

1. Following tissue collection, collect 5 replicate ponar samples following sample collection steps 4-6 and place each sample into a separately labeled bucket (be sure to

sample at different points on the boat so as not to sample the exact same location twice).

2. Place the contents of the sample into a U.S. Standard No. 30 mesh (0.600 mm opening) Nalgene sieve inside a washtub overhanging on the side of the boat. Gently wash the sample with lake water using a small impeller pump to remove small particles (clays and silts). Transfer the contents remaining in the sieve to a labeled wide mouth plastic sample jar (size may vary depending on amount of material). Add buffered 10 percent formalin with rose Bengal dye (wear Nitrile gloves and goggles during this operation), and fill the sample jar to just below the shoulder. Cap tightly and gently invert the sample several times to distribute the fixative solution. Double check the label(s), making sure all required information is recorded.
3. Proceed to the next location and repeat procedures for sample collection.
4. In the laboratory (under the laboratory exhaust hood), pour the contents of sample into a sieve with a mesh size of 500 µm. Rinse with tap water to remove any fine particles left in the sample from the field.
5. Transfer the sample to a sorting tray and distribute homogeneously over the bottom of the pan.
6. With the use of an over-head illuminated magnifier, scan the sample and remove 100 random organisms according to Bode et al (2002). For large samples, divide the sample into quarters to prevent biasing the data by selecting the larger easily located organisms. As they are removed, sort the organisms into major groups. After the major groups are sorted, place individual groups into four dram (0.5 ounce) vials containing 70 percent ethyl alcohol, and count them. Record the counts on the tally sheet.

   Note: If an entire sample is sorted and less than 100 organisms are found, make a note on the tally sheet stating that the entire sample was sorted.

   Note: Identify all organisms to order, with the exception of chironomids and oligochaetes.
7. Count all the zebra mussels within the first 100 random macroinvertebrate sorted (Sort 1). Close attention will be given to the identification of any quagga mussels. Next, sort out an equal number of non-zebra mussel macroinvertebrates from the original sample (or quarter) (Sort 2). Place the additional macroinvertebrates in separate vials from the initial sorting. Distinguish on the container labels as 1st and 2nd sorting. The objective is to obtain a sample of 100 macroinvertebrates including zebra mussels, and a sample of 100 macroinvertebrates without zebra mussels.
8. Once a 100 macroinvertebrate sample without zebra mussels is sorted, remove any remaining zebra mussels from the initial sample (or quarter), individually count, and document on the tally sheet. The additional zebra mussel count allows the calculation of the number of zebra mussels per square meter.

9. With an alcohol proof pen make a small label with date, Station ID, Replicate Number, Identification (order or family), and sampler initials and place into four dram (0.5 ounce) vials.
10. Place vials into a whirl-pak, fill out chain of custody and log sample into log book. Place chain of custody and whirl-pak with vials into a one gallon zip lock bag and place into QA/QC box.
11. Return remaining sample to original container in 70 percent ethanol and indicate on the cap that the sample was sorted, then initial and date.

QA/QC on Sample Sorting

The following quality assurance and quality control procedures shall be utilized for every sample location, and every replicate corresponding to that location.

1. Quality control checks will not be performed by the original sorter. Identify all samples that did not have 100 organisms sorted. Double check the original sample for any organisms that may have been overlooked.
2. With the logbook in hand, remove the first 10 samples sorted and identified. Following the steps listed below, determine if a sample passes of fails QA/QC. If all 10 "pass" the quality control, the sorter may randomly select one out of the next 10 samples. If this sample passes, randomly select one out of the next 10 samples again, utilizing this procedure for the entire sample.
3. Determine if sample passes or fails QA/QC:
   - If less than 100 organisms are present in sample. Check/sort the original full sample for additional organisms. If additional organisms are found, add to the tally (up to 100), sample fails QA/QC
   - Check counts for the breakdown by family. If incorrect sample fails QA/QC
   - If a sample fails quality control, the next 10 samples will be checked before the one in 10 procedure is resumed.
4. Once the QA/QC is corrected or confirmed, record this information on the chain of custody and in the log book.

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Benthic invertebrate community composition will be conducted by OCDWEP; tissue sampling and processing will be conducted by QEA. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this

procedure. Qualifications will be based on previous experience and health and safety training. An aquatic biologist with invertebrate experience will oversee the QA/QC for the various activities.

The sample remaining following initial sorting and qualified control checks will be sent to an outside laboratory (Aquatic Resources Center, Inc.) for identification to the lowest taxanomic level reasonably achievable.

6.0 REFERENCES

R.W. Bode, M. Novak, L. Abele, D. Heitzman, and A. Smith. 2002. Quality Assurance Work Plan For Biological Stream Monitoring in New York State. New York State DEC Division of Water.

STANDARD OPERATING PROCEDURE SB-3:

BIOTA TISSUE PROCESSING

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for biota tissue (fish and macroinvertebrates) sampling in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the tissue sampling. The scope of work including quantities and locations is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

2.0 EQUIPMENT LIST

- measuring board
- balance for weighing samples
- small and large baskets for weighing fish
- scale envelopes
- knife
- fillet knife
- deionized water
- 10 percent nitric acid solution
- alconox
- 6 mm dermal punch
- small spatual
- glass rod
- sample vials
- foil
- sample labels
- resealable plastic bags
- wet ice
- dry ice
- coolers

- cellular phone
- digital camera
- field notebook

3.0 PROCEDURES

3.1 Fish

Capture fish according to methods in the Fish Collection SOP.

Field Processing

1. Samples for tissue analysis will be collected if the required fish are collected at a station.
   - smallmouth bass (total length 305 to 500 mm)
   - walleye (total length 380 to 575 mm)
   - brown bullhead (total length 200 to 350 mm)
   - pumpkinseed sunfish (total length 130 to 200 mm)
   - prey fish in the minnow family (excluding carp and goldfish)
2. For each species, record the total length and weight on the field log (Figure 4). Remove several scales from the adult sport fish and place at least 10 scales in a scale envelope. Adult sport fish will be collected as individual samples; while prey fish will include a composite of 10 to 15 individuals of the same species (grouping fish by size to the extent possible).
3. Wrap fish in clean foil (shiny side out) and attach an identification label that includes the fish tag number, date, sample type, and location sampled (Figure 5).
4. Place the entire sample into a resealable plastic bag and place in a cooler on wet ice.
5. Prior to shipping the samples, print the chain of custody form and include with the shipment (Figure 6). Print the field collection log and retain a hard copy of the log (Figure 7).

Transportation

Store fish at a temperature below 4 degrees Celsius and ship immediately on wet ice to the analytical laboratory. Provide Fish Collection Records, Chain of Custody, and Analysis Request documents with the fish shipment.

Tissue Preparation

Fillets will be processed at the analytical laboratory according to procedures modified from the New York State Department of Environmental Conservation Fish Preparation Procedures for Contaminant Analysis. Tissue plugs will be collected from the adult sport fish based on

procedures in Peterson et al. (2005). Prey fish will be processed as whole body composites following analytical laboratory protocols. Bass, bullhead, walleye, and pumpkinseed sunfish will be aged by scales according to procedures in Devries and Frie, 1996, and prepared as standard fillets as follows:

1. Decontaminate all equipment prior to sampling each fish.
2. Remove scales from fish.
3. Do not remove skin from the smallmouth bass, walleye, or pumpkinseed. Remove brown bullhead skin.
4. Line an examination tray with clean foil and place fish in tray
5. Prior to removing the fillet, collect a tissue plug using a 6 mm dermal punch (Biopunch, Ray Products, Buffalo, NY or equivalent).
6. Insert the biopsy punch approximately 1 to 2 cm below the dorsal fin and with a slight twisting motion, cut through the skin and into the tissue.
7. Insert approximately 8 mm into the tissue and remove the punch carefully to retain the sample.
8. Remove the sample with a scalpel or small glass rod and place the sample (including skin) into a sterile 20 ml scintillation vial or other suitable container and freeze at -20 degrees Celsius until ready for analysis.
9. To remove the fillet, make a cut along the ventral midline of the fish from the vent to the base of the jaw.
10. Make a diagonal cut from the base of the cranium just below the gill, to the ventral side just behind the pectoral fin.
11. Remove the flesh and ribcage from one-half of the fish by cutting from the cranium along the spine and dorsal rays to the caudal fin. The ribs should remain on the fillet.
12. Complete sample preparation and analysis according to laboratory protocols.

Invertebrates

Collect and sort invertebrates according to the procedures in the Benthic Macroinvertebrate Sample Collection SOP.

Field Processing

1. After sorting and obtaining needed mass for each invertebrate taxon (1 g for total mercury and 0.1 g for methylmercury), place each invertebrate sample into a vial and label with sample ID, station location, date, and taxon and place in a cooler on dry ice.
2. Prior to shipping the samples, print the chain of custody form and include with the shipment. Print the field collection log and retain a hard copy of the log (Figure 8).

Transportation

Store invertebrates on dry ice and ship immediately on dry ice to the analytical laboratory, along with all Invertebrate Collection Records, Chain of Custody, and Analysis Request documents.

Tissue Preparation

Benthic invertebrates will be processed as composite samples according to laboratory protocols. Zebra mussel tissue will be removed from the shell in the laboratory using a Teflon™-coated spatula and processed by the laboratory.

3.3 Decontamination Procedures

Equipment used to process tissue samples will be decontaminated between each sample according to the following procedures.

1. Placed equipment in a wash tub or bucket containing Alconox (or other low-phosphate detergent) along with tap water, and scrub with a bristle brush or similar utensil.
2. This rinse shall utilize sufficient amounts of water to flush rather than just wet the surface.
3. Rinse with tap water followed by deionized water in a second wash tub
4. Rinse with 10 percent nitric acid.
5. Rinsed with deionized water.
6. Place equipment in a clean area and allow to air dry to the extent practicable. Following air-drying, the equipment that will be used for sampling will be wrapped in aluminum foil.

4.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. QEA will be responsible for conducting tissue sample processing tasks. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. An aquatic biologist with invertebrate experience and a certified fisheries professional will oversee the QA/QC as appropriate for the various activities.

5.0 REFERENCES

Devries and Frie. 1996. Determination of Age and Growth. Pages 483-512 in B.R. Murphy and E.W Willis (editors) Fisheries Techniques, Second Edition. American Fisheries Society, Bethesda, MD.

Peterson, S.A., J. Van Sickle, R.M. Hughes, J.A. Schacher, and S.F. Echols. 2005. A biopsy procedure for determining filet and predicting whole-fish mercury concentration. Arch. Environ. Contam. Toxicol. 48:99-107.

New York State Department of Environmental Conservation. 2000. Standard Operating Procedures for General Fish Collection and Handling. Bureau of Habitat, Division of Fish and Wildlife, New York State Department of Environmental Conservation. Albany, NY.

STANDARD OPERATING PROCEDURE SB-4:

FISH STOMACH SAMPLING

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for sampling fish stomach contents through gastric lavage in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the sampling. The scope of work including quantities and locations is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

Diet analysis will be performed using gastric lavage which, is commonly used to non-lethally obtain stomach contents in a wide variety of fish. A modified Seaburg (1957) method will be used which is described by (Light et al. 1983). Stomach contents of pumpkinseed, bluegill, largemouth bass, smallmouth bass, and brown bullhead will be identified.

2.0 EQUIPMENT LIST

- hand-pumped compression sprayer
- 1 mm polyethylene tubing
- funnel with 500 um mesh
- 20 mL vials
- 70 percent ethanol
- 10 percent buffered formalin
- live well or holding buckets
- cellular phone
- digital camera
- field notebook

3.0 PROCEDURES

1. Obtain fish for gastric lavage by a variety of active gears including, pop nets, electrofishing, and seining. Record the total length (in mm), and if applicable obtain a scale sample and place in a labeled scale envelope.
2. Perform gastric lavage with a hand-pumped compression sprayer attached to approximately 1 mm diameter flexible polyethylene tubing.

3. Fill the sprayer with water and attach the tubing.
4. Hold the fish over a funnel with a removable bottom equipped with 500 um mesh.
5. Insert the end of the polyethylene tubing into the mouth and stomach of the fish and inject water into the fish's stomach to flush out its contents.
6. The stomach and throat are flushed until no more food is being removed.
7. After the flushing is complete, remove the bottom of the funnel wash the contents on the mesh into a 20 mL vial and preserved with 75 percent ethanol (Light et al. 1983).
8. For fish that are too small for gastric lavage (i.e., less than 150 mm in total length per fish), sacrifice the entire fish and place in 10 percent buffered formalin. Analyze stomach contents in the laboratory.
9. Following gastric lavage, hold the fish in a separate live well until it is swimming normally prior to release.
10. Sort the contents of the stomachs using a stereomicroscope to the lowest taxonomic level reasonably achievable. Count each taxonomic representative and obtain a wet weight to the nearest 0.01 gram. Dry the samples in a 65 degrees Celsius oven for 24 to 28 hours to obtain a dry weight.

4.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Stomach analysis will be conducted by ESF personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. A certified fisheries professional will oversee the QA/QC for the various activities.

5.0 REFERENCES

Light, R. L., Peter A. H., and Dean, E. A. 1983. *Evaluation of gastric lavage for stomach analyses*. North American Journal of Fisheries Management. 3: 81-85.

STANDARD OPERATING PROCEDURE SB-5:

ADULT SPORT FISH POPULATION ESTIMATE

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for adult sport fish population estimation in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the population sampling. The scope of work is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

An intensive two week mark and recapture study will be conducted to estimate populations of largemouth bass, smallmouth bass, pumpkinseed sunfish, bluegill sunfish, and brown bullhead. Standard sampling techniques, including electrofishing, trap nets, and gillnets will be used to capture fish. Walleye, channel catfish, and brown trout are primarily susceptible to deep water gill nets which are very labor intensive for the low number of marked and recaptured fish, but these fish will be marked if they are encountered.

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

3.0 EQUIPMENT LIST

- Dip nets
- Fish holding tanks or live wells
- Knife of scissors for fin clips
- Tagging gun
- T-anchor tags
- Measuring board
- Marking gun

- Cellular phone
- Digital camera
- Field notebook

4.0 PROCEDURES

Sampling for mark recapture studies will be conducted following protocols for fish collection sampling (Fish Collection SOP), with specific details provided below. Sampling with trap nets will be conducted 5 days a week (Monday through Friday) at a total of 16 locations around the lake. Four nets will be sampled each day, with locations changed daily following sampling. Sampling with gillnets will be conducted for a maximum of eight nights over the two week sampling period. Gillnets will be set for one hour to reduce fish mortality since fish need to be marked and released live for the study. The entire lake shoreline will be sampled three times by electrofishing during the two week sampling period following the protocols in the Fish Collection SOP.

Mark/Recapture:

1. Fish will be placed in a live well or in holding buckets for processing. Data will be recorded on Mark/Recapture data sheets (Figure 9).
2. Non-target species captured in trap nets and gillnets with different mesh size panels will be counted and released.
3. Target species (largemouth bass, smallmouth bass, pumpkinseed, bluegill, and brown bullhead) will be measured for total length in mm and at least 10 scale samples collected from the appropriate position on the body. Scale samples will be placed in a scale envelope labeled with date, location, species, method of capture, and tag number (if appropriate).
    a. Scales will be taken during this two week mark and recapture study as long as it does not interfere with the goal of this portion of the sampling plan which is to mark and recapture as many fish as possible.
4. Fish will be marked by species:
    a. Largemouth bass and smallmouth bass 100 to 299 mm total length will be marked by clipping their left pelvic fin; fish at least 300 mm in total length will be marked using uniquely numbered t-bar anchor tags.
    b. Pumpkinseed and bluegill sunfish at least 100 mm in total length will have their left pelvic fin clipped.
    c. Brown bullhead at least 100 mm in total length will be marked by clipping the adipose fin. This is an easily recognizable mark that does not adversely affect the fish.

5. For fish marked with a unique T-bar tag, the tag will be inserted at an angle beneath the first and second dorsal ray and inserted behind the pterygiophores using a tagging gun (Murphy and Willis 1996).
6. The tag will include a unique tag number, SUNY ESF, and the SUNY ESF office telephone number printed on it.
7. The first week will be the marking period. All target fish captured will be marked and any recaptured fish will be released back into the lake.
8. The second week will be the recapture period. The number of fish of each target species will be counted based on if it was a recaptured fish or an unmarked fish.
9. The Petersen estimator (Ricker 1975) will be used to estimate the population size of each target species.

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. SUNY-ESF personnel will be conducting the mark-recapture study. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. A certified fisheries professional will oversee the QA/QC for the various activities.

6.0 REFERENCES

Murphy B.R. and D. W. Willis. 1996. Fisheries Techniques 2nd edition. American Fisheries Society. Bethesda, Maryland.

Ricker W.E. 1975. Computation and Interpretation of Biological Statistics of Fish Populations. Bulletin of the Fisheries Research Board of Canada. 191.

STANDARD OPERATING PROCEDURE SB-6:

FISH COMMUNITY ASSESSMENT

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for fish community assessment in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the community assessment. The scope of work including quantities and locations is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

Fish community sampling will occur from May to October during several sampling events. The sampling techniques to be used will include electrofishing, trap nets, gillnets, seining, and popnets (see the Fish Collection SOP).

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

3.0 EQUIPMENT LIST

- Fish holding tanks or live wells
- Measuring board
- Balance for weights
- Water quality meter
- Field notebook
- Cellular phone

4.0 PROCEDURES

Sampling for community studies will be conducted following protocols for fish collection sampling (see SOP for Fish Collection) and fish samples analyzed according to the procedures below. Sampling with trap nets will be conducted once a month for five days (Monday through

Friday) at a total of eight locations around the lake. Four nets will be sampled each day, with locations changed each day following sampling. The entire lake shoreline will be sampled monthly by electrofishing. Popnet sampling and beach seining will occur every three weeks from June to October to assess juvenile and prey fish communities at eight locations (same locations as tissue samples).

Fish Community Characterization:

1. Place fish in a live well for processing following collection.
2. Identify and count all fish collected during a sampling event. A maximum of 30 individuals of each species will be sampled for total length and weight and recorded in the field log.
3. During trapnet, popnet, and electroshocking sampling, stomach contents of fish will be evaluated using gastric lavage, or if the fish is too small for gastric lavage, by placing the fish in 70 percent ethanol for dissection of stomach contents in the laboratory (see Fish Stomach Sampling SOP). Stomach contents will be evaluated throughout the sampling events to evaluate potential seasonal changes in feeding preference.
4. For popnet samples, estimate the population density in the 9.3 square meter isolated area based on the Moran Zippin method (Zippin 1958).

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Personnel from SUNY-ESF and OCDWEP will be conducting the fish community assessments. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. A certified fisheries professional will oversee the QA/QC for the various activities.

6.0 REFERENCES

Zippin, C. 1958. The removal method of population estimation. J. Wildl. Manage. 22:82-90.

STANDARD OPERATING PROCEDURE SB-7:

SEDIMENT SAMPLE COLLECTION

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for surface sediment collection in Onondaga Lake. Surface sediment samples will be collected at locations sampled for benthic invertebrate tissue analysis. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the surface sediment sampling. The scope of work including quantities and locations is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

3.0 EQUIPMENT LIST

- Winch (if necessary);
- Boom arm or A-frame;
- Sediment core sampler (vibracore, piston tube, Wildco tube sampler, etc.);
- Core liners, core catchers, liner caps, etc.;
- Saw, knife, cutters to open or split core liners;
- 5 gal bucket
- mixing bowls
- spoon
- ruler/measuring device
- sampling vessel
- PFDs

- sample containers
- sample labels
- DGPS
- Digital camera
- Field notebook

4.0 PROCEDURES

Sample Collection

1. Upon arrival at a sampling station, position the boat in 1.0 to 1.5 m water depth.
2. Select a sediment core sampler (vibracore, piston tube, Wildco tube sampler, etc.) suitable for the bottom conditions, water depth expected, the volume of material needed, and the planned depth of sampling.
3. Select sediment coring tools of sufficient diameter and length to obtain the needed sample volume and depth of penetration. Depending on the volume of sediment needed, multiple sediment cores may need to be pushed. As much as possible, predetermine the number of cores required to avoid having to return to a location for additional cores/sample volume.
4. Set up the sediment coring tool and install the core liner tube, drive head, drive shoe, and/or core catcher, piston, and piston line, as appropriate for the specific sampler chosen and the proposed depth of sample/penetration.
5. Securely attach the core sampler to a winch with cable or line of sufficient strength to accommodate the weight of the sampler and sample (Vibracore) or other sampler (piston tube or Wildco tube sampler) to sufficient pipe to reach the maximum proposed sample depth.
6. Slowly lower the sampler through the moon pool or over the side until the sampler reaches the water/sediment interface. The sampler will be lowered on a winch cable and A-frame (Vibracore) or with the assistance of the winch and A-frame or boom to carry/control the weight of the pipe and piston tube or Wildco tube sampler. Note the depth to the top of sediment.
7. Advance the sediment core sampler into the sediment to the proposed depth or refusal, whichever comes first. If refusal is encountered, the sampling location will be moved slightly and the sample attempted again. The location where refusal was encountered will be noted. Three attempts will be made at a station. If a sample can not be collected after three attempts, the field crew will move on to the next station.
8. The Vibracore sampler will be advanced by the vibrating head. The Vibracore sampler will continue to be attached to the winch line and the rate of descent will be controlled during penetration into the sediment. The piston tube or Wildco tube samplers will be advanced manually. If necessary, the piston tube or Wildco tube

sampler may be advanced by tapping the top of the pipe with a rubber mallet. These samplers are intended for soft sediment and will not tolerate heavy abuse.

9. Slowly retrieve the sediment-coring tool. As soon as possible, cap the bottom of the sample tube to prevent loss of sample. Secure the sampling apparatus.
10. Remove the sediment core liner from the sampling apparatus.
11. Cap the bottom end of the core tube if it wasn't already capped.
12. Allow the core to drain, taking care not to disturb the surface of the sediment. At the first sign of sediment in the drained water sample, cease draining and tie or cap the sample liner to ensure that the sediment "fluff" layer is retained in the sample.
13. Cut off any empty core liner to eliminate head space. Cap the top of the core tube. Measure core recovery and confirm at least 15 vertical cm of sediment were collected. A core recovery of 70 percent or greater is required for the core samples.
14. Tape caps on so the caps do not leak or slip off during transport or storage.
15. Write the location ID and orientation (up arrow) on the outside of the core tube with a permanent marker. Record the top of sediment location on the core tube as well.
16. Store the core vertically on the vessel in a safe area where minimal disturbance to the sample will occur.
17. Transport sediment cores to the onshore processing area throughout the day.
18. Decontaminate the sediment coring apparatus in accordance with previously-implemented decontamination procedures (SOP 3; Parsons, 2005)
19. If insufficient core sample recovery (less than 60 percent) or refusal is encountered before reaching the proposed depth, repeat the process up to two more times in an attempt to obtain better recovery or better penetration. Select the core with the best percent recovery and penetration for sampling and analysis.
20. Process the core samples in accordance with previously implemented processing procedures (Parsons, 2008). Process the samples into intervals of 0 to 2 cm and 2 to 15 cm below the top of sediment. Record the total sample depth within each core and, if possible, mark the top of sediment location on the outside of each core tube.
21. Record a description of the sediment within the field log for each location sampled.

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Sediment collection will be conducted by OCDWEP or QEA personnel; core processing will be conducted by Parsons. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field

Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

REFERENCES

Parsons. 2005. Onondaga Lake Predesign Investigation: Standard Operating Procedures. Prepared for Honeywell. November 2005.

Parsons. 2008. Onondaga Lake Predesign Investigation: Phase III Addendum 6. SMU 8 Sampling to Monitor Natural Recovery. Prepared for Honeywell. Revised January 2008 (See Appendix A for the sediment sample collection procedure.)

STANDARD OPERATING PROCEDURE SB-8:

PHYTOPHILOUS MACROINVERTEBRATE SAMPLING

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for phytophilous macroinvertebrate sampling in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the phytophilous macroinvertebrate sampling. Phytophilous invertebrate sampling will be conducted to collect organisms for assessing community composition. Macroinvertebrates that are associated with the macrophyte structures above the sediments (and not including those associated with the root structure witin the sediments) will be sampled. The scope of work, including quantities and locations, is defined in the Work Plan. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, and falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

3.0 EQUIPMENT LIST

-petite ponar dredge

-19 liter (5 gallon) bucket

-600 micron mesh bottom bucket

-sampling vessel

-PFDs

-sample containers

-knife or scissors to remove roots

-10 percent buffered formalin

-rose bengal dye

-sample labels

-DGPS

-resealable plastic bags

-sample vials

-75 percent ethanol

-enamel pan

-plexiglass divider for subsampling

-forceps

-spatula

-600 micron sieve

-dissecting microscope

-petri dish

-digital camera

-field notebook

4.0 PROCEDURES

1. Determine ahead of time which transects will be sampled based on proximity to benthic invertebrate sampling locations.

2. Upon arrival at a transect, station the boat in 1.0 to 1.5 m [3.3 to 4.9 ft] water depth over a macrophyte bed.

3. Lower the petite ponar over the side of the boat with a cable or rope. Allow the sampler to freefall from the lake surface to allow it to penetrate the bottom. The closing mechanism is activated upon reaching the bottom.

4. Retrieve the sampler. Check the sample for acceptability. A sample is considered acceptable if it is not over-filled with sediment, overlying water is present and not excessively turbid, the sediment surface is relatively flat, and the desired plant material has been obtained. Cut the above grade portion of the aquatic macrophytes at the base. Discard the below grade portion of the sample.
5. Place the sample in a 600 micron mesh bottomed plastic bucket held over the side of the boat. Rinse excess sediment from the sample. Place the macrophytes in a resealable bag labeled with unique sample number, date, station, and sampler initials.
6. Add 10% buffered formalin with rose bengal dye to the bag to preserve the sample and bring to the lab for sorting and identification.
7. Repeat steps 3 through 6 until 5 replicates have been collected at a location.
8. Proceed to the next transect and repeat steps 2 through 7.
9. In the laboratory, rinse the sample with tap water in a 600 µm standard sieve to remove any fine particles left in the residues from field sieving.
10. Transfer the sample to an enamel pan and distribute homogeneously over the bottom of the pan.
11. Using a plexiglass divider split the sample into quarters.
12. Randomly select a single quarter and remove the sample with a spatula and forceps and place in a petri dish with water.
13. Examine this portion under a dissecting stereomicroscope and remove 100 organisms from the debris and plant material according to Bode et al. (2002).
14. As they are removed, sort the invertebrates into major groups and place in vials containing 75 percent ethanol. If less than 100 organisms are encountered, randomly select another quarter from the enamel pan and continue removing organisms from the debris. Continue subsampling until at least 100 organisms are removed. After 100 organisms are encountered, complete the subsample so an abundance estimate can be calculated (number per m2).
15. Identify the organisms to the lowest taxonomic level reasonably achievable. Identify macrophytes to species.
16. Record the number of individuals in each taxon, and the total number of individuals in the sample on a data sheet.

17. Archive samples in 75 percent ethanol at SUNY ESF. Label sample vials with unique sample number, date, station, replicate number, sampler, taxon, and number of individuals.

18. Retain the remainder of the sample in 75 percent ethanol for up to one year in case questions arise about taxanomic ID or counts of organisms. Label sample container with unique sample number, date, station, replicate number, and sampler initials.

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Phytophilous macroinvertebrate sampling will be conducted by SUNY-ESF personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. These considerations are discussed in more detail in the project safety plan.

6.0 REFERENCES

R.W. Bode M. Novak, L. Abele, D. Heitzman, and A. Smith. 2002. Quality Assurance Work Plan For Biological Stream Monitoring in New York State. New York State DEC Division of Water.

STANDARD OPERATING PROCEDURE SB-9:

LITTORAL ZONE SURFACE WATER SAMPLING

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for littoral zone surface water sampling in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the surface water sampling. The purpose of littoral water sampling is to understand the movement of mercury/methylmercury generated from the hypolimnion during and following fall turnover into the surface waters of the lake for assessing exposure to biota. Littoral water samples will be collected at six fish sampling locations within the littoral zone (four in the south basin and two in the north basin). These water samples will be collected during three events - one event prior to fall turnover (July or August) and two events following fall turnover (late October to mid-to-late November). These samples will be analyzed for total mercury and for methylmercury (unfiltered). These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager in consultation with NYSDEC.

Before samples are collected, the sample collection vessels and sample containers will be cleaned by the laboratory using detergent, mineral acids, and reagent water. Reagent water is defined as water prepared by the laboratory in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method(s). After cleaning, sample containers will be filled with weak acid solution, and individually double-bagged using resealable plastic bags. Sample collection vessels will be placed in plastic bags to minimize contact with metal or atmospheric deposition of particles containing metal.

Upon arrival at the sampling site, one member of the two-person sampling team will be designated to perform duties that may result in contact with potential contaminants, and will not perform any tasks that result in direct contact with samples ("dirty hands"). The second member will perform all activities that may result in contact with the sample containers or transfer of the sample ("clean hands"). Sampling personnel are required to wear clean gloves at all times when handling sampling equipment and containers.

Preservation of samples with dilute nitric acid will be performed immediately upon arrival at the laboratory, where the samples will be allowed to equilibrate for a minimum of 48 hours prior to analysis.

Appropriate field documentation will be maintained using a computerized sample tracking system.

2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, and falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

3.0 EQUIPMENT LIST

Equipment needed for collection of water samples for mercury and methyl mercury analysis includes:

- pre-cleaned glass or Teflon sample collection vessels
- disposable gloves
- reagent water (free of metals; supplied by laboratory)
- 5 gallon plastic carboy (for storage of dilute acid wastes from pre-cleaned sample containers)
- plastic (polyethylene) resealable food storage bags
- plastic (polyethylene) food wrap
- plastic (polyethylene) trash bags
- dedicated, clean cooler with ice
- boat and motor
- Global Positioning System (GPS)
- lap top computer and printer
- field log-Sampling vessel
- PFDs
- digital camera
- field notebook

- sample labels

4.0 PROCEDURES

Sample Collection

1. Navigate the sampling vessel to the desired sampling station using GPS.

2. From this point forward, sample handling procedures will follow USEPA's "clean hands/dirty hands" protocols whenever handling materials that may come in contact with the sample. One person of the two person sampling crew will be designated to perform the "clean hands" duties, while the other will perform the "dirty hands" duties.

3. Both sampling personnel will put on two pairs of disposable gloves. The outer pair of gloves will be changed any time there is potential for the outer gloves coming in contact with potential contaminants.

4. Pre-cleaned sample containers will be pre-labeled and double bagged using resealable food storage bags, and placed in a clean, dedicated cooler. Sample containers will be labeled in accordance with the QAPP.

5. "Dirty hands" will open the cooler and the outer plastic bag containing the appropriate sample container.[both should change gloves after handling the sampler and prior to opening the outer and inner bags] "Clean hands" will then open the inner plastic bag, poor the dilute acid solution out into a carboy container designated for waste storage.

6. "Clean hands" will immerse the sample container into the lake without disturbing the sediment. The sample will be collected from the top 12 inches of the water column.

7. "Clean hands" will then place the cap back on the container, and place it inside the inner bag, and then place the inner bag inside the outer bag, held by "Dirty hands". "Dirty hands" will then close the outer bag, and place the double bagged container back in the cooler. This process will be repeated at each location.

Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in the QAPP. Samples will be collected in accordance with the procedures described in Section 7 above. Each container will be placed in two re-sealable food storage bags (double bagged, one inside the other), and placed in a clean dedicated cooler. The samples will be chilled with ice to approximately 4° C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be shipped by overnight delivery to the laboratory at the end of each day and preserved with nitric acid upon arrival. Samples will be allowed to equilibrate after preservation

for a minimum of 48 hours prior to analysis. Chain of custody procedures will be followed, as specified in the QAPP.

Data and Records Management

Data from water sample collection will be recorded in the field database using a laptop computer. Upon completion of sampling at one location, all data from the location will be entered into the database and the field log for that location printed and the hard copy stored in the field notebook. This will limit the risk of losing sample information due to computer failure. Blank field log sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in the QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected are blind duplicate samples, equipment blank samples, and matrix spike samples. One set of field QA/QC samples will be collected for each sampling event. Blind duplicate samples and matrix spike samples will be prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each sampling event. Equipment blank samples will be prepared as follows:

1. Prepare for “clean hands/dirty hands” procedures (put on new disposable gloves).

2. “Clean hands” will pour the dilute acid solution out into a carboy container designated for waste storage.

3. “Clean hands” will then slowly pour laboratory supplied reagent water into a clean sample container while “dirty hands” hold the container stable.

4. After collection, handle equipment blank samples in a manner that is consistent with all other environmental samples.

5.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Surface water sampling will be conducted by QEA personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed

to perform this procedure. Qualifications will be based on previous experience and health and safety training. These considerations are discussed in more detail in the QEA project safety plan.

6.0 REFERENCES

USEPA. 1996. Method 1669. Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency. Office of Water Engineering and Analysis Division (4303). July, 1996.

SOP LB-1

MERCURY (COLD VAPOR TECHNIQUE)
SW-846 METHOD 7471A

Title: Mercury (Cold Vapor Technique)
[SW-846 Method 7471A]

Approvals (Signature/Date):

William S. Cicero — 12/27/07 Date
Laboratory Director

Jessica A. Holzschuh — 12/27/07 Date
Current Department Manager

Kirstin L. McCracken — 12/27/07 Date
Quality Assurance Manager

Bryce E. Stearns — 12/27/07 Date
Technical Director

Bryce E. Stearns — 12/27/07 Date
Interim Health & Safety Coordinator

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-HG-7471.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

STL BURLINGTON
STANDARD OPERATING PROCEDURE

MERCURY (COLD VAPOR TECHNIQUE)
SW-846 Method 7471A
Applicable Matrix: Solid and Chemical Materials

APPROVAL SIGNATURES

William S. Cicero
Laboratory Director
Date: January 31, 2007

Kirstin L. McCracken
Quality Assurance Manager
Date: January 31, 2007

Nicholas J. Rosner
Department Supervisor
Date: January 31, 2007

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials.

1.2 The routine RL for solid samples is 0.033 mg/Kg based on a sample digestion weight of 0.3 grams and a final volume of 50 mL.

2.0 SUMMARY OF METHOD

2.1 A portion of solid sample is acid digested for 2 minutes at a temperature of 95°C then digested with potassium permanganate and potassium persulfate for 30 minutes at a temperature of 95°C. Hydroxylamine hydrochloride is added to each digestate in order to reduce excess permanganate. The digestate is placed on a closed-system mercury autoanalyzer and stannous chloride is added to each sample. The elemental mercury released is measured spectrophotometrically at a wavelength of 253.7 nm. The concentration is calculated from the response of the sample absorbance applied against the calibration curve.

2.2 This procedure is based on SW-846 Method 7471A, Revision 1, September 1994.

3.0 DEFINITIONS

3.1 A list of terms and definitions is given in Appendix A.

4.0 INTERFERENCES

4.1 Potassium permanganate is added to the samples to eliminate possible interference from sulfide. Copper has also been noted as an interferent but per reference method SW-846 7471A concentrations as high as 10mg/Kg had no effect on recovery of mercury from spiked samples.

4.2 Samples high in chlorides may require additional permanganate because during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253nm. Care must be taken to ensure free chlorine is not present and this is accomplished by the addition of hydroxylamine hydrochloride and stannous chloride.

5.0 SAFETY

5.1 Employees must be trained on and adhere to the policies and procedures for safety in the Corporate Safety Manual and this document.

5.2 Safety Concerns or Requirements

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added. Protective clothing

such as a lab coat, safety glasses and latex gloves must be worn while performing this procedure.

5.3 Primary Materials Used

Table 1, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 Mercury Auto-Analyzer; Leeman Labs PS 200 and Leeman Labs Hydra AA with Autosampler or equivalent.

6.2 Block Digester, capable of maintaining temperature at 90-95°C: Environmental Express or equivalent.

6.3 Polyethylene Digestion Vessels, 100mL volume with Volumetric Indicators: Environmental Express or equivalent,.

6.4 Volumetric Autopipettes, Range of use 0.2-1.0mL & 1.0-5.0mL: Finpipette or equivalent.

6.5 Top Loading Balance capable of measurements to 0.1mg.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagent Water

Aqua Regia: Prepare by carefully adding 3 volumes of concentrate HCl to one volume of concentrated nitric acid.

Nitric Acid (HNO_3), Concentrated: Reagent Grade: J.T. Baker or equivalent.

Hydrocloric Acid (HCl), Concentrated: Reagent Grade: J.T. Baker or equivalent.

Hydroxalimine Hydrochloride: Reagent Grade: J.T. Baker or equivalent.

Potassium Permanganate: Reagent Grade: J.T. Baker or equivalent.

Stannous Chloride Dihydrate Crystal ($SnCl_2$): Reagent Grade, J.T. Baker or equivalent.

HCl (10%): Add 100mL of concentrated HCl to a 1 L volumetric flask containing ~800 mL of reagent water. Adjust to final volume with reagent water.

Stannous Chloride Solution: Add 200 g of $SnCl_2$ to 2 L of 10% hydrochloric acid.

Hydroxylamine Hydrochloride: Dissolve 240 g of Hydroxylamine Hydrochloride in 2 L of reagent water.

Potassium Permanganate ($KMNO_4$): 5% solution w/v: Dissolve 100g of $KMNO_4$ in 2 L of reagent water.

7.2 Standards

Mercury (Hg) Stock Standard Solution (1000mg/L), Spex.

Hg Mercury Intermediate Standard (10,000ug/L): Add 1.0 mL of 1000 mg/L Hg Stock Standard Solution and 0.15 mL of concentrated HNO_3 to a 100 mL volumetric flask that contains approximately 80 mL reagent water. Adjust to volume with reagent water. Assign an expiration date of six months from the date made, or the manufacturers date, whichever is sooner.

Hg Working Standard (100 ug/L): Add 1.0 mL of the Hg Intermediate Standard Solution and 0.15 mL of concentrated HNO_3 to a 100 mL volumetric flask that contains approximately 80 mL reagent water. Adjust to volume with reagent water. Use this standard to prepare the calibration standards (ICAL & CCV). Prepare this standard each day of use.

ICV Stock Standard Solution (1000 mg/L), Inorganic Ventures.

ICV Intermediate Standard Solution (10,000 ug/L): Add 1.0 mL of the 1000 mg/L ICV Stock Standard Solution and 0.15 mL of concentrated HNO_3 to a 100 mL volumetric flask that contains approximately 80 mL reagent water. Adjust to volume with reagent water. Assign an expiration date of six months from the date made, or the manufacturers date, whichever is sooner.

ICV Working Standard Solution (30 ug/L): Add 1.5 mL of the ICV Intermediate Standard Solution and 0.75 mL of concentrated HNO_3 into a 500 mL volumetric flask that contains approximately 300 mL reagent water. Adjust to volume with reagent water. Assign an expiration date of six months from the date made, or the manufacturers date, whichever is sooner.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Samples should be collected in glass or polyethylene containers. Immediately following collection the samples should be cooled to a temperature of 4°C (±2) and maintained at that temperature until digestion.

8.2 The holding time is 28 days from collection of the sample.

8.3 Unless otherwise specified by client or regulatory program, after digestion and analysis, samples are retained for 60 days and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1 QC Requirements

The following QC samples are analyzed with each digestion batch: Method Blank (MB) Laboratory Control Sample (LCS), a Matrix Spike (MS), and a Sample Duplicate (SD). Some clients and/or regulatory programs may require a Matrix Spike Duplicate (MSD) instead of and/or in addition to the sample duplicate.

In addition to calibration (ICAL), instrument standardization is checked with the following QC samples, Initial Calibration Verification (ICV), Continuing Calibration Verification (CCV), and Calibration Blanks (ICB/CCB). A low level standard (CRI) is analyzed per client request. Sample results that exceed the range of calibration are diluted and reanalyzed such that the diluted sample result in near the midpoint or in the upper half of the calibration range.

The minimum frequency requirements, acceptance criteria and recommended corrective action for QC samples are summarized in Table 2, Section 18.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration

Calibrate the autoanalyzers daily with five calibration standards and a blank using the instrument operating conditions established by the instrument manufacturer. Prepare the calibration standards daily by making successive dilutions of the Hg Working Standard Solution (100 ug/L) in reagent water to achieve a final volume of 50 mL. The final concentration of the prepared calibration standards is as follows:

Calibration Standards

Level	Hg Standard 100ug/L (mL)	Final Volume (mL)	Final Concentration (ug/L)
Blank	0	50	0
Level 1	0.1	50	0.2
Level 2	0.25	50	0.5
Level 3	0.5	50	1
Level 4	2.5	50	5
Level 5	5	50	10

Process the calibration standards following the procedures given in Section 11.1. The instrument data system constructs a standard curve by plotting the instrument response from each standard solution against the final concentration and using linear regression, the data system calculates the correlation coefficient. The correlation coefficient must be greater than or equal to 0.995.

10.2 Initial Calibration Verification (ICV)

Following calibration, analyze the ICV. The ICV is a second source standard whose concentration (3 ug/L) is near the midpoint of the calibration range but at a different concentration than the CCV (5 ug/L). Process the ICV following the procedure given in Section 11.1. The percent recovery of the ICV must be within 90-110%.

10.3 Continuing Calibration Verification (CCV).

Analyze a CCV following the ICB, after every 10^{th} sample and at the end of the sample run. The CCV standard is at a concentration of 5 ug/L and is prepared from the same source of standard used for the calibration standards. Process the CCV following the procedure given in Section 11.1. The percent recovery of the CCV must be 80-120%.

10.4 Calibration Blanks (ICB/CCB)

Analyze an initial calibration blank (ICB) after the ICV. Analyze a continuing calibration blank (CCB) after each CCV. The results of each calibration blank must be less than the RL.

10.5 Support Equipment Calibration

Check the calibration of the auto-pipettes and the top-loading balance on the day of use prior to use and record the calibration check in the logbook designated for this purpose.

11.0 PROCEDURE

11.1 Sample, QC & Standard Preparation

Weigh 0.3 g of sample into a polyethylene digestion vessel. Add 5 mL of reagent water. Use reagent water for the method blank (PBS), the laboratory control sample (LCS), and each calibration blank. Add 1 mL of the Hg working standard solution (100 ug/L) to the LCS and the matrix spike.

To prepare the ICV, transfer 5 mL of the ICV working standard solution (30 ug/L) to a labeled polyethylene digestion vessel and add 45 mL of reagent water.

For each CCV, transfer 2.5 mL of the Hg working standard solution (100 ug/L) to a labeled polyethylene digestion vessel and add 47.5 mL of reagent water.

If analysis of a low-level standard is requested, transfer 0.1 mL of the Hg working

standard solution (100 ug/L) to a labeled polyethylene digestion vessel and adjust the volume to 50 mL with reagent water.

11.2 Digestion

To each sample, standard, and blank add 2.5 mL of aqua regia. Heat for 2 minutes in a digestion block at 95°C. Allow the samples to cool then add 20 mL of reagent water, 7.5 mL of potassium permanganate, and swirl to mix. Return to the block for 30 minutes. Cool and, when ready to analyze, add 3 mL of hydroxylamine hydrochloride to reduce the excess permanganate. Swirl each vessel to ensure that any soluble residue dissolves back into solution. If the color of any sample is still purple, add hydroxylamine hydrochloride in 3 mL increments until the purple color disappears. Add 25 mL of reagent water to each vessel and transfer the digestate to individual autoanalyzer tubes for analysis.

11.3 Instrument Set Up & Analysis

Turn the instrument lamp, gas and pump on and allow 15 minutes for the instrument to warm up. Fill the rinse bath with 10% hydrochloric acid solution. Check all tubing connections and reset the calibration curve. Check the stannous chloride reductant reservoir and fill if necessary.

Select the autosampler template and enter the sample IDs in the order of analysis. Place the samples, calibration blanks, calibration standards, and performance check standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis. An example analytical sequence is given below:

Example Analytical Sequence:
Calibration Blank
0.2 Calibration Standard
0.5 Calibration Standard
1.0 Calibration Standard
5.0 Calibration Standard
10.0 Calibration Standard
ICV
ICB
CRI (if requested)
CCV
CCB
PBS
LCS
7 Samples*
CCV
CCB
9 Samples*

CCV
CCB

**The number of samples between each CCB/CCV (10) includes the method blank, laboratory control sample, matrix spikes, and sample duplicates.*

During analysis, the data processing system constructs a calibration curve by plotting the absorbances of standards versus units of mercury and sample concentrations are determined from the calibration curve.

After analysis is complete, review the data against the criteria given in Table 2, Section 18.0 and perform corrective action, as needed. Dilute and reanalyze any samples that exceed the linear range.

12.0 CALCULATIONS

12.1 Concentration

$$C_{(mg/Kg\ drywt.)} = \frac{\mu g}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\ solids}$$

Where:
$\mu g/L_{dig}$ = Instrument result adjusted for dilution factors
V_{dig} = Final digestate volume in liters
g_{samp} = Sample weight in grams
% Solids = Percent solids to nearest 0.1%

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the acceptance criteria in Table 2, Section 18.0. If the results do not fall within the established limits or criteria, corrective action is required as contained in Table 2. Recommended corrective action is provided in Table 2. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 A demonstration of analyst capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC procedures are further described in the laboratory SOP for employee training.

14.2 A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. The procedure and acceptance criteria for MDL studies are given in the laboratory SOP for method detection limit studies.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 The following waste streams are produced when this method is carried out.

- Acid Waste, Digested Samples, Expired Hg Standards

→ *Satellite Waste Container: 55 Gallon Closed Topped Poly labeled "CORROSIVE"*

Transfer the waste stream to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waster storage room for future disposal in accordance with Federal, State and Local regulations, The procedures for waste management are further given in the laboratory SOP LP-LB-001 *Hazardous Waste.*

16.0 REVISION HISTORY

16.1 Title Page: Changed to reflect current management team.

16.2 Section 6.0; replaced water bath with digestion block

16.3 Section 7.0: Added vendor detail.

16.4 Section 7.1: Removed Potassium Persulfate and Potassium Persulfate, 5% Solution. Added Stannous Chloride Dihydrate Crystal. Stannous Chloride Solution changed Stannouse Chloride Dihydrate Crystal grams used and changed liters of hydrochloric acid used.

16.5 Section 7.2: Changed concentration of ICV Working Standard Solution. Also changed mLs of ICV intermediate standard used for that solution.

16.6 Section 11: Added "if requested" to analytical sequence, changed water bath reference in procedure to block digester. Eliminated redundant sample table entry information (duplicate sentence)

16.7 Section 11.1: Changed all volumes in the second and third paragraph. All cut in half.

16.8 Section 11.2: volume of Hydroxylamine hydrochloride used if color still purple cut in half.

16.9 Section 11.3: Added PBS and LCS to analytical sequence.

16.10 Seciton 15.2: Satellite waste container information.

16.11 Table 2; changed DoD blank criteria to 2X MDL

17.0 REFERENCES

17.1 Method 7471A Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique), Revision 1, September 1994. Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986.

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1: Primary Material Used
18.2 Table 2: QC Summary, Acceptance Criteria, Recommended Corrective Action

Table 1: Primary Materials Used (Mercury / CVAA)

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Frequency, Criteria and Recommended Corrective Action (SW-846 7471A)

QC Check	Acronym	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	ICAL	Daily	r ≥ 0.995	Correct problem and repeat calibration
Initial Calibration Verification	ICV	After each calibration, prior to sample analysis.	±10% of expected value	Correct problem, verify second source standard. If that fails, repeat calibration.
Initial Calibration Blank	ICB	Beginning of analytical sequence after ICV	No analytes ≥RL DoD: ≥2XMDL	Correct problem and reanalyze
Low Level Standard	CRI	Per Client Request	%R (30-131) [1]	Correct problem, then reanalyze
Continuing Calibration Verfication	CCV	Beginning of sequence, after every 10 samples and at the end of the analytical sequence	±20% of expected value	Correct problem, reanalyze CCV. If that fails, repeat calibration and reanalyze all samples since last successful calibration.
Calibration Blank	CCB	After every 10 samples and at end of the sequence (i.e. after each IPC)	No analytes ≥RL DoD: ≥2XMDL	Correct problem and reanalyze the calibration blank and previous 10 samples.
Method Blank	MB	One per digestion batch	No analytes ≥RL DoD: ≥2XMDL	Correct problem, redigest and reanalyze MB and associated samples.
Laboratory Control Sample	LCS	One per digestion batch	%R (85-115)	Correct problem, redigest and reanalyze LCS, MB and associated samples for failed analytes if sufficient sample volume is available.
Matrix Spike	MS	One per batch of twenty samples or less	%R (85-115)	Examine project DQO's with Project Manager. Evaluate data to determine if outage is related to analytical error or matrix effect.
Matrix Spike Duplicate	MSD	Per client request Arizona: 1 MS/MSD per batch	%R (85-115)	Examine project DQO's with Project Manager. Evaluate data to determine if outage is related to analytical error or matrix effect.
Sample Duplicate	SD	One per batch of twenty samples or less	RPD ≤ 20	Examine project DQO's with Project Manager. Evaluate data to determine source of difference between results

[1] *The control limits for the low level standard (CRI) are based on control charts and are subject to change each time control charts are generated.*

Appendix A: Terms & Definitions

Analyte: The element or ion an analysis seeks to determine; the element of interest.

Analytical Sequence: The actual instrumental analysis of the samples from the time of instrument calibration through the analysis of the final CCV or CCB.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards.

Calibration Blank: A blank solution containing all of the reagents and in the same concentration as those used in the analytical sample preparation.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Interferents: Substances which affect the analysis for the element of interest.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Relative Percent Difference (RPD): As used in the SOW and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

Sample: A portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

SOP LB-2

ANALYSIS OF POLYCHLORINATED DIOXINS/FURANS BY HIGH RESOLUTION GAS CHROMATOGRAPHY/HIGH RESOLUTION MASS SPECTROMETRY (HRGC/HRMS) BASED ON METHODS 8290, 1613B, 23, 0023A, AND TO-9A

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 1613B, 23, 0023A, and TO-9A

(SUPERSEDES: KNOX-ID-0004, Rev. 6)

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1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 8290, 1613B, 23, 0023A, or TO-9A is specified.

1.2 The seventeen 2,3,7,8-substituted PCDDs/PCDFs listed in Table 1 may be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In addition, total homologs (i.e., Total TCDD, Total TCDF, etc.) may be identified by this method.

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be quantitated with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 13 and Table 15. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged with hexane. The extract is then subjected to one or more cleanup steps to remove the sample of interferences. The final extract is prepared by adding a known amount of the labeled recovery standards (13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acid coextractables. If such interferences are not removed before column chromatography, they may cause a shift in the predicted elution pattern.

Conditions which may indicate the need for this procedure are: samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances. The identification of 2,3,7,8-TCDF is confirmed on an isomer specific (DB-225) GC column.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 5 and Table 6.

3.4 Cleanup Standard: $^{37}Cl_4$-2,3,7,8-TCDD which is added to samples, blanks, quality control samples, and calibration solutions. It is added to the samples after extraction but prior to extract cleanup, and is used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley < 25%).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 5 and Table 6.

3.8 Detection Limit (DL): The minimum concentration of the target analyte that can be detected. Sample specific detection limits are calculated from the instrument noise level and internal standard response.

3.9 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.10 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal in the same retention time region as a target analyte but which does not meet the other qualitative identification criteria defined in the procedure.

3.11 GC: Gas chromatograph or gas chromatography

3.12 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.13 HRGC: High resolution GC

3.14 HRMS: High resolution MS

3.15 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the initial calibration to verify the concentration of the Initial Calibration Standards.

3.16 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.17 IPR: Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

3.18 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.19 Laboratory Blank: See Method Blank.

3.20 Laboratory Control Sample: See Ongoing Precision and Recovery Standard (OPR).

3.21 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.22 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix, free of the targets of interest and interferences, that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.23 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.24 MS: Mass spectrometer or mass spectrometry.

3.25 Multiple Ion Detection (MID): A MS operational mode in which only selected ions are monitored rather than scanning the instrument to obtain a complete mass spectrum.

3.26 OPR: Ongoing precision and recovery standard; a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.27 PAR: Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.28 PCDD: Polychlorinated dibenzo-p-dioxins.

3.29 PCDF: Polychlorinated dibenzofurans.

3.30 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.31 Recovery Standard: $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standard.

3.32 Relative Percent Difference (RPD): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.33 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples.

3.34 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.35 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.36 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

3.37 Additional definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2 The use of high purity reagents and solvents helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile clean room gloves are worn. For operations using solvents that splash, silver shield gloves are recommended. Silver shield gloves protect against breakthrough for most of the solvents used in this procedure

5.3 Finely divided dry soils contaminated with PCDDs and PCDFs may be particularly hazardous because of the potential for inhalation and ingestion. Such samples are to be processed in a confined environment, such as a hood or a glove box.

5.4 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.5 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.6 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source may be removed from the vacuum manifold through a vacuum interlock.

5.7 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument may be left on.

5.8 Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.9 When using a scalpel, cut away from yourself. If you are holding something, cut away from your hand.

5.10 Equipment goggles or a face shield must be used when employees are using solvents to rinse or clean glassware.

5.11 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	Corrosive, Oxidizer, Dehydradator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive, Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Hydrochloric Acid	Corrosive, Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methylene chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Cyclohexane	Flammable, Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. High concentrations have a narcotic effect.
Tetradecane	Irritant	None established	Inhalation of vapors may cause difficulty breathing, headache, intoxication and central nervous system damage.
Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim may experience tightness in the chest, breathlessness, and loss of consciousness.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation.
Potassium Hydroxide	Corrosive, Poison	2 mg/m3 ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on the severity of exposure. Symptoms may include coughing, sneezing, and damage to the nasal or respiratory tract. High concentrations can cause lung damage. Corrosive! Contact with skin can cause irritation or severe burns and scarring with greater exposures.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.11.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8-substituted PCDD or PCDF isomers.

Note: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.12 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.13 The preparation of all standards and reagents and glassware cleaning procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.14 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

5.15 Training: Workers must complete the employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.16 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.17 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Benchtops should be covered with plastic backed absorbent paper.

5.18 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.19 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

6. Equipment and Supplies

6.1 Sample Extraction Equipment.

Note: All glassware used in extraction and cleanup procedures is solvent rinsed twice before use with acetone, toluene, methylene chloride and hexane in that order. Pre-extract the Soxhlet apparatus with toluene for at least 4 hours. Rinse glassware with all 4 solvents once. See SOP KNOX-QA-0002, current revision, “Glassware Cleaning”, for details.

6.1.1 Aqueous Sample Extraction

6.1.1.1 Multi-position separatory funnel rotator.

6.1.1.2 2000 mL separatory funnels with PFTE stopcocks and PFTE stoppers.

6.1.1.3 100 mm glass funnels with short stems.

6.1.1.4 Class A 1 mL pipettes.

6.1.1.5 1000 mL graduated cylinders.

6.1.1.6 PFTE squirt bottles, 500 mL.

6.1.1.7 Syringes.

6.1.1.8 Glass wool, precleaned with methylene chloride.

6.1.1.9 Buchner funnels, filter flasks, rubber stopper and GF/D filters

6.1.1.10 Vacuum source.

6.1.2 Soxhlet Extraction

6.1.2.1 Analytical balance, capable of weighing to 0.01 g.

6.1.2.2 Stainless steel spatula.

6.1.2.3 Stainless steel tweezers.

6.1.2.4 Soxhlet extractor or Dean-Stark Soxhlet extractor.

6.1.2.5 Heating mantles with temperature controls.

6.1.2.6 500 mL evaporative flask, round bottom.

6.1.2.7 Glass condenser, compatible with the dean-stark extractor.

6.1.2.8 Class A 1 mL pipettes.

6.1.2.9 Glass wool, precleaned with methylene chloride.

6.1.2.10 High purity glass fiber Soxhlet thimble.

6.1.2.11 Boiling beads, 6 mm glass.

6.1.2.12 PFTE boiling chips.

6.1.3 Waste Dilution

6.1.3.1 Analytical balance, capable of weighing to 0.01 g.

6.1.3.2 40 mL vial, with PFTE lined cap.

6.1.3.3 5 ¾ inch borosilicate glass pipets.

6.1.3.4 Rubber bulbs.

6.1.3.5 1 ml Class A pipette.

6.2 Sample Cleanup Equipment.

6.2.1 Acid-base cleanup

6.2.1.1 Disposable Pasteur pipets and rubber bulbs.

6.2.1.2 Graduated cylinder, 100 mL volume.

6.2.1.3 Vials, 40 mL volume, with PFTE lined caps.

6.2.2 Dual column cleanup

6.2.2.1 Disposable glass columns.

6.2.2.1.1 20mm x 240mm custom glass column with support ring and tapered tip.

6.2.2.1.2 16mm x 240mm custom glass column with support ring and tapered tip.

6.2.2.2 Aluminum support rack for custom columns.

6.2.2.3 Amber-colored glass jar with a PFTE lined screw cap, 250mL.

6.2.2.4 Volumetric flask, 100 mL volume.

6.2.2.5 Disposable Pasteur pipets and rubber bulbs.

6.2.2.6 Bottletop solvent dispenser.

6.2.2.7 40 mL vials with PFTE lined screw caps.

6.2.2.8 Volumetric flask, 100mL

6.2.2.9 Graduated cylinder, 100 ml.

6.2.2.10 Solvent waste collection jars, 125mL.

6.2.2.11 Marking pen.

6.2.3 Activated carbon cleanup

6.2.3.1 10 mL disposable pipet for use as the column.

6.2.3.1.1 All disposable carbon columns are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order).

6.2.3.2 Glass wool, precleaned with methylene chloride.

6.2.3.3 25 mL graduated cylinder

6.2.3.4 40 mL vials.

6.3 Sample Concentration Equipment.

6.3.1 Macro Concentration Equipment – Rapid-Vap

6.3.1.1 Labconco Rapid-Vap concentrator

6.3.1.2 600 mL sample concentrator tubes, Labconco or equivalent.

6.3.1.3 Borosilicate 5.75 inch and 9.0 inch disposable pipettes.

6.3.1.4 Rubber bulbs.

6.3.1.5 Borosilicate 40 mL disposable vials with PFTE lined screwcaps.

6.3.2 Macro Concentration – Snyder Column

6.3.2.1 Heating mantles with temperature controls.

6.3.2.2 Three-ball macro Snyder column.

6.3.2.3 Rubber bulbs.

6.3.2.4 Nine inch borosilicate glass pipets.

6.3.2.5 40 mL vial, with PFTE lined cap.

6.3.2.6 PFTE boiling chips.

6.3.3 Micro Concentration – N-Evap

6.3.3.1 Nitrogen blowdown apparatus (N-EVAP or equivalent).

6.3.3.2 Mini vials, 1.1 mL capacity with a tapered bottom; with PFTE faced, rubber septa and screw caps.

6.4 Sample Analysis Equipment.

6.4.1 Gas Chromatograph --- Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specification in Section 10.

6.4.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD --- 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent.

6.4.1.2 GC column for isomer specificity for 2,3,7,8-TCDF --- 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent.

6.4.2 Mass Spectrometer --- Electron impact ionization with the filament eV's optimized for best instrument sensitivity, stability and signal to noise ratio. Shall be capable of

repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and shall meet all of the performance specifications in Section 10.

6.4.3 GC/MS Interface --- The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam

6.4.4 Data System --- Capable of collecting, recording, and storing MS data.

7. Reagents and Standards

7.1 Sample Pre-Treatment

7.1.1 Hydrochloric acid (HCl), concentrated 37% wt in water (ACS), Mallinkcrodt AR Select or equivalent.

7.1.2 1N HCl - Carefully add 83mL of concentrated HCl to 917 mL of reagent water in a glass container.

7.2 Aqueous Extraction

7.2.1 Acetone, pesticide quality or equivalent.

7.2.2 Toluene, pesticide quality or equivalent.

7.2.3 Methylene chloride, pesticide quality or equivalent.

7.2.4 Hexane, pesticide quality or equivalent.

7.2.5 Tetradecane, pesticide quality or equivalent.

7.2.6 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 mega ohm (MΩ) resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2.7 Sodium sulfate, reagent grade, granular, anhydrous (J.T Baker 3375, or equivalent)- Sodium Sulfate is cleaned by putting approximately 600g of Sodium Sulfate in large amber-colored glass jars and completely covering with methylene chloride, stirring the mixture with a stirring rod and letting the Sodium Sulfate soak for 5 minutes. The methylene chloride is drained and this step is repeated. After the methylene chloride is drained the Sodium Sulfate is transferred to a Buchner Funnel fitted onto a Vacuum Flask and is rinsed 2 times with methylene chloride while a vacuum is being applied to the apparatus. The Sodium Sulfate is then placed into shallow borosilicate glass dishes where it is allowed to dry. After drying, the Sodium Sulfate is transferred into pre-cleaned glass jars with fluoropolymer lined screw caps and are placed in a desiccator until needed.

7.3 Soxhlet extraction

7.3.1 Acetone, pesticide quality or equivalent.

7.3.2 Toluene, pesticide quality or equivalent.

7.3.3 Methylene chloride, pesticide quality or equivalent.

7.3.4 Hexane, pesticide quality or equivalent.

7.3.5 Benzene, pesticide quality or equivalent.

7.3.6 Tetradecane, pesticide quality or equivalent.

7.3.7 Sand, prepared by extracting with methylene chloride and/or baking at 450 °C for a minimum of 4 hours. After cooling store in a dessicator.

7.3.8 Sodium sulfate, reagent grade, granular, anhydrous (J.T Baker 3375, or equivalent)- Refer to Section 7.2.7 for details of sodium sulfate preparation.

7.3.9 Dry Ice, purchased from local vendor.

7.3.10 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 mega ohm (MΩ) resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.4 Waste Dilution

7.4.1 Hexane, pesticide quality or equivalent.

7.4.2 Benzene, pesticide quality or equivalent.

7.5 Acid-Base Cleanup

7.5.1 Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.5.2 Potassium hydroxide, 20% aqueous. Prepare by cautiously adding, 200 g of potassium hydroxide pellets to 800 mL of deionized water. This solution is stored at room temperature in a plastic bottle.

7.5.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in reagent grade water.

7.5.4 Hexane, pesticide quality or equivalent.

7.5.5 Benzene, pesticide quality or equivalent.

7.5.6 Sodium sulfate, reagent grade, granular, anhydrous (J.T Baker 3375, or equivalent)- Refer to Section 7.2.7 for details of sodium sulfate preparation.

7.6 Silica Gel/Alumina Column Cleanup

7.6.1 Sodium sulfate, reagent grade, granular, anhydrous (J.T Baker 3375, or equivalent)- Refer to Section 7.2.7 for details of sodium sulfate preparation.

7.6.2 Methylene chloride pesticide quality or equivalent.

7.6.3 Hexane, pesticide quality or equivalent.

7.6.4 Acetone, pesticide quality or equivalent.

7.6.5 Toluene, pesticide quality or equivalent.

7.6.6 Silica gel, F679-212, Fisher Chromatographic Silica Gel, 100-200 mesh or equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to a shallow, borosilicate glass dish and air dry. After drying, cover with aluminum foil and activate in an oven at 130°C for a minimum of four (4) hours. Store in labeled glass jars in a desiccator until use.

7.6.7 3.3% Deactivated silica gel – To prepare add 6.6 mL of reagent water to 200 g of silica gel (section 7.6.6) in a 250 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar.

7.6.8 Acidic silica gel - To prepare, add 57 mL of concentrated sulfuric acid to 180 g silica gel (section 7.6.6) in a 250 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar.

7.6.9 Alumina, Neutral - Super I - Scientific Absorbents. Purchase and use only activated alumina. Store in an oven at 130°C when not in use.

7.6.9.1 Each new lot of alumina must be tested upon receipt and before use. Elute a solution containing all of the ^{13}C internal standards and native analytes through a column packed with the new lot of alumina. Collect the 5% and 60% fractions together and analyze by HRMS. Archive the 80 mL of hexane in a separate container. The target analytes and internal standard recoveries must be greater than 85% in the final fraction. If the recovery is less than 85% for any compound or internal standard, the ratios and volumes of the elution solvents must be optimized and the test is repeated until all compounds meet the recovery criteria.

7.6.10 5% methylene chloride in hexane. Add 15 mL methylene chloride to 285 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.6.11 65% methylene chloride in hexane - add 390 mL methylene chloride to 210 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.7 Activated Carbon Cleanup

7.7.1 Refer to section 7.6.6

7.7.2 J.T Baker Carbon, Activated Powder, E345-07, or equivalent

7.7.3 Thoroughly mix 5% (by weight). Activated J.T Baker carbon and 95% (by weight) Fisher Chromatographic silica gel (100-200 mesh). Activate in an oven at 130°C for 6 hours. Store in a desiccator in an amber colored bottle with a PTFE lined lid until use. Do not label the bottle until oven activation is completed to avoid heat damage to the label.

7.7.4 Toluene, pesticide quality or equivalent.

7.7.5 Methylene Chloride, pesticide quality or equivalent.

7.7.6 Benzene, pesticide quality or equivalent.

7.7.7 Methanol, pesticide quality or equivalent.

7.7.8 Cyclohexane, pesticide quality or equivalent.

7.7.9 Tetradecane, pesticide quality or equivalent.

7.7.10 Hexane, pesticide quality or equivalent.

7.7.11 Acetone, pesticide quality or equivalent.

7.8 Standard and Calibration Solutions: Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PFTE-lined caps.

7.8.1 Nonane, pesticide quality or equivalent.

7.9 Stock Solutions: Standards are used as received after being sonicated and transferred to 1.0 mL amber glass vials with PFTE lined caps.

7.9.1 Initial Calibration Standards:

7.9.1.1 1613B/8290: CS1-CS5. CIL Catalog No. EDF-9999. (See Table 5).

7.9.1.2 23/0023A/TO-9A: CS1-CS5. CIL Catalog No. EDF-4052. (See Table 6)

7.9.2 Initial Calibration Verification Standard: Wellington Laboratories Catalog No. EPA-1613-CS3.

7.9.3 Daily Calibration Verification Standards

7.9.3.1 1613B/8290: CS3. CIL Catalog No. EDF-9999-3. (See Table 7).

7.9.3.2 1613B/8290: CS3. CIL Catalog No. EDF-4141. (See Table 7).

Note: This standard may be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution.

7.9.3.3 23/0023A/TO-9A: CS3. CIL Catalog No. EDF-4052-3. (See Table 8)

7.9.4 PAR Native Standard Stock Solution: CIL Catalog No. EDF-7999-10x (see Table 11) 400-4000 ng/mL in nonane, 1.2 mL.

7.9.5 Internal Standard Stock Solution

7.9.5.1 1613B/8290: CIL Catalog No. EDF-8999, (see Table 13), 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.9.5.2 23/0023A/TO-9A: CIL Catalog No. EDF-4053, (see Table 15), 1000 ng/mL ($^{13}C_{12}$-OCDD 2000 ng/mL) in nonane, 1.2 mL.

7.9.6 23/0023A/TO-9A Surrogate Standard Stock Solution: CIL Catalog No. EDF-4054, (see Table 16), 1000 ng/mL in nonane, 1.2 mL.

7.9.7 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, (see Table 14), 50 μg/mL in nonane, 1.2 mL.

7.9.8 $^{13}C_{12}$-2,3,7,8-TCDD Labeled Standard Stock Solution: CIL Catalog No. ED-900, 50 μg/mL in nonane, 1.2 mL.

7.9.9 $^{13}C_{12}$-2,3,7,8-TCDF Labeled Standard Stock Solution: CIL Catalog No. EF-904 50 μg/mL in nonane, 1.2 mL.

7.9.10 $^{13}C_{12}$-1,2,3,4-TCDD Labeled Standard Stock Solution: CIL Catalog No. ED-911, 50 μg/mL in nonane, 1.2 mL.

7.9.11 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Labeled Standard Stock Solution: CIL Catalog No. ED-996, 50 μg/mL in nonane, 1.2 mL.

7.9.12 PCDD/PCDF Window Defining and Isomer Specificity Mixture: CIL Catalog No. EDF-4147 (see Table 18 and Table 19). This standard is used for qualitative purposes only and is not considered quantitative.

7.10 Secondary Stock Solutions

7.10.1 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solution in section 7.9.7 to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 μg/mL.

7.10.2 Cleanup Standard Working Stock Solution: Dilute 0.120 mL of the stock solution in section 7.10.1 to 3.0mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.10.3 $^{13}C_{12}$ TCDD/TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions in sections 7.9.8 and 7.9.9 to 5 mL in a volumetric flask with nonane to a final concentration of 1000 ng/mL.

7.10.4 Recovery Standard (RS) Secondary Stock Solution: Dilute 1.0 mL of the stock solutions in sections 7.9.10 and 7.9.11 to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 μg/mL.

7.10.5 Native Standard Working Stock Solution – Dilute 0.300 mL of stock solution in 7.9.4 to 3.0 mL in a volumetric flask with nonane for a final concentration of 40-400 ng/mL.

7.11 Standards and Spiking Solutions

7.11.1 PCDD/PCDF Window Defining and Isomer Specificity Standard: Combine 25 μL of the standard solution in section 7.9.12, 5 mL of the IS spiking solution in section 7.11.3, 5 μL of the RS stock solution in section 7.10.4, and 500 μL of nonane in a 10

mL vial. Concentrate the solution to 500 µL with a stream of nitrogen and transfer to 1.0 mL amber glass vials with PFTE lined cap.

7.11.2 PAR Native Standard Spiking Solution: Dilute 200 µL of the working stock solution in section 7.10.5 to 40 mL in a graduated cylinder with acetone to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each IPAR, OPR, LCS or MS/MSD sample. See Table 11 for a complete list of compounds and their concentrations.

7.11.3 1613B/8290 Internal Standard Spiking Solution: Dilute 500 µL of the stock solution in section 7.9.5.1 to 50 mL in a graduated cylinder with acetone to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.11.4 23/0023A/TO-9A Internal Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.9.5.2 to 100 mL in a graduated cylinder with acetone to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.11.5 23/0023A/TO-9A Surrogate Standard Spiking Solution: Dilute 500 µL of the stock solution in section 7.9.6 to 25 mL in a graduated cylinder with nonane to a final concentration of 20 ng/mL. 100 µL of this solution is added to each sample train components before sampling. See Table 16 for a complete list of compounds and their concentrations.

7.11.6 Cleanup Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.10.2 to 100 mL in a volumetric graduate with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract prior to cleanup. See Table 14 for a complete list of compounds and their concentrations.

7.11.7 $^{13}C_{12}$ TCDD/TCDF Internal Standard Spiking Solution: Dilute 100 µL of the stock solution in section 7.10.3 to 100 mL in a volumetric flask with acetone to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract that are extracted for TCDD and/or TCDF analysis only.

7.11.8 Recovery Standard Spiking Solution: Dilute 200 µL of the stock solution in section 7.10.4 to 10 mL in a volumetric flask with nonane to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank, and QC sample extract.

7.12 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes should be analyzed periodically, and should be assayed against reference standards before further use.

7.13 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log In of Commercial Samples, current revision. Sample container and preservation recommendations are listed in the table below.

Sample Holding Times, Containers, and Preservation

Method:	1613B	8290[1]	23	0023A[1]	TO-9A
Holding Times	Samples – 1 year Extracts – 1 year	Samples – 30 days from collection Extracts – 45 days from extraction Tissue Extracts –45 days from collection	Samples – 30 days from collection Extracts – 45 days from extraction	Samples – 30 days from collection Extracts – 45 days from extraction	Samples – 7 days from collection Extracts – 40 days from extraction
Containers	Amber Glass	Amber Glass	See KNOX-ID-0012	See KNOX-ID-0012	See KNOX-ID-0012
Preservation:					
Aqueous Samples	0-4 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate. If pH > 9, adjust to pH 7-9 with sulfuric acid	4 °C ± 2 °C in the dark	N/A	N/A	N/A
Solid Samples	<-10 °C in the dark	4 °C ± 2 °C in the dark	N/A	N/A	N/A
Tissue Samples	<-10 °C in the dark	<-20 °C in the dark[2]	N/A	N/A	N/A
Air Samples	N/A	4 °C ± 2 °C in the dark	4 °C ± 2 °C in the dark	4 °C ± 2 °C in the dark	≤4 °C in the dark

Note:

1 For method 8290 and 0023A the holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed may be as high as a year for certain matrices. The results of samples analyzed after the holding time expiration date should be considered to be minimum concentrations and should be identified as such in the final report. Sample extracts, however, should always be analyzed within 45 days of extraction. (For the State of South Carolina – The holdings times for 8290 are as listed in the table and are not considered recommendations.)

2 If the freezer used to store 8290 samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, a storage higher temperature is acceptable as long as it is <-10 °C.

9. Quality Control

9.1 Initial Demonstration of Capability

9.1.1 Initial precision and recovery (IPR) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.2 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sand or sodium sulfate spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. It is recommended that a method blank be prepared with the IPR samples.

9.2 Extracts should be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

9.2.1 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration(s) in ng/mL for each compound.

9.2.2 For each compound, compare s and X with the corresponding limits for initial precision and recovery in Table 9 for method 1613B and Table 10 for methods 8290, 23, 0023A, and TO-9A. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.3 The method detection limit (MDL) study described in Section 13 must be completed with acceptable results before analysis of samples may begin.

9.4 A laboratory method blank must be run along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The method blank is normally analyzed immediately after the calibration standards. The method blank consists of reagent water for aqueous samples, and a clean solid matrix (sand or sodium sulfate) for solid samples. The method blank must meet the following acceptance criteria;

- The concentration of target analytes in the method blank must be less than the MDL.
- If the concentration of target analytes in the method blank is greater than the MDL but less than the minimum level (ML), corrective action is required but the associated samples may be reported. At a minimum, corrective must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the MDL.
- If the concentration of target analytes in the method blank is greater than minimum level (ML) but less than 5% of the concentration in the associated samples, corrective action is required but the associated data may be reported. At a minimum, corrective action must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the ML and documentation in the case narrative.
- If the method blank sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.
- If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be done in consultation with the client.

9.4.1 The method blank internal standard recoveries must be within the established control limits. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. If the method blank internal standard recoveries are outside the QC limits and the decision is made to report the sample results, an NCM must be initiated and the reason for accepting the sample results clearly documented. Consultation with the client before acceptance must take place.

9.4.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," an NCM is initiated and appropriate comments made in the report narrative to provide further documentation.

9.4.3 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.5 Instrument Blank

9.5.1 Instruments must be evaluated for contamination during each 12 hour analytical run. This is accomplished by analysis of a method blank if available. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.6 Laboratory Control Sample (LCS) or Ongoing Precision and Recovery (OPR)

9.6.1 An LCS/OPR sample is analyzed along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. LCS/OPR spike components, concentrations, and control limits are given in Table 11.

9.6.2 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the LCS/OPR sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

- If the batch is not re-extracted and reanalyzed, an NCM must be initiated and the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of an acceptable reason for not reanalyzing might be that the matrix spike and matrix spike duplicate recoveries are within control limits, the method blank and sample internal standard recoveries are within limits, and the data clearly demonstrates that the problem was confined to the LCS/OPR).

- For method TO-9A calculate the precision (%D) relative to the previous TO-9A LCS. The precision must be within ± 30%.

9.6.3 Ongoing monitoring of the LCS/OPR provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.7 Internal Standards.

Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 for methods 1613B and 8290 or in Table 15 for methods 23, 0023A, and TO-9A.

9.7.1 If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than the lower control limit, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the minimum levels (ML's), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (ML's), re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 12). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented in the report narrative.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the analysis is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCSD should be analyzed. The LCSD is evaluated using the same acceptance criteria as the LCS. The RPD of the LCS and LCSD are compared to the acceptance limits in Table 12.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.9 Surrogate Standards – Methods 23, 0023A, TO-9A

Field surrogate standards are added to the collection media prior to sample collection when performing methods 23, 0023A, or TO-9A. The surrogate recoveries are calculated relative to the internal standards and are a measure of sampling efficiency. The recovery of the surrogate standards should be within the limits specified in Table 16. Poor recoveries of the surrogate standards may indicate breakthrough in the sampling train.

9.9.1 If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Flag the results that are outside control limits and notify the Project Manager. The client must be notified and consulted for additional corrective action.

10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 5 for methods 1613B and 8290 or in Table 6 for methods 23, 0023A, or TO-9A. Store calibration standards at room temperature in the dark. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). For method 1613B adjust the GC conditions to meet the relative retention times for the PCDDs/PCDFs listed in Table 3. The cycle time for MID descriptors must be $\leq$ 1 sec.

10.2.3 By using a PFK molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to the m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 is greater than 10,000 (10 percent valley).

10.2.4 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.5 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution or Mixture Solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of ≤ 25, where

$$\% \text{ Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8 - TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\% \text{ Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8 - TCDF}} \times 100$$

10.2.6 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 3 for methods 1613B and 8290 or in Table 4 for methods 23, 0023A, and TO-9A using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7 Calculate the mean relative response factor and the standard deviation of the relative response factors using the equations in the LQM for each calibration standard solution.

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met for each initial calibration standard before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, follow the procedure in STL Policy P-T-001(see reference section 16.9).

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors must be within the acceptance criteria listed in Table 5 for methods 1613B and 8290 or in Table 6 for methods 23, 0023A, and TO-9A.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 22.

10.2.8.4 For method 1613B the absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.9.2 after the completion of the initial calibration prior to sample analysis. Calculate the concentration of the ICV using the RRF's from the CS3 standard analyzed in section 10.2.6. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{\left(C_{Exp} - C_{Calc}\right)}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the ICV Standard.
C_{Calc} = The calculated concentration of the ICV Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is less than or equal to ±35% for all native and labeled compounds. The warning limits for percent difference is ±35 - 55%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits shall be documented as an NCM. Corrective action must be taken and may include the following

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A calibration check is also required at the end of a 12 hour period when performing method 8290 or 0023A.

10.3.2 Document the mass resolution performance as specified in section 10.2.3. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.4 and 10.2.5.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations using the formulas in section 12.3.

Note: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.9.3.2 may be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period that samples are analyzed. If acceptable beginning continuing calibration criteria is not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive beginning continuing calibration does not meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing beginning continuing calibrations by the analysis of two consecutive acceptable beginning continuing calibrations or by analysis of a new initial calibration.

10.3.5.1 The measured concentration or percent difference for each compound must be within the acceptance criteria limits in Table 7 for methods 1613B and 8290 or in Table 8 for methods 23, 0023A, and TO-9A.

10.3.5.2 For method 1613B the relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 3.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) ≥ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 22.

10.3.5.5 When performing method 8290 or 0023A, if the continuing calibration fails at the beginning of a 12-hour shift, the instructions in section 10.3.5 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than ±25 percent RPD for unlabeled native analytes and ±35 percent RPD for labeled standards, the closing standard may not be used as a beginning calibration standard for the next 12-hour shift and the requirements in section 10.3.5 must be met before analysis may continue. Use the mean RRF from the two daily continuing calibration runs to compute the analyte concentrations, instead of the RRFs obtained from the initial calibration. If the continuing calibration check performed at the end of a 12 hour period fails by more than ±25 percent RPD for unlabeled native analytes and ±35 percent RPD for labeled standards initiate corrective action and reanalyze all positive sample extracts analyzed during the 12 hour period encompassing the failed end of shift calibration check.

It is realized that it may not always be possible to achieve all RF criteria. For example, the RF criteria for 13C12-HpcDD and 13C12-OCDD were not met, however the RF values for the corresponding unlabeled compounds were within the criteria established in this procedure. The data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must consult with the group manager and the project manager to assess the impact on the data quality objectives on the affected samples. Corrective action must be taken and any decision to report sample data in this situation must be made in conjunction with the client. An NCM must be initiated if the data is to be reported.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard.

10.3.6.1 For methods 1613B, 23, TO-9A The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

10.3.6.2 For method 8290, 0023A - The Continuing Calibration Standard check and mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12-hour shifts, the Window Defining Mixture and/or Column Performance Solution Mixture must be analyzed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Screening process for samples with high concentration of Dioxins/Furans.

11.2.1 Samples received are carefully reviewed before starting the extraction process. Any samples that are received from known Dioxin/Furan sites and samples that contain keywords such as PCP (pentachlorophenol) site, wood treaters, PCB sites, and fire/burn sites may be subjected to the screening process.

11.2.2 Screening is done as a precaution to minimize the chance of having high level samples exposing the preparation and analytical areas to excessive amounts of Dioxin/Furan's, thereby potentially contaminating areas and other samples contained in those areas. See Figure Attachment I for LRMS Dioxin Screen Strategy.

11.2.3 Mix Sample well, weigh out 2.5 g and place in a 40 mL vial.

11.2.4 Add 10 mL of toluene and shake on a shaker table for 3 hours.

11.2.5 After contents have settled, remove the toluene from the vial and place in a fresh, clean vial containing 100 uL of tetradecane as a keeper. Rinse vial 3 times with 1 mL. of toluene to insure complete transfer of extract.

11.2.6 Solvent exchange the extract by placing it on the nitrogen concentration device. Concentrate the extract to near dryness. Add 4 mL of hexane and concentrate to near dryness again. Repeat again and then bring the extract to volume with 2 mL of hexane.

11.2.7 Run the extract thru a silica gel/alumina column cleanup as detailed in section 11.9.3. After the silica gel/alumina column cleanup is completed, put the extract back on nitrogen concentration device and concentrate to approximately 0.5 mL.

11.2.8 Transfer the concentrated extract to a 2 mL, clear, crimp top vial marked at 1.0 mL Rinse the 40 mL vial several times with small amounts of hexane to complete the transfer. Adjust volume of the extract to 1.0 mL. Take extract to GC/MS group for analysis.

11.3 Sample Pretreatment

11.3.1 Tissue Samples

11.3.1.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is blended to provide a homogeneous sample. At least 20 g of tissue should be homogenized if possible to allow for reanalysis if necessary.

11.3.1.2 Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender.

11.3.1.3 Weigh out 10 grams of the homogenized tissue sample, record the sample weight on the sample prep sheet or in a logbook. Add the 10 g sample along with 20 g of sodium sulfate to a laboratory blender. Blend the tissue/sodium sulfate mixture, while adding small chips of dry ice as necessary, to achieve a powder like consistency.

11.3.2 Fly Ash Samples

11.3.2.1 If the sample matrix is fly ash and is to be analyzed by method 8290, pretreat the sample with HCl as follows:

11.3.2.2 Weigh 10±0.05 g of the fly ash sample and transfer to a 240 mL glass jar. Record the sample weight on the sample prep sheet. If a sample is

designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD samples.

11.3.2.3 Add 150 mL of 1N HCl to the sample. Seal the jar with a PFTE lined screw cap and shake for 3 hours at room temperature.

11.3.2.4 Rinse a glass fiber filter with reagent water, carefully fit the glass fiber filter into a Buchner funnel and filter the sample through the glass fiber filter, placed in the Buchner funnel attached to a 1 L vacuum flask. Rinse the sample bottle twice with small amounts of reagent water, making sure that all particulate matter is transferred onto the glass fiber filter. Wash the fly ash cake with approximately 500 mL reagent water.

11.3.2.5 Add 1.0 mL of the internal standard spiking solution (see section 7.11.3) to the sample. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry. Extract the sample and glass fiber filter by Dean-Stark Soxhlet extraction in section 11.5.

11.4 Aqueous Sample Extraction

11.4.1 Remove samples from the refrigerator and allow them to come to room temperature before measuring the volume or performing the extraction. Inspect the samples carefully for biphasic sample characteristics. If this condition exists, document the observation, contact project manager for instructions before proceeding with the extraction.

11.4.2 For aqueous samples that contain visible solids, a percent solid determination must be performed using the following procedure.

Add 10 mL of the well shaken sample to a pre-weighed aluminum weighing dish. Weigh the dish to three significant figures. Dry the dish overnight in an oven at 105 °C. Reweigh the dish and calculate the percent solids using the following equation.

$$\%solids = \frac{\text{weight of dish plus sample after drying} - \text{weight of dish}}{\text{weight of dish plus sample before drying} - \text{weight of dish}} \times 100$$

11.4.3 8290 aqueous extraction and analysis: For samples with ≤ 1% solids follow normal extraction proceedure. For sample with ≥ 1% , consult project manager for further instruction befor proceeding with the extraction.

Note: Samples can be filtered, and extracted as a solid or aqueous separately or both fractions of solid and aqueous can also be combined after extraction at client's request.

11.4.4 1613 aqueous extraction and analysis: For samples with ≤ 1% solids, samples must be filtered and extracted as solid and aqueous fractions. The extracts from each fraction are then

combined into one extract. See Section 11.4.9.1 for filtration. For samples with > 1%, consult project manager for further instructions before proceding with extraction.

11.4.5 Refer to Knoxville SOP, KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire and replace any glassware found to be damaged.

11.4.6 Place separatory funnels, one for each sample, the method blank, and the OPR, in the positions in the rotary extractor.

11.4.7 Place a 600 mL concentration tube directly beneath each separatory funnel in the tube holder.

11.4.8 Plug a glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the funnel stops dripping, place the funnel on top of the concentrator tube.

11.4.9 If solids are not observed in the sample, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. Using a 1000 mL graduated cylinder measure out 1000 mL of reagent water and add to the separatory funnels marked for the method blank , LCS/OPR, and LCSD (if required).

11.4.9.1 Sample Filtration

11.4.9.1.1 Assemble a Buchner funnel with a rubber stopper on top of a clean vacuum filter flask. Insert a 15 cm diameter, 2.7 um particle retention glass fiber filter into the funnel. Wet the filter paper with a few mLs of reagent water and apply vacuum to the filter flask.

11.4.9.1.2 Apply vacuum to the flask, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.4.9.1.3 Rinse the sample bottle twice with approximately 10 mL portions of reagent water to transfer any remaining particles onto the filter. Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.4.9.1.4 If the percent solids are ≤ 1%, extract the filtrate in a separatory funnel by proceeding to section 11.4.10. Extract the solids on the filter and the filter itself following the procedure in section 11.5. **Do not add internal standards to this portion of the sample, only add internal standards to the aqueous portion of the sample!** The resulting extract is combined with the extract of the aqueous portion during the macro concentration step in section 11.8.

11.4.10 Using a Class A 1 mL volumetric pipet, add 1 mL of the ^{13}C labeled internal standard spiking solution, as specified in section 7.11.3, to each sample, the method blank, LCS/OPR, LCSD, and MS/MSD samples . Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

11.4.11 Using a Class A 1 mL volumetric pipet, add 1 mL of the PAR native spiking solution, as specified in section 7.11.2, to the designated LCS/OPR, LCSD (if required), and MS/MSD samples. Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

Note: If the volume of standard in the stock container is less than 10 mL after use, discard the remaining portion and prepare a new batch as specified in section 7.11.2.

11.4.12 Add 60 mL of methylene chloride to the sample bottle and shake. Then carefully pour the methylene chloride into the separatory funnel. Add 60 mL of methylene chloride to the method blank, LCS/OPR , and LCSD (if required) as well.

11.4.13 Secure the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles may be worn when performing this procedure.

11.4.14 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.4.15 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the concentrator tube. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed. If at least 10 minutes has elapsed and other ways of breaking up or reducing the size of the emulsion have failed the following steps may be tried to reduce the impact of the emulsion on the sodium sulfate.

11.4.15.1 Place a large piece of pre-cleaned glass wool in the funnel containing the sodium sulfate.

11.4.15.2 Spread the glass wool out, covering the entire surface of the sodium sulfate to about a depth of about 5 to 10 mm. If the emulsion is hard to break up and persistent, a small, additional layer of sodium sulfate may be added on top of the glass wool.

11.4.15.3 Drain the solvent and emulsion layer into the funnel being careful to drain no more than 60 mL of volume if a clear phase layer cannot be determined.

11.4.15.4 If this procedure is used the funnel should be rinsed with an extra 30 mL of methylene chloride to ensure all analytes are rinsed into the concentrator tube after the third portion of methylene chloride has drained through the sodium sulfate in section 11.4.17.

11.4.16 Repeat steps 11.4.12 through 11.4.15 two more times.

11.4.17 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.4.18 Remove the separatory funnel from the hood and pour the extracted water into the extracted water waste's carboy.

11.4.19 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the volume of sample used on the benchsheet.

11.4.20 Proceed to Macro Extract Concentration by Rapid-Vap in section 11.8.

11.5 Soxhlet Extraction

11.5.1 Prepare and label the required number of Soxhlet systems.

NOTE: If samples have a high water content (e.g., sludges, pulp samples, etc.) or are to be extracted by method 1613B, a Dean-Stark extractor should be used to remove the water from the sample. The Dean-Stark apparatus is installed between the Soxhlet body and the condenser when the components are assembled.

11.5.2 The Soxhlet is prepared by cleaning and rinsing per section 6.1.

11.5.3 For 1613 solids only: Calculate the amount of solids to be weighed out to achieve a 10 g dry weight of sample. See Attachment II for example of moisture spreadsheet.

11.5.3.1 Batch samples in Quantims and access an EXCEL template to determine the amount of solids to weigh out to achieve a 10 g "dry weight" sample. In EXCEL, select General Template file menu on the right, then select STL Knx SOG tab to open the "SOG Moist.xlt". Click on "Instruction tab" at the bottom of spreadsheet for instructions.

11.5.4 Transfer 10 ± 0.05 g of the solid sample (wet weight) into a glass fiber extraction thimble or glass fiber filter paper and put the thimble or filter inside the Soxhlet. If tissue samples are being extracted, add the entire sample and sodium sulfate mixture prepared in section 11.3.1.3. Record the sample weight on the sample prep sheet. Initial and date the entry. If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD samples.

Note: The MS and MSD samples must be prepared at the same weight as the OS to avoid calculation errors in the RPD values.

11.5.4.1 For the method blank, LCS/OPR and LCSD (if required) add 10 ± 0.05 g of sodium sulfate to a glass fiber extraction thimble.

11.5.4.2 If the matrix is tissue samples, sodium sulfate and dry ice are used for method blank, LCS/OPR, and LCSD (if required). Transfer 20 ± 0.5 g of the sodium sulfate and several small chips of dry ice into an extraction thimble.

11.5.4.3 Record the blank matrix type and lot number on the bench sheet.

11.5.5 Pour approximately 350 mL toluene into a 500 mL round bottom flask. Place the flask in the heating mantle. Add 10-15 boiling beads and several PFTE boiling chips.

11.5.6 Place the extraction thimble in the glass Soxhlet extractor.

11.5.7 Assemble the Soxhlet system and secure to the lab supports.

11.5.7.1 Place the method blank and QC samples in random positions within the available prep positions in the hood (i.e., do not use the same positions each time for the method blank and QC samples).

11.5.8 Spike each sample with 1.0 ml of the internal standard spiking solution (see section 7.11.3) and add a small amount of glass wool if needed to secure the sample material to the top of the extraction thimble. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

11.5.8.1 Spike the LCS/OPR, LCSD (if required), and MS/MSD samples with 1.0 ml of the PAR native spiking solutions (see section 7.11.2) prior to adding the glass wool. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

Note: If the volume of standard in the stock container is less than 10 mL after use, discard the remaining portion and prepare a new batch as specified in section 7.11.2.

11.5.9 Adjust the temperature of the heating mantle to bring the toluene in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour. Record the date and time that the Soxhlet extraction was started on the benchsheet and initial and date.

11.5.10 Soxhlet extract the sample in the above manner for a minimum of 16 hours. At the end of the extraction period, turn off the heating mantles. Record the date and time that the Soxhlet extraction was completed on the benchsheet and initial and date.

11.5.11 Remove the condensers. If a Dean Stark condenser is used, drain water from Dean Stark (the bottom layer of liquid). Then drain the remaining liquid into the soxhlet. Empty the Soxhlet extractor chamber into the round bottom flask and remove the Soxhlet extractor from the 500 mL round bottom flask.

11.5.12 Add several (2-3) fresh boiling chips to the flask. Insert a three-ball macro Snyder column into the top of the 500 mL round bottom flask.

11.5.13 Apply heat to the 500 mL flask in the heating mantle and reduce the extract volume to approximately 10-15 mL.

11.5.14 Transfer the extract into a 40 mL vial containing 100 uL of tetradecane, rinsing the 500 mL flask 3 times with 3 mL of toluene. Add the rinsings to the 40 mL vial.

11.5.15 Place the 40 mL vials into the nitrogen concentration device and reduce the volume to near dryness. Add 4 mL of hexane and swirl the vial. Reduce the volume of hexane to near dryness again to complete the solvent exchange. If the sample

exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the residue. Adjust the final volume of the extract with hexane to 12 mL for acid-base cleanup or 2 mL for column cleanup. Proceed to sample cleanup in section 11.9.

11.6 Waste Dilution

11.6.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.6.2 Tare a clean 40 mL VOA vial on a laboratory balance. Add an appropriate amount of sample (e.g., 1.0 g) to the VOA vial. If a sample is designated for MS/MSD analysis, prepare two additional portions of the sample and label them as the MS and MSD samples. Prepare method blank, LCS/OPR, and LCSD (if required) samples by adding 12 mL of hexane to a 40 mL VOA vial.

11.6.3 Record the weights and volumes used on the laboratory bench sheets and initial and date.

11.6.4 Add 1.0 ml of the internal standard spiking solution (see section 7.11.3) to the samples, method blanks, and QC samples. Record the spike solution number and the volume spiked on the sample prep sheet. Initial and date the entry. Add hexane to bring the volume to 12 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the sample.

11.6.5 Add 1.0 ml of the PAR native spiking solutions (see section 7.11.2) to the LCS/OPR, LCSD (if required), and MS/MSD samples. Record the spike solution identification number and the volume spiked on the sample prep sheet. Initial and date the entry.

11.6.6 Proceed to sample extract cleanup in section 11.9.

11.7 Air Sampling Trains

11.7.1 For media and sample preparation of air sampling trains refer to Knoxville SOP, KNOX-ID-0012.

11.8 Macro Extract Concentration by Rapid-Vap

11.8.1 Preheat the unit to the appropriate temperature for the solvent used in the extraction.

11.8.2 Set the operating parameters on the programmer. For example, if there is 300 ml of a methylene chloride extract, the following parameters may be used and should be adjusted as needed:

Temperature	30 °C
Vortex Speed	30%, to be increased at a later time
Nitrogen	7-9 psi
Timer Set	30 minutes

11.8.3 Place 600 ml concentrator tubes containing the extract in the Rapid-Vap. Begin concentrating the extract, adjust the vortex speed for the proper rate of concentration.

11.8.4 When the extract has been concentrated to less than 20 mL, add approximately 60 mL of hexane. Concentrate the extract to a final volume of approximately 2 ml (that is the volume contained in the reservoir tip of the Rapid-Vap). Shut off the nitrogen flow and turn off the Rapid-Vap or remove the 600 mL concentrator tube to prevent further concentration.

11.8.5 Transfer the extract to a 40 mL vial with a 9" disposable pipet, rinsing the sample tube three times with 2 mL of hexane. Reduce the volume in the 40 mL vial using the N-Evap to approximately 2 mL and proceed to extract cleanup in section 11.9. If no additional cleanups are to be performed continue with the following steps to dry the extract.

11.8.6 Prepare a small funnel by placing a small plug of pre-cleaned glass wool at the bottom of the funnel and adding a layer of sodium sulfate on top of the glass wool.

11.8.7 Pipet the extract from the Rapi-Vap concentrator tube and through the funnel containing the sodium sulfate into a 40 mL vial.

11.8.8 Rinse the concentrator tube 3 times with approximately 3 mL of hexane for each rinse. The sodium sulfate funnel then should be rinsed with an additional 2 mL of hexane. Proceed to micro concentration in section 11.10.

11.9 Sample Extract Cleanup

11.9.1 For 1613B samples, add 1.0 mL of the ^{37}Cl-,2,3,7,8-TCDD cleanup standard (see section 7.11.6) to each sample extract as well as the method blank and OPR sample extracts.

11.9.2 Acid-Base Cleanup

The acid-base cleanup is employed when sample extracts are colored and/or oily in appearance, or if specified by the client or project manager.

11.9.2.1 Bring the extract volume up to ~15 mL with hexane in a 40 mL vial.

NOTE: If the extracts are from fish tissue, omit sections 11.9.2.2 and 11.9.2.3.

11.9.2.2 Wash the extract by adding 10 mL of 20% aqueous potassium hydroxide to the vial and gently shaking for 20 seconds. If an emulsion begins to form, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer (the bottom layer) with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the base washing until no color is visible in the base layer (perform a maximum of four base washings).

11.9.2.3 Add 10 mL of 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the

aqueous layer (the bottom layer) with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion.

11.9.2.4 Slowly add 15 mL of concentrated sulfuric acid to the vial and shake for 30 seconds. If an emulsion remains from the previous, slowly add concentrated sulfuric acid (drop by drop) to the vial. **CAUTION: HEAT MAY BE GENERATED DURING THIS STEP**. If an emulsion still exists, discontinue shaking. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion settles out. Carefully remove the aqueous layer (the bottom layer) with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.9.2.5 Add 10 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. Vent the vial frequently to prevent pressure build up. Let the vial stand for 10 minutes or longer until any emulsion present settles out. Carefully remove the aqueous layer (the bottom layer) with a glass pipet, taking care not to remove any of the solvent layer or remaining emulsion. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.9.2.6 Reduce the extract volume to approximately 2 ml.

11.9.2.7 Proceed to section 11.9.3, silica gel/alumina column cleanup.

11.9.3 Silica Gel/Alumina Column Cleanup

Silica gel/alumina column cleanup is employed when sample extracts are clear or after other cleanup techniques have been employed. If treated drinking water samples are being analyzed, further cleanup may not be necessary.

11.9.3.1 Prepare a 20 mm diameter column and a 16mm diameter column for each extract by rinsing, in order, with acetone, toluene, methylene chloride and hexane. Place a large ball of pre-cleaned glass wool in the bottom of each column.

11.9.3.2 Mark the level to which the column packings will be added with a marking pen starting at the top of the glass wool plug and proceeding from bottom to top. The levels for each type column are as follows;

20 mm Silica Gel column
12 mm – 2g of 3.3% deactivated silica gel
16 mm – 4g of acidic silica gel
12 mm - 2g of 3.3% deactivated silica gel
10 mm – sodium sulfate
16 mm Alumina Column
40 mm – 6 g of neutral alumina
10 mm – sodium sulfate

11.9.3.3 Place the columns to the lab supports in the hood so that the 20 mm silica gel column is above the 16 mm alumina column. Offset the columns slightly so that the packings can be added and the columns rinsed.

11.9.3.4 Add the column packing in the order listed above while tapping with a marking pen to column to settle the contents to prevent channeling. When the columns have been completely packed, remove the lower columns from the support rack and remove the ink markings with a paper towel moistened with methylene chloride. Replace the columns in the rack.

11.9.3.5 Place a 125 mL glass jar under the lower alumina column to catch the solvent wastes and eluants as they filter through the column.

11.9.3.6 Add 20 mL of hexane to each column to rinse the packing. Collect the hexane from the columns in the 125 mL glass jar, the columns must be aligned so that the waste does not drip on the surface of the hood. When the level of solvent in the silica gel column approaches the top of the packing, move the upper column support so that the tips of the upper columns are inserted into the tops of the lower columns and the solvent will drip into the lower columns.

11.9.3.7 Just as the level of hexane reaches the top of the packing in the silica gel column transfer the sample extract into the top of the column. Rinse the extract vial 3 times with 1.5 mL of hexane and add each of these rinsings to the silica gel column.

11.9.3.8 Just as the solvent level reaches the top of the column packing add 70 mL of hexane (via a solvent bottle top dispenser) into the top of the silica gel column and allow this to drip into and through the alumina column and into the collection jar. When the hexane has completely drained from the silica gel column, remove the column from the support rack and dispose of it in the appropriate waste container.

11.9.3.9 Just as the level of hexane reaches the top of the packing in the alumina column using a solvent dispenser add 10ml of 5% methylene chloride/hexane mixture. Immediately after adding the 5% mixture replace the 125 mL glass jar containing the solvent waste with 40ml vial which has been labeled with the sample workorder number. Dispose of the solvent waste in the 125 mL glass jar in the appropriate waste collection container.

11.9.3.10 Just as the level of the 5% mixture reaches the top of the packing in the alumina column add 30 mL of 65% methylene chloride/hexane using a solvent dispenser and continue to catch the eluants in the 40 mL vial.

11.9.3.11 When the solvent has completely drained from the alumina column, cap the 40 mL vial containing the eluant and dispose of the alumina column in the appropriate waste container.

11.9.3.12 If no further cleanup is to be performed, proceed to final extract micro concentration detailed in Section 11.10. Otherwise, reduce the volume of

the extract to approximately 2 mL using the nitrogen micro concentration apparatus and proceed to the next cleanup.

11.9.4 Activated Carbon Cleanup

Carbon column cleanups should be performed when site history indicates carbon columns are necessary for removal of interferences. Carbon columns should also be run if, when running the extracts through dual columns, it is noticed that the acid silica layer becomes colored along the entire length of the acid silica. Most solid samples meet these criteria.

11.9.4.1 Prepare a 10 mL disposable pipette by cutting off the tapered end to achieve a 12-cm column. Insert a glass-wool plug of about 1 cm in length at one end and pack the column with 4.1 cm of the J.T Baker Carbon/Silica Gel mixture (section 7.7.8). Hold the packing by inserting an additional glass wool plug, again about 1 cm in length, in the other end.

11.9.4.2 Pre-elute the column with 10 mL of cyclohexane/methylene chloride (50:50 v/v). Turn the column over and pre-elute in the opposite direction with another 5 mL of cyclohexane/methylene chloride (50:50 v:v).

11.9.4.3 When the solvent reaches the glass wool, add the sample extract. Rinse the sample vial 2 times with 2 mL of 50/50 cyclohexane/methylene chloride. Add these rinses to the column. Elute the column with the following sequence of solvents:

11.9.4.3.1 6 mL of cyclohexane/methylene chloride (50:50 v/v).

11.9.4.3.2 5 mL of methylene chloride/methanol/benzene (75:20:5 v/v).

11.9.4.4 Allow the 75:20:5 methylene chloride/methanol/benzene to drain completely. Turn the column over and in the direction of reverse flow elute the PCDD/ PCDF fraction with 30 mL toluene into a 40 mL vial.

11.9.4.5 Place vials containing the extract in the nitrogen concentration apparatus and reduce the solvent volume to approximately 0.3 ml.

11.10 Micro Extract Concentration by Nitrogen Blowdown.

11.10.1 When all cleanups have been completed on the sample, add 20 uL of the labeled recovery standard spiking solution (see section 7.11.8) to an empty clean 1.1 mL tapered minivial that has been labeled with the sample ID. Mark the level of the recovery standard on the minivial (mark half the level, 10 µL, if the extracts are from treated drinking waters). Record the volume of recovery standard added on the benchsheet.

11.10.2 Transfer the concentrated extract into the mini-vial. Rinse the 40 ml vial at least twice with a small amount of hexane and add the rinses to the minivial. Put the minivial on the N-EVAP nitrogen blowdown and reduce the volume to the mark on the vial. Put the cap with PFTE-faced septa securely on the vial. Record the final extract volume on the benchsheet.

11.10.3 All items listed on the data review check list must be checked by both the prep analyst who performed the extraction and cleanups and the prep analyst who performed the second level review. An example data review check list is shown in Figure 4.

11.10.4 Transfer the extracts and paperwork to the GC/MS group for analysis.

11.11 Sample Extract Analysis

11.11.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 μL into the GC/MS and acquire data until OCDF has eluted from the column.

11.11.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename
Analyst
Lab sample identification
Additional information may be recorded in the logbook if necessary.

11.11.3 Generate ion chromatograms for the masses listed in Table 21 that encompass the expected retention windows of the PCDD and PCDF homologous series.

12. Data Analysis and Calculations

12.1 Refer to Figure 4 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.2.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.2.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.2.3 The ratio of the integrated areas of the two exact m/z's specified in Table 21 must be within the limits specified in Table 22, or alternatively when performing method 1613B, within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.2.4 Method 1613B only - The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 3.

12.2.5 Method 8290 and 0023A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within -1 to +3 seconds of the isotopically labeled standard.

12.2.6 Method 23 and TO-9A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within ±3 seconds of the isotopically labeled standard.

12.2.7 Method 8290, 23, 0023A, and TO-9A only - For 2,3,7,8-substituted isomers, which do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration.

12.2.8 The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.4.

12.2.9 No peaks detected in the polychlorinated diphenyl-ether (PCDPE) mass channel in the same retention time region (± 2 sec for method 8290 & 0023A) as a PCDF peak.

12.3 Quantitation for PCDD's and PCDF's.

12.3.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$\text{Ris} = \frac{\text{Ais} \times \text{Qrs}}{\text{Ars} \times \text{RRFis} \times \text{Qis}} \times 100\%$$

where:

Ais	=	sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars	=	sum of the areas of the quantitation ions of the recovery standard
Qrs	=	ng of recovery standard added to extract
Qis	=	ng of internal standard added to sample
RRFis	=	mean relative response factor of internal standard obtained during initial calibration

Note: In some situations, such as high-volume water sampling or air train samples, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = \frac{Crs \times Vrs}{S}$$

Where:

Qrs	=	ng of recovery standard added to extract
Crs	=	concentration of recovery standard added to the split portion of the extract
Vrs	=	volume of recovery standard added to the split portion of the extract
S	=	split ratio of the extract (decimal fraction of the extract used)

12.3.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards. The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:

Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.
Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.
Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.3.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard should be within the limits specified in Table 13 for method 1613B or 8290 or in Table 15 for method 23, 0023A, or TO-9A. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the internal standard. If the S/N is ≥ 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed.

12.3.4 Calculate the concentration of target analytes according to the following equation:

$$C = \frac{Ata \times Qis}{Ais \times RRF \times Ws \times Ssl}$$

Where:

Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a particular level of chlorination, the average of the individual 2,3,7,8-isomer RRF's is used in the calculation.

12.3.6 Calculate the total concentration of all isomers within each homologous series of PCDD's and PCDF's by summing the concentrations of the individual PCDD or PCDF isomers.

12.3.7 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRFs \times Ws \times Ssl}$$

Where:

N	=	average peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His	=	peak height of quantitation ions for appropriate internal standard
Qis	=	ng of internal standard added to sample
RRFs	=	mean relative response factor of compound for the shift opening and closing standards
W	=	amount of sample spiked and extracted (grams or liters)
Ssl	=	decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.8 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.2.3, calculate an Estimated Maximum Possible Concentration (EMPC). Two different calculation formulas may be used depending upon specific client requirements.

12.3.8.1 When performing method 8290 for EPA regulated analyses where the currently promulgated method is required by law (e.g. Trial Burns) and for all other analyses unless the client has specified otherwise, use the equation in section 12.3.4, except that Ata should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.3.8.2 When the client has specifically requested, use the equation in section 12.3.4 without correcting the areas. This method will give an EMPC which is always higher than the method above and would be considered the worst case.

12.3.9 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of

the peak using the equation in section 12.3.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.3.10 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For the other congeners (including OCDD and OCDF), however, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Dilutions of up to 1/10 may be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed.

12.3.11 Evaluate the ion chromatograms of the PFK lock mass and calibration mass for each MID group. The PFK mass intensity should be consistent throughout the retention time of the target compounds. Negative excursions or variations in the PFK mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results should be carefully evaluated when there is evidence of ion suppression present in the PFK mass traces.

12.4 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.5 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\,\text{min} \times Vfe}{W\text{s}}$$

Where:

Cmin	=	the concentration the analyte in the lowest calibration standard
Ws	=	amount of sample spiked and extracted (grams or liters)
Vfe	=	the final volume of the extract, corrected for all splits and dilutions

$$\mathrm{V}fe = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.6 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$\mathrm{M}axL = \frac{C\,\mathrm{max} \times Vfe}{W\mathrm{s}}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard Vfe and Ws are defined in Section 12.5.

12.7 Flag all compound results in the sample that were detected in the method blank with a "B" qualifier.

12.8 Flag all compound results in the sample that are below the minimum level with a "J" qualifier.

12.9 Flag all compound results in the sample that are above the upper calibration limit with an "E" qualifier.

12.10 Flag all compound results in the sample that are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.11 Flag compound results in the sample that exhibit chromatographic evidence of co-eluting compounds with a "C" qualifier.

12.12 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier.

12.13 Data Review

12.13.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.13.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.13.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies

are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.13.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.13.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. An example data review check list is shown in Figure 4.

13. Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP S-Q-003, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in STL Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1 All procedures shall be conducted in a manner to minimize, as far as practical, the use of solvents, reagents and other chemicals.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 See the current revision of the KNOX-HS-0002 for specific waste handling guidelines.

15.3 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Waste solvents including acetone, toluene, methylene chloride, and hexane from glassware rinsing and sodium sulfate pre-rinsing shall be placed in the flammable waste

stream, contained in a steel satellite accumulation container type or flammable solvent container.

- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous shall be placed in the incinerable laboratory waste stream, contained in a poly satellite accumulation container.
- Extracted PUF filters, XAD-2 resin, paper funnel filters, glass wool, fish/crawfish and soil contaminated with solvents shall be placed in the incinerable laboratory waste stream, contained in a poly satellite accumulation container.
- Contaminated sulfuric acid used during extract cleanup shall be placed in the acidic laboratory waste stream, contained in a poly satellite accumulation container or 55 gallon poly drum.
- Extracted aqueous samples, contaminated with methylene chloride shall be placed in the organic water waste stream, contained in a poly satellite accumulation container.
- Silica gel, alumina, carbon and sodium sulfate, from column clean-ups, contaminated with various solvents and eluates shall be placed in the incinerable laboratory waste stream, contained in a poly satellite accumulation container.

16. References

16.1 STL Quality Management Plan (QMP), current revision.

16.2 STL Knoxville Laboratory Quality Manual (LQM), current revision.

16.3 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins And Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994

16.4 USEPA SW-846 “Test Methods for Evaluating Solid Waste” Third Edition, Method 8290 and 0023A.

16.5 USEPA Method 23 – Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. 40 CFR Part 60 Appendix A.

16.6 Method TO-9A: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition EPA/625/R-96/010b.

16.7 STL SOP, KNOX-ID-0012, Method 0023A and Method 0010 Sampling Train Pre-Sampling Preparation and Sample Extraction Procedure (Includes TO-9A Sampling Components).

16.8 STL SOP, KNOX-QA-0002, Glassware Cleaning, current revision.

16.9 STL Policy, P-T-001, Selection of Calibration Points.

17. Miscellaneous

17.1 Deviations from Reference Method.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 Method 1613B employs a gravimetric determination of sample size rather than a volumetric determination. This procedure employs a volumetric determination of sample size to allow reporting of sample concentration in the standard units of pg/L (ppq). This modification has no impact on the performance criteria of this method.

17.1.3 The determination of solids content procedure used for aqueous samples is the same as the 1613B procedure used for solid samples rather than the 1613B procedure for aqueous samples. The aqueous sample procedure in 1613B is subject to error if the sample density is not exactly 1.0 g/mL.

17.1.4 The amount of hexane used in the solvent exchange step has been reduced from that specified in the reference methods. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.5 Method 1613B specifies that the sample bottle is rinsed twice with 5 mL of reagent water after the sample is transferred to the separatory funnel. This procedure specifies that the sample bottle is rinsed three times with methylene chlorideafter the sample is transferred to the separatory funnel. This modification improves the removal of target compounds from the sample bottle.

17.1.6 The separatory funnel is only rinsed once with methylene chlorideafter the sample is extracted instead of three times as specified in Method 1613B. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.7 Toluene volumes and cycle rates for Soxhlet extractors have been optimized for the specific size of glassware used and may not be the same as those specified in the referenced method. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.8 Soxhlet extracts are not filtered before concentration and solvent exchange. The use of glass wool in the extraction thimbles eliminates the transfer of particles to the extraction solvent. The column cleanup procedures remove any particulate that may not be removed by the glass wool. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.9 Particle size determination and reduction as specified in method 1613B is not performed on a routine basis. Silica and sand is not added to the Soxhlet extraction thimble as specified in method 1613B. Fish tissues are extracted with toluene rather than methylene chloride/hexane as specified in method 1613B. These procedures are considered to be outside the scope of the laboratories routine extraction procedures and are only performed on a client specific or project specific basis. These procedures, if required, will be specified and documented in the appropriate QAPPs.

17.1.10 Benzene is used to aid in dissolving the samples and/or extracts in hexane. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.11 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.12 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.13 The acid-base cleanup procedure is carried out in a VOA vial instead of a separatory funnel. Disposable glassware is used to decrease the risk of cross contamination. The volumes of the washes used have been adjusted for use in the VOA vials. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.14 The silica gel/alumina column cleanup used in this procedure has been optimized relative to amount and order of packings and may vary from the various columns and packings specified in the referenced methods. The solvent volumes and mixtures have been optimized based on evaluation of the elution of native and labeled standards. The silica gel and alumina are heated in an oven at 130°C instead of 110°C. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.15 The carbon column used in this procedure is based on the column specified in method 8280. Silica gel is used as the carbon column support instead of Celite 545® as specified in methods 8290 and 1613B. It has been determined that silica gel is less likely to contain contaminants and interferences which are not removed by the a precleaning procedures than Celite 545®, yet performs similarly. The solvents and elution schemes used are as specified in method 8280 rather than 8290 and 1613B. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.16 Method 8290 does not require dilution and reanalysis of samples for which OCDD exceeds the calibration range. Although this allowance is not made by method 1613B, this procedure does not require dilution for OCDD on samples analyzed by that method.

17.1.17 The calibration standards specified in method 23 are used for method 0023A and TO-9A.

17.1.18 Extracts are stored at room temperature rather than at <10 °C. The reference method requires that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation and irreversible adsorbtion to the inside surface of

the vial. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.2 Summary of modifications to SOP

17.3 Summary of reivisions to SOP for revision 7

17.3.1 Changed: "Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.9.2 after the completion of the initial calibration prior to sample analysis.

17.3.2 Added the preparation of sodium sulfate and it vendor in sections 7.2.7.

17.3.3 Added the amount of potassium hydroxide and DI water in 7.5.2

17.3.4 Added the amounts of sulfuric acid, DI water, silica gel, and methylene chloride in sections 7.6.7, 7.6.7, 7.6.11, 7.7.1

17.3.5 Added vendor for activated carbon and activation process in 7.7.2 and 7.7.3

17.3.6 Added PAR native solution in 7.9.4

17.3.7 Added standard solution information in 7.10.2,7.10.3, 7.10.5 and 7.11.2, 7.11.8

17.3.8 Added the grade and preparation of silica gel in 7.6.6

17.3.9 Added screening process in 11.2

17.3.10 Edited aqueous and solid extraction process.

17.4 Summary of revisions to SOP for revision 6.

17.4.1 Added an exception to 1613B allowing OCDD over calibration range.

17.4.2 Added RLs for biological tissues in Table 2.

17.4.3 Added health and safety information to section 5.10 and waste handling information to section 15.2.

17.4.4 Changed the preparation of sodium sulfate in sections 7.2.7, 7.3.8, 7.5.6, 7.6.1.

17.4.5 Changed the oven temperature for alumina and silica gel in section 7.6.6 and 7.6.9.

17.5 Summary of revisions to SOP for revision 5.

17.5.1 Added information to sections 3.37, 8.1, 12.1, 13.1, Appendix I.

17.6 Summary of revisions to SOP for revision 4.

17.6.1 Corrected the %D for 13C12-1,2,3,6,7,8-HxCDD and –HxCDF for 23 and TO-9A. Updated sections 5 and 15 to meet corporate EH&S requirements.

17.7 Summary of modifications to SOP for revision 3.

17.7.1 Incorporated all PCDD/PCDF analysis methods including 8290, 23, 0023A, and TO-9A into this method.

17.7.2 Revised all Tables to reflect requirements for each analysis method.

17.7.3 Removed instruction to follow carbon cleanup with silica gel/alumina cleanup.

17.7.4 Modified the solids determination procedure in section 11.4.9.1 from that specified by method 1613B.

17.8 List of tables and figures referenced in the body of the SOP.

17.8.1 Table 1 – Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

17.8.2 Table 2 – Methods – All, Minimum Levels by Matrix

17.8.3 Table 3 – Methods – 1613B and 8290, Retention Time References, Quantitation References, and Relative Retention Times

17.8.4 Table 4 – Methods – 23, 0023A, and TO-9A, Retention Time References and Quantitation References.

17.8.5 Table 5 – Methods – 1613B and 8290, Initial Calibration Standard Concentrations and Acceptance Criteria.

17.8.6 Table 6 – Methods – 23, 0023A, and TO-9A, Initial Calibration Standard Concentrations and Acceptance Criteria.

17.8.7 Table 7 – Methods – 1613B and 8290, Daily Verification Standard (VER) Concentrations and Acceptance Criteria.

17.8.8 Table 8 – Methods – 23, 0023A, and TO-9A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria.

17.8.9 Table 9 – Method – 1613B, Initial Precision and Recovery (IPR) Acceptance Criteria.

17.8.10 Table 10 – Methods – 8290, 23, 0023A, and TO-9A, Initial Precision and Recovery (IPR) Acceptance Criteria.

17.8.11 Table 11 – Laboratory Control Sample (LCS/OPR) Spiking Solution Component Concentrations and Acceptance Limits.

17.8.12 Table 12 – Method – 8290. Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits.

17.8.13 Table 13- Methods – 1613B and 8290, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.8.14 Table 14 – Method – 1613B, Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.8.15 Table 15 – Methods – 23, 0023A, and TO-9A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.8.16 Table 16 – Methods – 23, 0023A, and TO-9A, Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits.

17.8.17 Table 17 – Methods – All, Recovery Standard Spiking Solution Component Concentrations.

17.8.18 Table 18 – Rtx-5/DB-5 Column Window Defining Standard Mixture Components. – Rtx-5 (DB-5) Column Performance Standard Mixture Components.

17.8.19 Table 21 – DB-225 (Rtx-225) Column Performance Standard Mixture Components.

17.8.20 Table 21 – Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs.

17.8.21 Table 22 – Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs.

17.8.22 Figure 1 – Recommended GC Operating Conditions.

17.8.23 Figure 2 – Recommended MID Descriptors.

17.8.24 Figure 3 – Example Sample Prep Benchsheet

17.8.25 Figure 4 – Example Data Review Checklist.

17.8.26 Figure 5 – Aqueous sample Extraction Flowchart

17.8.27 Figure 6 – Solid Sample Extraction Flowchart

17.8.28 Figure 7 – Sample Cleanup Flowchart

17.8.29 Figure 8 – Analysis of PCDD’s and PCDF’s by HRGC/HRMS Flowchart.

History of Revisions

HISTORY OF REVISION PAGE

REV NO.	DATE	PAGES AFFECTED	REASON FOR REVISION
0	02/26/97	All	Initial version of the SOP
1	08/31/99	All	Procedure review.
2	01/28/02	All	Procedure review.
3	04/26/03	All	Procedure review
4	11/12/03	56 of 83	Corrected the %D for $^{13}C_{12}$-1,2,3,6,7,8-HxCDD and – HxCDF for 23 and TO-9A. Updated sections 5 and 15 to meet corporate EH&S requirements.
5	6/18/04	All	Added information to sections 3.37, 8.1, 12.1, 13.1, Appendix I.
6	9/27/05	All	Added an exception to 1613B allowing OCDD over calibration range. Added health and safety information to section 5.10 and waste handling information to section 15.2. Updated reagent preparation information for sodium sulfate, alumina and silica gel. Added RLs for biological tissues in Table 2.
7	2/17/07	All	Added dioxin screening and moisture sections in order to determine the appropriate sample dry weight for extraction. Edited reagent and standard preparation sections.

Table 1

Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

PCDD's/PCDF's [1] Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD $^{37}Cl_4$-2,3,7,8-TCDD	76523-40-5 85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	none	

Notes:

1. Polychlorinated dioxins and furans

TCDD	=	Tetrachlorodibenzo-p-dioxin	TCDF	=	Tetrachlorodibenzofuran
PeCDD	=	Pentachlorodibenzo-p-dioxin	PeCDF	=	Pentachlorodibenzofuran
HxCDD	=	Hexachlorodibenzo-p-dioxin	HxCDF	=	Hexachlorodibenzofuran
HpCDD	=	Heptachlorodibenzo-p-dioxin	HpCDF	=	Heptachlorodibenzofuran
OCDD	=	Octachlorodibenzo-p-dioxin	OCDF	=	Octachlorodibenzofuran

Table 2

Methods – All
Minimum Levels by Matrix

Analyte	Extract (ng/mL) [1]	Water (pg/L) [2]	Solids (pg/g) [3]	Biological Tissue (pg/g) [3]	Waste (pg/g) [4]	Air/Wipe (pg) [5]
2,3,7,8-TCDD	0.5	10	1	1	10	10
2,3,7,8-TCDF	0.5	10	1	1	10	10
1,2,3,7,8-PeCDD	2.5	50	5	5	50	50
1,2,3,7,8-PeCDF	2.5	50	5	5	50	50
2,3,4,7,8-PeCDF	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDD	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDF	2.5	50	5	5	50	50
2,3,4,6,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDF	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDD	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDF	2.5	50	5	5	50	50
1,2,3,4,7,8,9-HpCDF	2.5	50	5	5	50	50
OCDD	5.0	100	10	10	100	100
OCDF	5.0	100	10	10	100	100

Notes:
1 Concentration in the extract assuming a 20 µL volume.
2 Based on a sample volume of 1.0 L.
3 Based on a sample volume of 10.0 g.
4 Based on a sample volume of 1.0g.
5 Based on extraction of the entire sample.

Table 3

Methods – 1613B and 8290
Retention Time References, Quantitation References, and Relative Retention Times

Analyte	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard		
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard		
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	--[1]	1.000-1.019
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

Notes:
1 The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

Table 4

Methods – 23, 0023A, and TO-9A
Retention Time References and Quantitation References

Analyte	Retention Time and Quantitation Reference
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard	
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard	
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDD	$^{13}C_{12}$-OCDD
OCDF	$^{13}C_{12}$-OCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

Table 5

Methods – 1613B and 8290
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	1613B	8290
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**
Native PCDD's and PCDF's							
2,3,7,8-TCDD	0.5	2.0	10	40	200	±20	±20
2,3,7,8-TCDF	0.5	2.0	10	40	200	±20	±20
1,2,3,7,8-PeCDD	2.5	10	50	200	1000	±20	±20
1,2,3,7,8-PeCDF	2.5	10	50	200	1000	±20	±20
2,3,4,7,8-PeCDF	2.5	10	50	200	1000	±20	±20
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000	±20	±20
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000	±20	±20
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000	±35	±20
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000	±20	±20
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000	±20	±20
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000	±20	±20
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000	±20	±20
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000	±20	±20
OCDD	5.0	20	100	400	2000	±20	±20
OCDF	5.0	20	100	400	2000	±35	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	±35	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±35	±30
Labeled Cleanup Standard							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2.0	10	40	200	±35	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

Table 6

Methods – 23, 0023A, and TO-9A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	23 / TO-9A	0023A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**
Native PCDD's and PCDF's							
2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±20
2,3,7,8-TCDF	0.5	1.0	5	50	100	±25	±20
1,2,3,7,8-PeCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8-PeCDF	2.5	5	25	250	500	±25	±20
2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±20
OCDD	5.0	10	50	500	1000	±25	±20
OCDF	5.0	10	50	500	1000	±30	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±30	±30
Surrogate Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

Table 7

Methods – 1613B and 8290
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

Analyte	VER (ng/mL)	1613B All Isomers (ng/mL)	1613B Tetra only (ng/mL)		8290 Shift Open %D	8290 Shift Close[1] %D
Native PCDD's and PCDF's						
2,3,7,8-TCDD	10	7.8-12.9	8.2-12.3		±20	±25
2,3,7,8-TCDF	10	8.4-12.0	8.6-11.6		±20	±25
1,2,3,7,8-PeCDD	50	39-65	-		±20	±25
1,2,3,7,8-PeCDF	50	41-60	-		±20	±25
2,3,4,7,8-PeCDF	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,6,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,7,8,9-HxCDD	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDF	50	45-56	-		±20	±25
1,2,3,6,7,8-HxCDF	50	44-57	-		±20	±25
2,3,4,6,7,8-HxCDF	50	44-57	-		±20	±25
1,2,3,7,8,9-HxCDF	50	45-56	-		±20	±25
1,2,3,4,6,7,8-HpCDD	50	43-58	-		±20	±25
1,2,3,4,6,7,8-HpCDF	50	45-55	-		±20	±25
1,2,3,4,7,8,9-HpCDF	50	43-58	-		±20	±25
OCDD	100	79-126	-		±20	±25
OCDF	100	63-159	-		±20	±25
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121	85-117		±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140	76-131		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130	-		±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85-117	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143	-		±30	±35
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129	-		±30	±35
$^{13}C_{12}$-OCDD	200	96-415	-		±30	±35
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7	8.3-12.1		±30	±35
Labeled Recovery Standard						
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-		-	-

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 8

Methods – 23, 0023A, and TO-9A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

			0023A	
	VER	23 and TO-9A	Shift Open	Shift Close[1]
Analyte	**(ng/mL)**	**%D**	**%D**	**%D**
Native PCDD's and PCDF's				
2,3,7,8-TCDD	5	±25	±20	±25
2,3,7,8-TCDF	5	±25	±20	±25
1,2,3,7,8-PeCDD	25	±25	±20	±25
1,2,3,7,8-PeCDF	25	±25	±20	±25
2,3,4,7,8-PeCDF	25	±25	±20	±25
1,2,3,4,7,8-HxCDD	25	±25	±20	±25
1,2,3,6,7,8-HxCDD	25	±25	±20	±25
1,2,3,7,8,9-HxCDD	25	±25	±20	±25
1,2,3,4,7,8-HxCDF	25	±25	±20	±25
1,2,3,6,7,8-HxCDF	25	±25	±20	±25
2,3,4,6,7,8-HxCDF	25	±25	±20	±25
1,2,3,7,8,9-HxCDF	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDD	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDF	25	±25	±20	±25
1,2,3,4,7,8,9-HpCDF	25	±25	±20	±25
OCDD	50	±25	±20	±25
OCDF	50	±30	±20	±25
Labeled Internal Standards				
$^{13}C_{12}$-2,3,7,8-TCDD	100	±25	±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	±25	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	±30	±30	±35
$^{13}C_{12}$-OCDD	200	±30	±30	±35
Surrogate Standards				
$^{37}Cl_4$-2,3,7,8-TCDD	5	±25	±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	±25	±30	±35
Labeled Recovery Standard				
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-	

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

Table 9

Method – 1613B
Initial Precision and Recovery (IPR) Acceptance Criteria

	Test	1613B			1613B Tetra Only	
Analyte	Conc. (ng/mL) [1]	s^2 (ng/mL) [1]	X^3 (ng/ml) [1]		s^2 (ng/mL) [1]	X^3 (ng/ml) [1]
Native PCDD's and PCDF's						
2,3,7,8-TCDD	10	2.8	8.3-12.9		2.7	8.7-12.4
2,3,7,8-TCDF	10	2.0	8.7-13.7		2.0	9.1-13.1
1,2,3,7,8-PeCDD	50	7.5	38-66		-	-
1,2,3,7,8-PeCDF	50	7.5	43-62		-	-
2,3,4,7,8-PeCDF	50	8.6	36-75		-	-
1,2,3,4,7,8-HxCDD	50	9.4	39-76		-	-
1,2,3,6,7,8-HxCDD	50	7.7	42-62		-	-
1,2,3,7,8,9-HxCDD	50	11.1	37-71		-	-
1,2,3,4,7,8-HxCDF	50	8.7	41-59		-	-
1,2,3,6,7,8-HxCDF	50	6.7	46-60		-	-
2,3,4,6,7,8-HxCDF	50	7.4	37-74		-	-
1,2,3,7,8,9-HxCDF	50	6.4	42-61		-	-
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65		-	-
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56		-	-
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63		-	-
OCDD	100	19	89-127		-	-
OCDF	100	27	74-146		-	-
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	50	18.5	14-67		17.5	16-57.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17.5	15.5-56.5		17	17.5-49.5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	19.5	13.5-92		-	-
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	17.0	13.5-78		-	-
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	19.0	8-139.5		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	20.5	14.5-73.5		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	19.0	17-61		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	21.5	13.5-76		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	17.5	15-61		-	-
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	18.5	14.5-68		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20.0	12-78.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	17.5	17-64.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20.5	16-55		-	-
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20.0	14-70.5		-	-
$^{13}C_{12}$-OCDD	100	47.5	20.5-138		-	-
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4		3.4	4.5-13.4

Notes:

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the concentration

3 X = average concentration. The acceptance range for average recovery may be normalized (shifted to center on 100% recovery) to compensate for the bias in the collaborative study used to develop the acceptance criteria.

Table 10

Methods – 8290, 23, 0023A, and TO-9A
Initial Precision and Recovery (IPR) Acceptance Criteria

Analyte	Test Conc (ng/mL) [1]	s[2] (%Rec)	X[3] (%Rec)
Native PCDD's and PCDF's			
2,3,7,8-TCDD	10	15[4]	70-130[4]
2,3,7,8-TCDF	10	15[4]	70-130[4]
1,2,3,7,8-PeCDD	50	15[4]	70-130[4]
1,2,3,7,8-PeCDF	50	15[4]	70-130[4]
2,3,4,7,8-PeCDF	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDD	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDD	50	15[4]	70-130[4]
1,2,3,4,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,6,7,8-HxCDF	50	15[4]	70-130[4]
2,3,4,6,7,8-HxCDF	50	15[4]	70-130[4]
1,2,3,7,8,9-HxCDF	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDD	50	15[4]	70-130[4]
1,2,3,4,6,7,8-HpCDF	50	15[4]	70-130[4]
1,2,3,4,7,8,9-HpCDF	50	15[4]	70-130[4]
OCDD	100	15[4]	70-130[4]
OCDF	100	15[4]	70-130[4]

Notes:
1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.
2 s = standard deviation of the percent recovery
3 X = average percent recovery
4 In-house generated historical control-limits may be used in place of the specified limit.

Table 11

Laboratory Control Sample (LCS/OPR) Spiking Solution Component Concentrations and Acceptance Limits

Analyte	LCS Solution Conc. (ng/mL)[1]	Final Extract Conc (ng/mL)[2]	1613B OPR Conc (ng/mL)[2]	8290, 23, 0023A, TO-9A Recovery (%Rec)
2,3,7,8-TCDD	0.2	10	6.7-15.8	70-130[4]
2,3,7,8-TCDF	0.2	10	7.5-15.8	70-130[4]
1,2,3,7,8-PeCDD	1.0	50	35-71	70-130[4]
1,2,3,7,8-PeCDF	1.0	50	40-67	70-130[4]
2,3,4,7,8-PeCDF	1.0	50	34-80	70-130[4]
1,2,3,4,7,8-HxCDD	1.0	50	35-82	70-130[4]
1,2,3,6,7,8-HxCDD	1.0	50	38-67	70-130[4]
1,2,3,7,8,9-HxCDD	1.0	50	32-81	70-130[4]
1,2,3,4,7,8-HxCDF	1.0	50	36-67	70-130[4]
1,2,3,6,7,8-HxCDF	1.0	50	42-65	70-130[4]
2,3,4,6,7,8-HxCDF	1.0	50	35-78	70-130[4]
1,2,3,7,8,9-HxCDF	1.0	50	39-65	70-130[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	35-70	70-130[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	41-61	70-130[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	39-69	70-130[4]
OCDD	2.0	100	78-144	70-130[4]
OCDF	2.0	100	63-170	70-130[4]
Tetras Only				
2,3,7,8-TCDD	0.2	10	7.3-14.6	70-130[4]
2,3,7,8-TCDF	0.2	10	8.0-14.7	70-130[4]

Notes:

1 1.0 mL of this solution is added to the OPR sample before extraction (see section 7.11.1).

2 The final extract concentration is based on an extract volume of 20-µL.

3 Spike concentrations are based on a 1.0 L extraction for Water, 10.0g extraction for Solids, and entire sample extraction for Air/Wipe samples.

4 In-house generated historical control-limits may be used in place of the specified limit.

Table 12

Method - 8290
Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits[1]

Analyte	LCS Solution Conc. (ng/mL)[2]	Final Extract Conc (ng/mL)[3]	8290 Recovery (%Rec)	8290 Precision (RPD)
2,3,7,8-TCDD	0.2	10	70-130[4]	±15[4]
2,3,7,8-TCDF	0.2	10	70-130[4]	±15[4]
1,2,3,7,8-PeCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
2,3,4,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
2,3,4,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	70-130[4]	±15[4]
OCDD	2.0	100	70-130[4]	±15[4]
OCDF	2.0	100	70-130[4]	±15[4]

Notes:
1 If insufficient sample exists for MS/MSD analysis, these limits apply to LCS/LCSD samples.
2 mL of this solution is added to the OPR sample before extraction (see section 7.11.2).
3 The final extract concentration is based on an extract volume of 20-µL.
4 In-house generated historical control-limits may be used in place of the specified limit.

Table 13

Methods – 1613B and 8290
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B OPR Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	8290 Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	10.0-87.5	12.5-82.0	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	11.0-76.0	12.0-84.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	10.5-113.5	12.5-90.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	10.5-96.0	12.0-92.5	40-135
$^{13}C_{12}$-2,3,4,7,8-PeCDF	1.0	50	6.5-164.0	10.5-89.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1.0	50	10.5-96.5	16.0-70.5	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	12.5-81.5	14.0-65.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1.0	50	9.5-101.0	13.0-76.0	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	10.5-79.5	13.0-61.5	40-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	1.0	50	11.0-88.0	14.0-68.0	40-135
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1.0	50	8.5-102.5	14.5-73.5	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	13.0-83.0	11.5-70.0	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	10.5-79.0	14.0-71.5	40-135
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1.0	50	10.0-93.0	13.0-69.0	40-135
$^{13}C_{12}$-OCDD	2.0	100	13.0-198.5	17.0-157	40-135
Tetras Only					
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	12.5-70.5	15.5-68.5	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	13.0-63.0	14.5-70.0	40-135

Notes:
1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to extraction (see section 7.11.3).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 14

Method – 1613B
Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B OPR Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	1613B OPR Tetra Only Conc (ng/mL)[2]	1613B Sample Tetra Only Conc (ng/mL)[2]
$^{37}Cl_4$-2,3,7,8-TCDD	0.2	10	3.1-19.1	3.5-19.7	3.7-15.8	4.2-16.4

Notes:
1 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to cleanup (see section 7.11.4).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 15

Methods – 23, 0023A, and TO-9A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-OCDD	2.0	100	25-130	40-135	40-120

Notes:
1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to extraction (see section 7.11.3).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 16

Methods – 23, 0023A, and TO-9A
Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{37}Cl_4$-2,3,7,8-TCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-2,3,4,7,8-PeCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	20	100	70-130	70-130	40-120

Notes:
1 100 µL of the Surrogate Standard Spiking Solution is added to each sample train prior to sampling (see section 7.11.5).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 17

Methods – All
Recovery Standard Spiking Solution Component Concentrations

Labeled Analyte	Solution Conc (µg/mL)[1]	Test Conc. (ng/mL)[2]
$^{13}C_{12}$-1,2,3,4-TCDD	0.1	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.1	100

Notes:
1 20 µL of the Recovery Standard Spiking Solution is added to each sample, method blank and LCS/OPR sample prior to analysis (see section 7.11.8).
2 Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 18

Rtx-5/DB-5 Column Window Defining Standard Mixture Components

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,6,8-/1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-/1,2,4,6,8,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

Table 19

Rtx-5 (DB-5) Column Performance Standard Mixture Components

Isomer
1,2,3,7/1,2,3,8-TCDD
1,2,3,9-TCDD
2,3,7,8-TCDD

Table 20

DB-225 (Rtx-225) Column Performance Standard Mixture Components

Isomer
2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 21

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
1	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	342.9792	QC	C_8F_{13}	PFK
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	330.9792	LOCK	C_7F_{13}	PFK
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	380.9760	QC	C_8F_{15}	PFK
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760	LOCK	C_8F_{15}	PFK
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	404.9760	QC	$C_{10}F_{15}$	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

Table 21 (Continued)

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
4	404.9760	LOCK	$C_{10}F_{15}$	PFK
	407.7818	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF
	409.7788	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0$	HpCDF
	417.8250	M	$^{13}C_{12}H\ ^{35}Cl_7\ 0$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF (S)
	423.7767	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD
	425.7737	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD (S)
	442.9728	QC	$C_{10}F_{17}$	PFK
	479.7165	M+4	$C_{12}H\ ^{35}Cl_7\ ^{37}Cl_2\ 0$	NCDPE
5	430.9728	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0$	OCDF
	443.7399	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0$	OCDF
	457.7377	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD
	459.7348	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD
	469.7780	M+2	$^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD (S)
	480.9696	QC	$C_{10}F_{19}$	PFK
	513.6775	M+4	$C_{12}\ ^{35}Cl_8\ ^{37}Cl_2\ 0$	DCDPE

Notes:

1 Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

Table 22

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

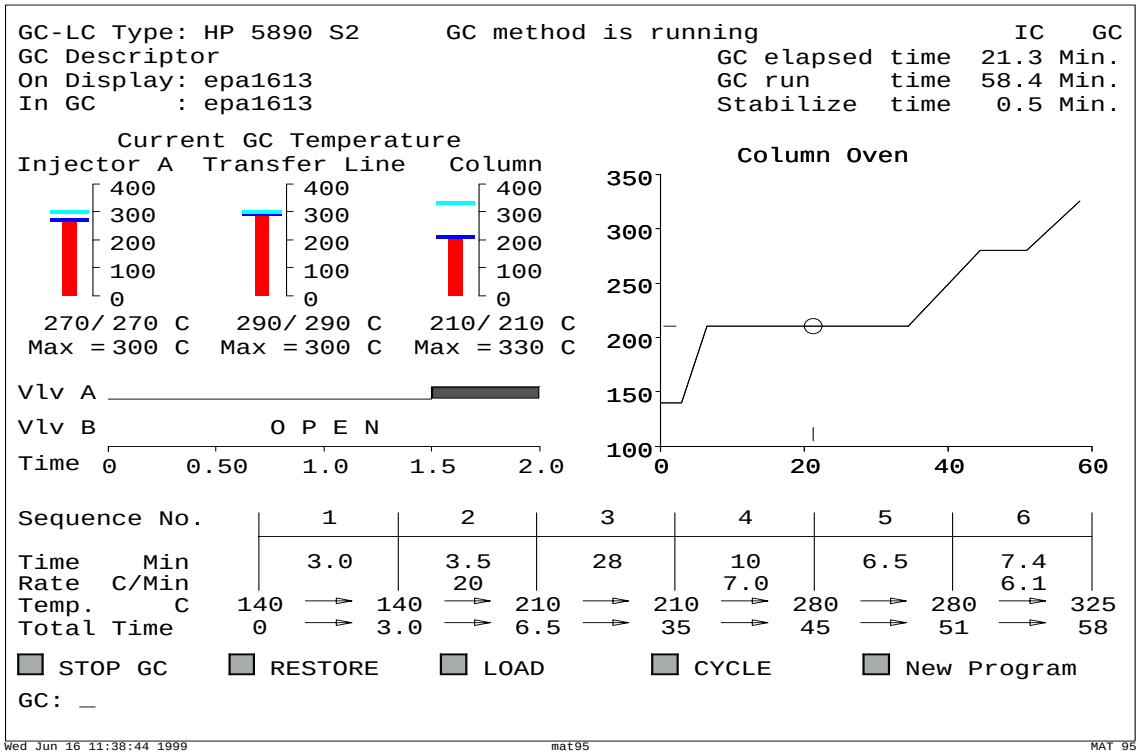
Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [1]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04/1.05[3]	0.88	1.20
7 [2]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

Notes:

1 Used for ^{13}C-HxCDF (IS).
2 Used for ^{13}C-HpCDF (IS).
3 Method 1613B Theoretical Ratio

Figure 1

Rtx-5 Recommended GC Operating Conditions



DB-225 Recommended GC Operating Conditions

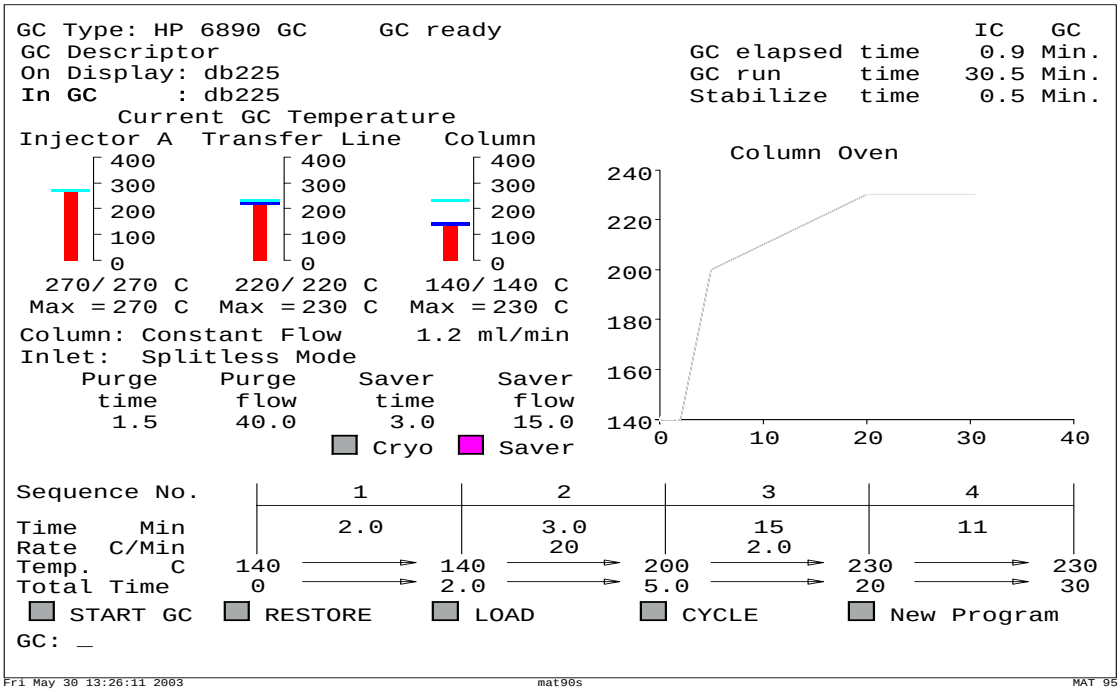
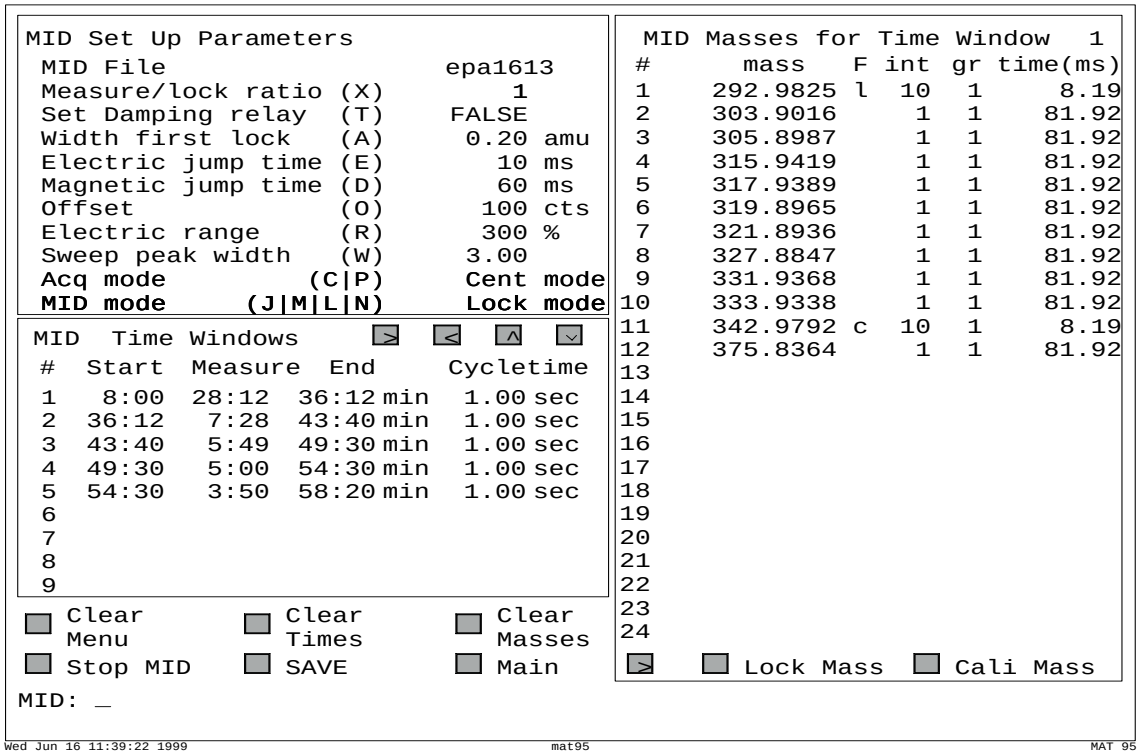


Figure 2

Rtx-5 Recommended MID Descriptors



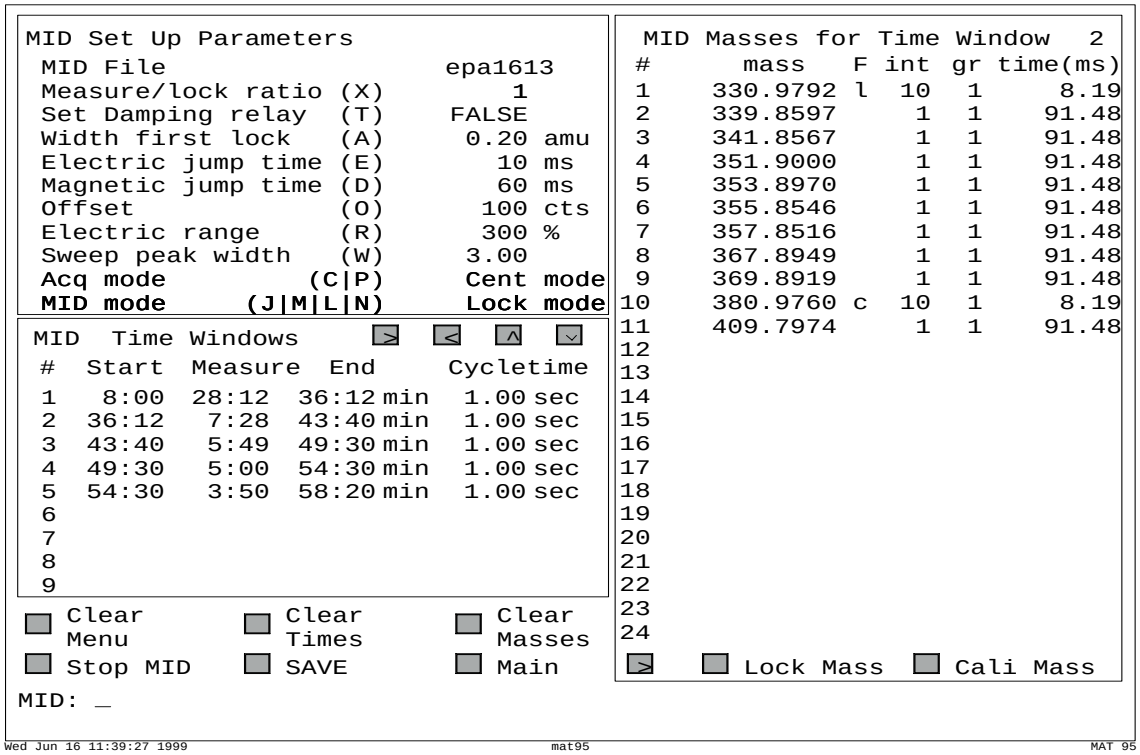
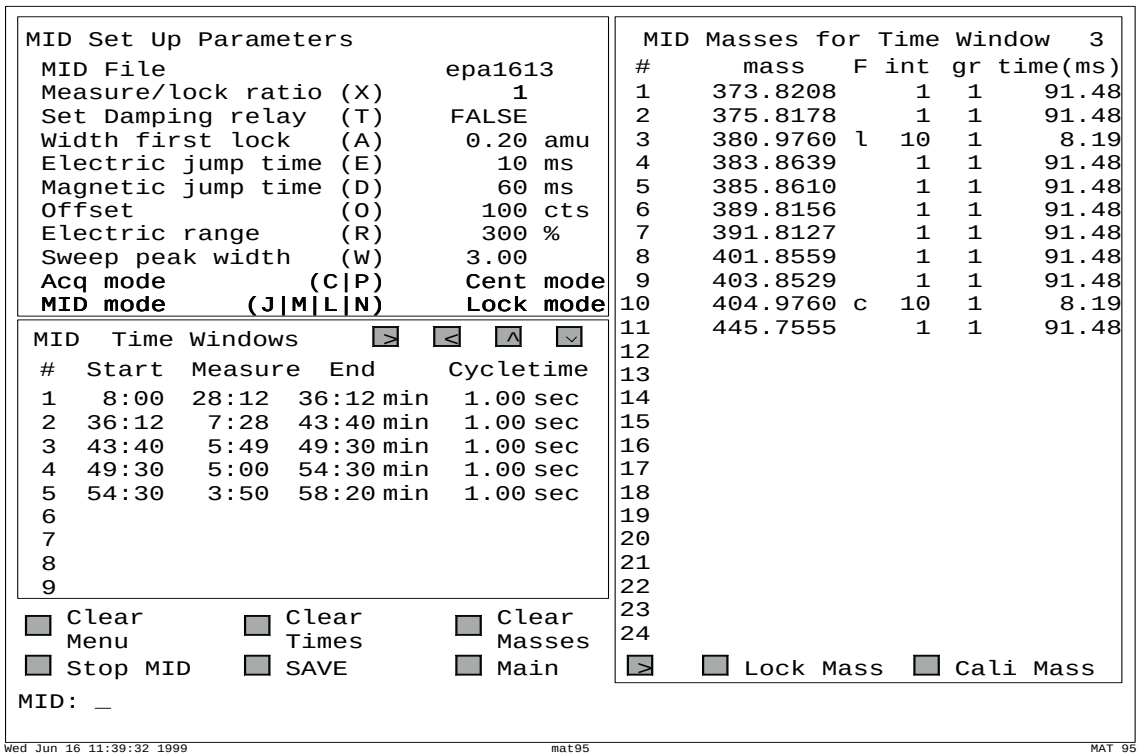


Figure 2 **Continued**

Rtx-5 Recommended MID Descriptors



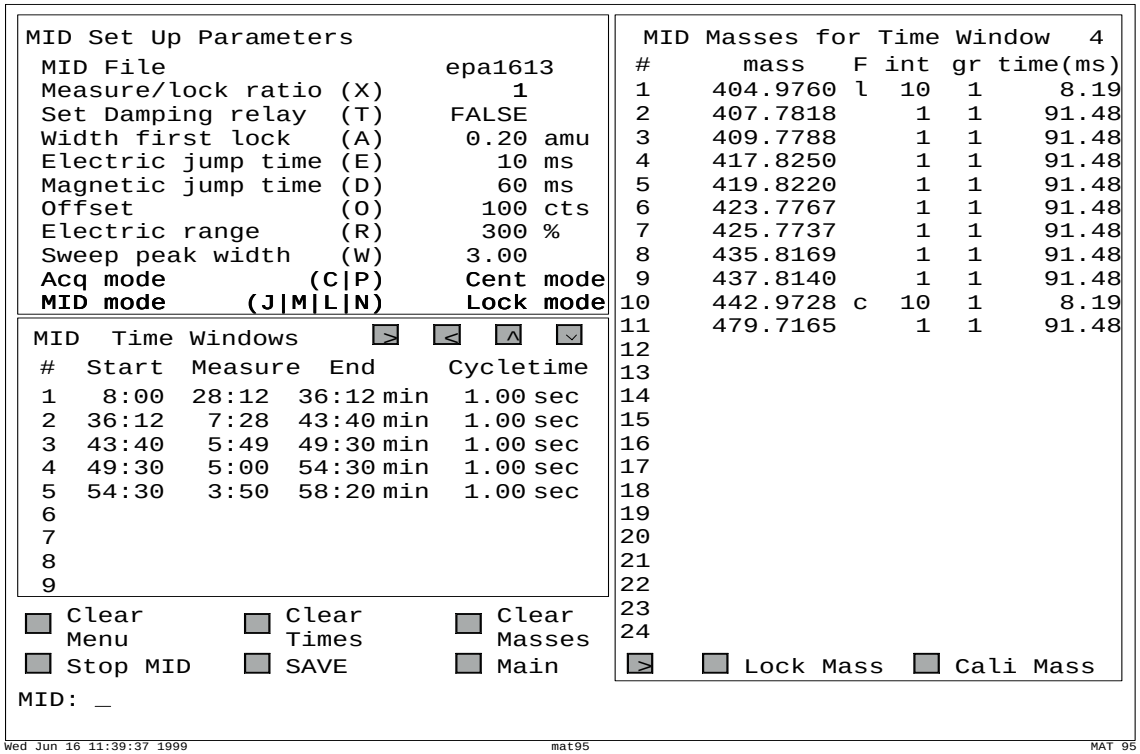
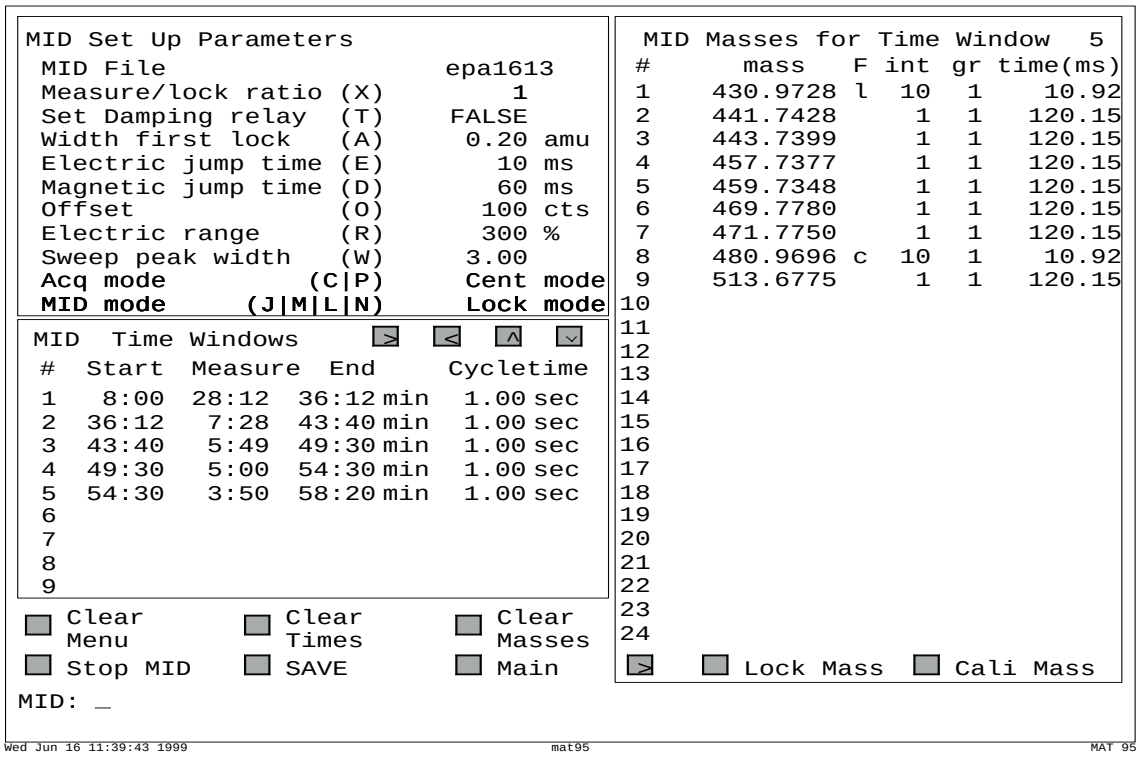


Figure 2 Continued

Rtx-5 Recommended MID Descriptors



DB-225 Recommended MID Descriptor

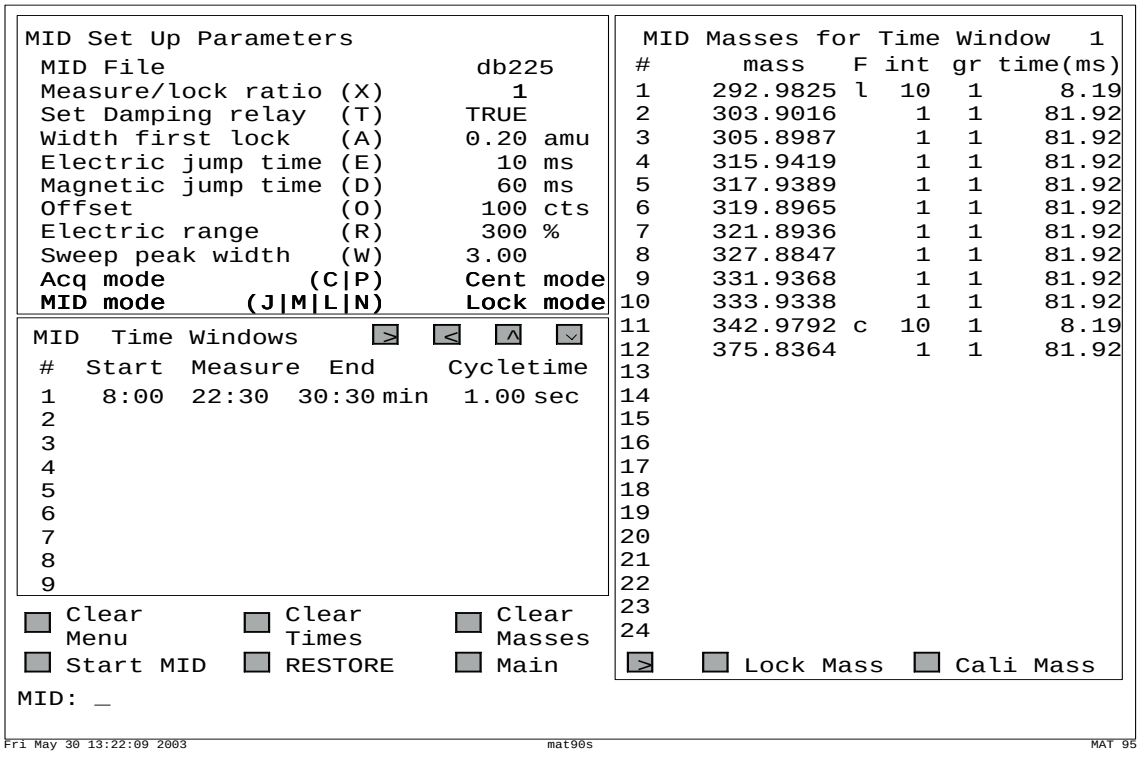


Figure 3

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group

QC Batch No: 6132072 Internal Std. Spiked By: _____ Verified By: _____ Date: _____

Sodium Sulfate Lot: _____ Native LCS/D Spiked By: _____ Verified By: _____ Date: _____

(only for Waters) Native MS/D Spiked By: _____ Verified By: _____ Date: _____

Work Order Number	Filtered Y/N?	Vol of Sampling Surrogate (uL)	Soxhlet Started (Date/Time)	Soxhlet Finished (Date/Time	Blow Down (Initial/Date)	Recovery Standard (Book:Page)	Recovery Std Vol (uL)	Vol Delivered (uL)	Comments
H4GE42AA									
H4GE41AA									
H4GE92AA									
H4GE91AA									
H4GFD2AA									
H4GFD1AA									
H4GFH2AA									
H4GFH1AA									
H4GFX1AA									
H48TC1AA	B								
H48TC1AC	C								
H48TC1AD	L								

Comments: _____ Volume of Alt Standard: _____

Split Ratios: Post I.S. _____

Post F.C. _____

Post C.S. _____

Post R.S. _____

Blk Matrix: _____ W.B. Temp _____

Extraction Solvent: _____ Lot #: _____

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Figure 3 Continued

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group

QC Batch No: 6132072 **Cleanup Std. Spiked By:** _____ **Verified By:** _____ **Date:** _____

Lot #s: _____ _____

Work Order Number		Cleanup Spike (Book:Page)	Cleanup Spike Volume (uL)	SilicaGel Alumina Col (Initial/Date)	Acid/Base Wash (Initial/Date)	Carbon Column (Initial/Date)	Florisil Column (Initial/Date)	Mercury Cleanup (Initial/Date)	TBA Cleanup (Initial/Date)	Other Cleanup (Initial/Date)	Comments
H4GE42AA											
H4GE41AA											
H4GE92AA											
H4GE91AA											
H4GFD2AA											
H4GFD1AA											
H4GFH2AA											
H4GFH1AA											
H4GFX1AA											
H48TC1AA	B										
H48TC1AC	C										
H48TC1AD	L										

Comments: _____

_____

_____

_____

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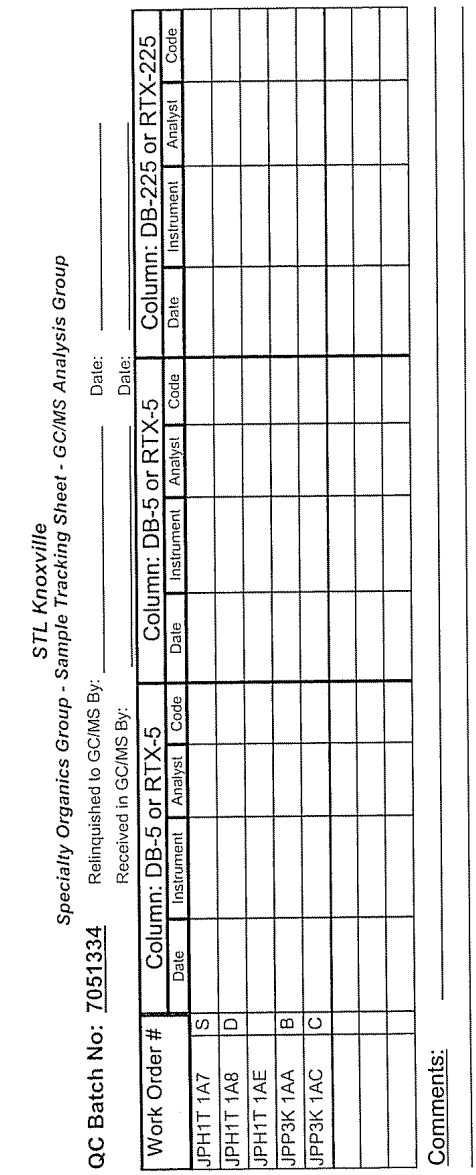
Figure 3 Continued

Example Sample Prep Benchsheets



STL Knoxville
Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group

QC Batch No: 7051334 Relinquished to GC/MS By: _____ Date: _____
Received in GC/MS By: _____ Date: _____

Work Order #		Column: DB-5 or RTX-5				Column: DB-5 or RTX-5				Column: DB-225 or RTX-225			
		Date	Instrument	Analyst	Code	Date	Instrument	Analyst	Code	Date	Instrument	Analyst	Code
JPH1T 1A7	S												
JPH1T 1A8	D												
JPH1T 1AE													
JPP3K 1AA	B												
JPP3K 1AC	C												

Comments: _____

Figure 4

Example Sample Prep Data Review Checklist

STL Knoxville **Specialty Organics Prep Batch Review/Checklist** **Batch #_____**

□ KNOX-ID-0004, rev. 7 (PCDD/F extraction) □ KNOX-ID-0012, rev. 1 (Air Train extraction) □ KNOX-ID-0013, rev. 5 (PCB extraction) □ KNOX-ID-0016, rev. 5 (LR-SIM PAH extraction)

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Does the batch contain no more than 20 field samples? (Excluding MB, LCS, LCSD, MS, & MSD)					
2. Were the samples extracted by the proper method?					
3. Were the samples extracted within the required holding times?					
4. For waters by 1613B, if visible solids were present, were solids determined to be ≤ 1%?					
5. Were all project specific requirements met as noted on the Lot Checklists and Sample Worksheets?					
6. Were all required QC samples prepared & extracted with the batch at method required frequency?					
7. Were MS Run# properly assigned and samples entered on QC tracking Sheet?					
8. Were samples requested properly and request form completed, signed, and dated?					
9. Were the correct weights and volumes entered in Quantims for all samples?					
10. Were the internal standards properly spiked and the spikes verified? Were the spike solution ID and spike volumes entered correctly and verified?					
11. Were alternate standards properly spiked and the spikes verified? Were the spike solution ID and spike volumes entered correctly and verified?					
12. Were all cleanup steps properly documented by initials and date?					
13. Was the final volume checked and verified against the supplemental benchsheet and Quantims?					
14. Are the final extracts free of water, precipitates, multiple phases, and color?					
15. Were all appropriate notes and observations recorded on the prep benchsheet and in Quantims?					
16. Were all Quantims batch information completed including; • Batch reviewed • Correct volumes entered • Correct completion date entered • Samples released					
17. Does the prep batch paperwork package contain all required documentation which has been properly and completely filled out, including; • Prep Benchsheet • Supplemental Benchsheet • Standard concentration forms or copies of logbook pages, for all IS, RS, SS, CS, Native and Alternate standards. • Lot Checklists for all lots in the batch • Sample worksheets for all samples in the batch in proper order as recorded on tracking sheet					
18. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

Figure 4 Continued

Example Sample Data Review Checklist

STL Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 8290 - KNOX-ID-0004-R7

PFK Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
6. Were the five calibration standard solutions, at the concentrations specified in Table 5 of the SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 5), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
10. Are %RSD ≤20% for all unlabeled native analytes?					
11. Are %RSD ≤35% for all labeled internal standards?					
12. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
13. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
14. Was the second source (Wellington) ICV standard analyzed, and the %D calculated and within the acceptance criteria of < ±35%?					
15. If manual integrations were performed, are they clearly identified, initialed and dated?					
16. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
17. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard, ICV Summary Table, Calculation Summary, and chromatograms?					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 8290 - KNOX-ID-0004-R7

Start PFK:		**VER Filename:**		**Win Filename:**		**Inst:**	
End PFK:		**VER Filename:**		**Col Perf Filename:**		**ICAL Date:**	

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
7. Were continuing calibrations performed at the beginning and end of the 12-hour period, with successful mass resolution and GC resolution performance checks?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 3), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the measured RRFs for each compound within the specified control limits in Table 7 for all PCDDs/PCDFs?					
10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the CCAL folder contain **complete** data in the following order: Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards?					

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist LOT #_____
Method: 8290 - KNOX-ID-0004-R7 **Page 1 of 2**

Batch Number:	

Review Items **A. Initial Calibration**	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd Level**
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration					
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results					
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Was date/time of analysis verified between analysis header and logbook as correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____ _____				☐ HT expired upon receipt. ☐* Client requested analysis after HT expired. ☐ Re-extraction done after HT expired. ☐ See Comment no. _____.	
5. Are internal standards within QC limits specified in Table 13? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____				☐* **[sup]** Ion suppression due to matrix. ☐* **[low]** Low recovery. S/N >10 and EDL<ML. ☐ **[sam]** Not enough sample to re-extract. ☐ **[dil]** Dilution showed acceptable %R. ☐ **[mtx]** Obvious matrix interference. Further cleanup not possible. ☐* **[unk]** At client's request, data was flagged as estimated and released without further investigation. ☐ **[com]** See Comment no. _____.	
6. Were the following qualitative criteria met for all reported PCDD/Fs: • All 2378 isomers within the RRT limits specified in Table 3 and both ions maximized within ±2 seconds. • All non-2378 isomers within established RT windows and both ions maximized within ±2 seconds. • The ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22. • All peaks ≥2.5 S/N. • No corresponding peak at PCDPE mass.					
7. Were peaks ≥2.5 S/N, which did not meet the above criteria, properly calculated and reported as EMPCs?					
8. Were all positive 2378-TCDF hits confirmed by analysis on DB-225?					
9. Are positive results within calibration range? *If no, list samples:* _____ _____				☐ OCDD/F or non-2378 exceeded calibration range ☐ Sample extracted at lowest possible volume	
11. If manual integrations were performed, are they clearly identified, initialed and dated?					
12. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
13. Was a narrative prepared and all deviations noted?					

* Such action must be taken in consultation with client.

Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist **LOT #**_____
Method: 8290 - KNOX-ID-0004-R7 **Page 2 of 2**

D. Preparation/Matrix QC	N/A	Yes	No	Why is data reportable?	2nd Level
1. LCS(OPR) done per prep batch and all analytes within the limits specified in QuantIMS reference data? *If no, list LCS(OPR) ID:* _____				□* Reanalysis not possible-insufficient sample. □ LCS %R high and affected analyte(s) were <ML in associated samples. □ See Comment no._____.	
2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____				□* Internal standards are high and blank demonstrates that analysis is free of contaminants. □* Sample internal standards OK and there is no analytes >ML in samples associated with blank.	
4. Are all analytes present in the method blank ≤ ML? *If no, list blank ID:* _____ _____ _____				□ Sample results are > 20x higher than blank. □* There is no analyte > RL in the samples associated with method blank. □* Reanalysis not possible-insufficient sample	
4. MS/MSD done per batch and are all recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD ID:* _____ _____ _____ _____ _____				□ LCS showed acceptable results indicating sample matrix effects. □ LCS showed acceptable results. High native analyte concentration relative to spike level. □ LCS showed acceptable results. RPD out due to lack of sample homogeneity. □ See Comment no. _____.	
E. Other					
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	Date:	Analyst:	Date:
Comments:		Comments:	

* Such action must be taken in consultation with client.

Figure 5

Aqueous Sample Extraction Flowchart

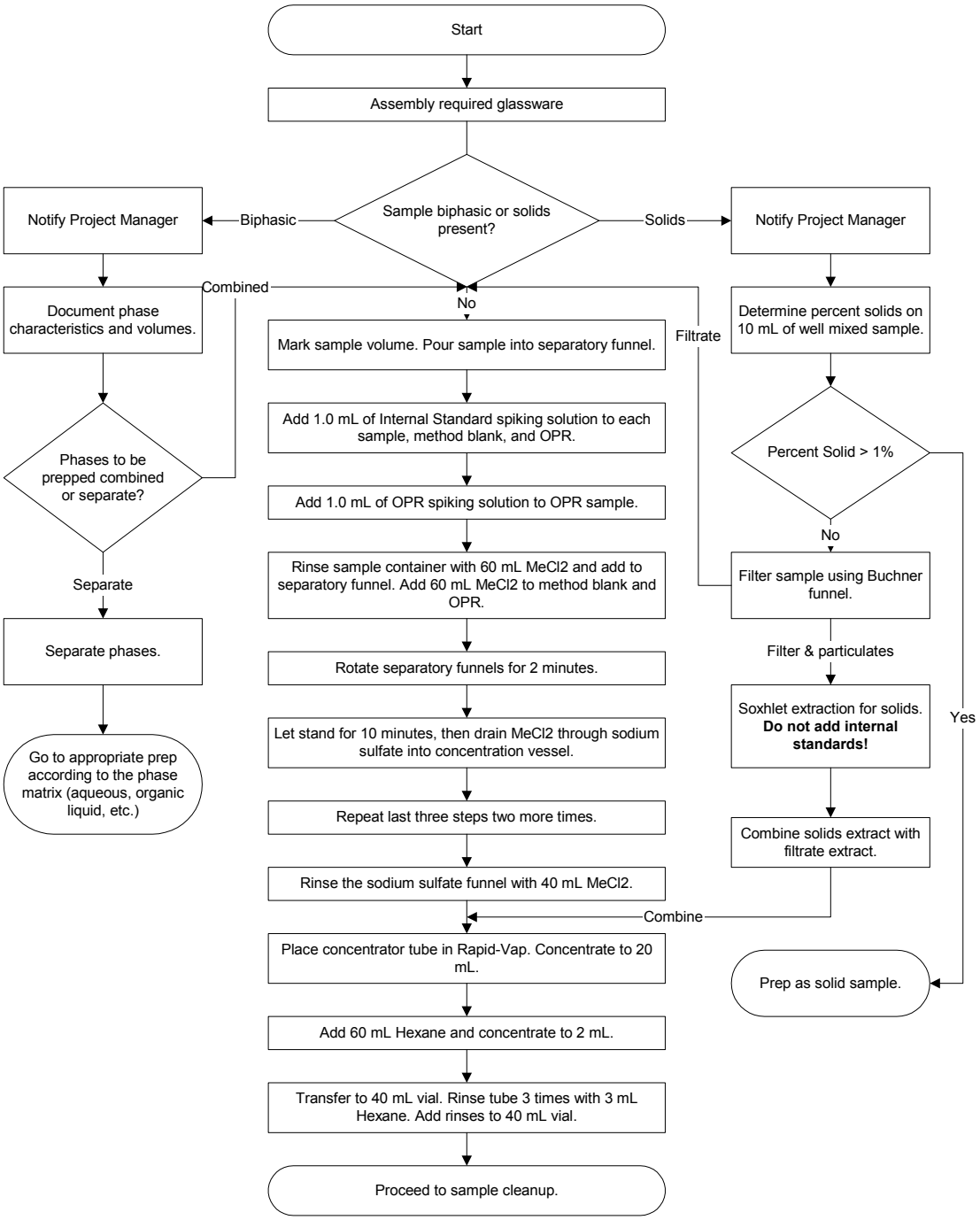


Figure 6

Solid Sample Extraction Flowchart

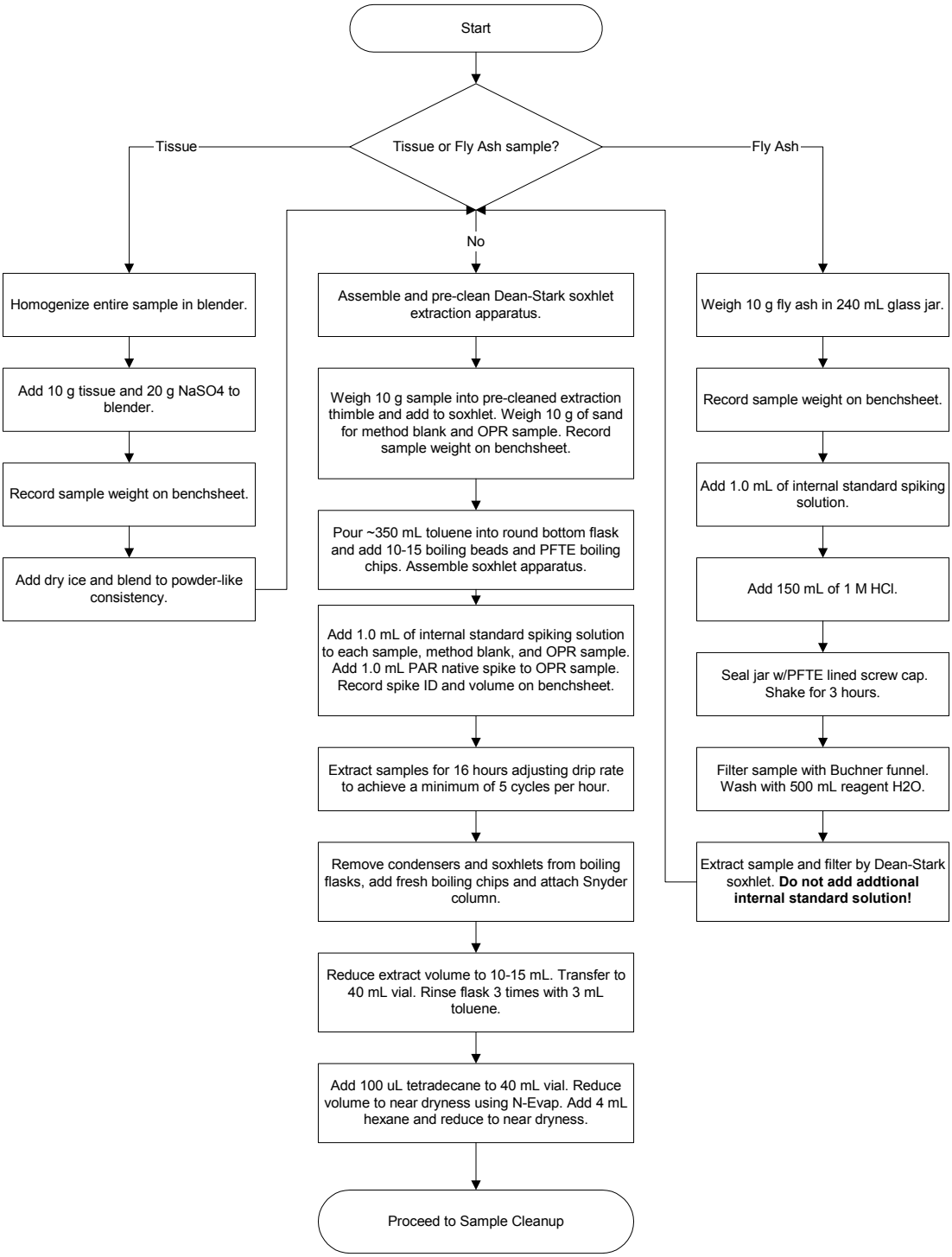


Figure 7

Sample Cleanup Flowchart

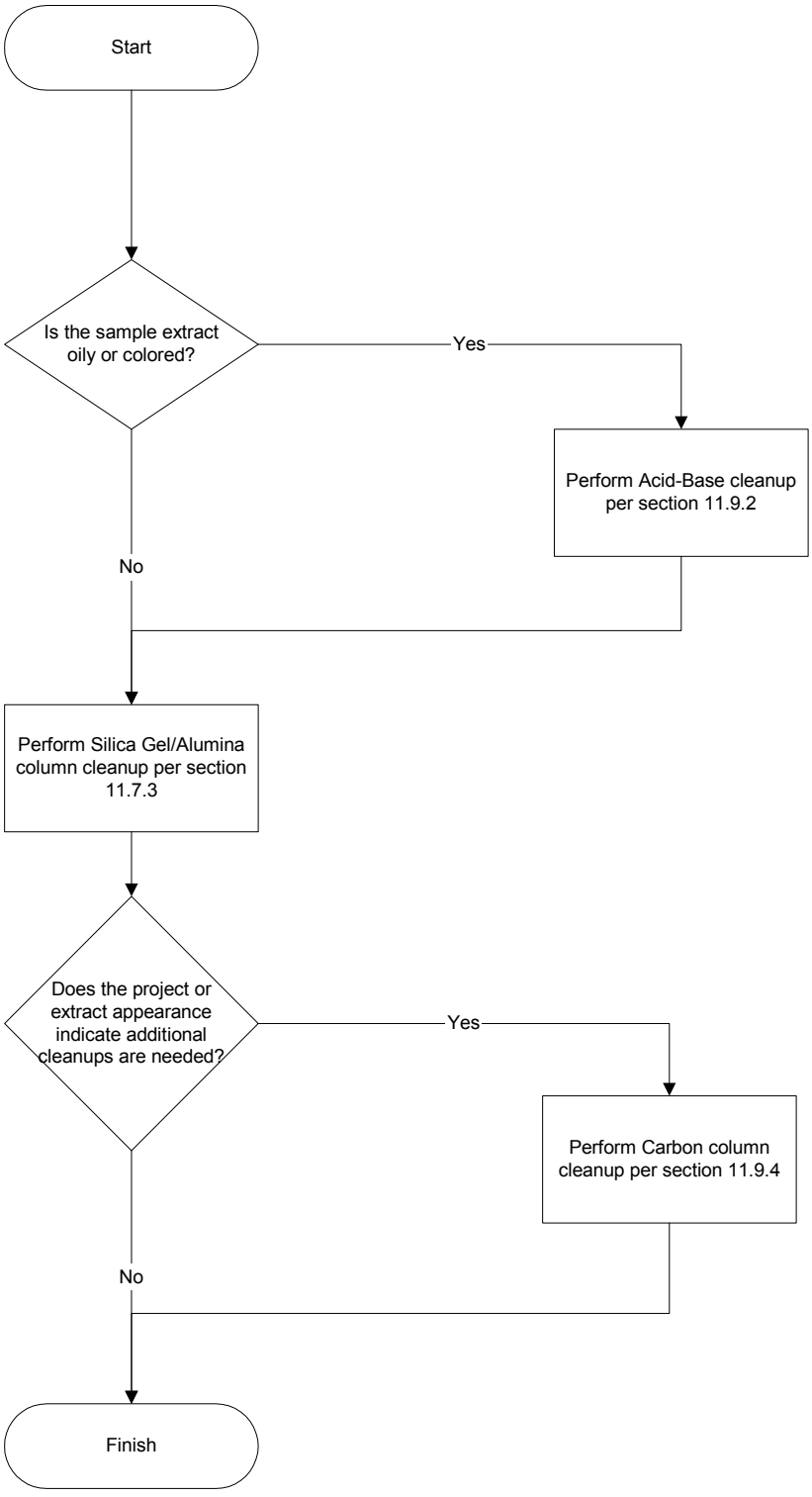
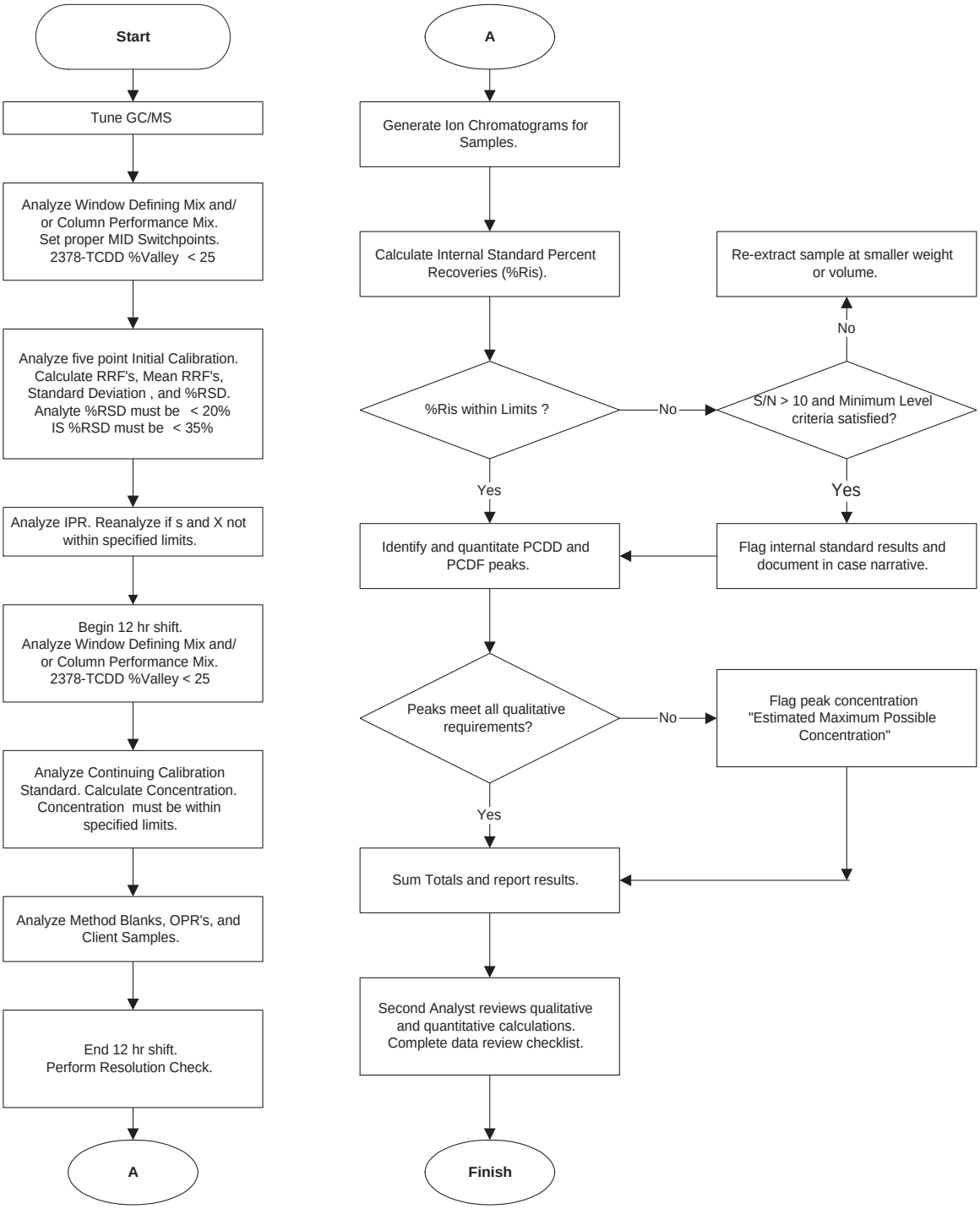


Figure 8

Analysis Of PCDD's and PCDF's by HRGC/HRMS



Appendix I

Evaluation of Method Blank Criteria for USACE Programs

18. Scope and Application

18.1 This modification to the standard procedure is designed to meet analytical program requirements for USACE Hazardous, Toxic and Radioactive Waste (HTRW) Projects. This procedure is based on the document entitled "Shell for Analytical Chemistry", US Army Corps of Engineers (USACE), EM200-1-3, Appendix I, 1 Feb 01.

18.2 This procedure modifies the evaluation and acceptance criteria for Method Blanks.

18.3 This procedures establishes Method Quantitation Levels (MQLs) based on Minimum Levels (MLs) and extract volumes that are specified in USEPA Method 8290.

19. Summary of Method

19.1 Same as the base procedure with the following exception.

19.2 Method blanks are evaluated based on the criteria specified in section 11.4.1 of the USACE "Shell".

20. Definitions

20.1 MDL Check Sample Concentration - The MDL Check sample concentration is one half of the Method Quantitation Level (MQL).

20.2 MQL - Method Quantitation Level - The MQL represents the value that the laboratory has demonstrated the ability to reliably quantitate target analytes. The MQLs for this method have been established based on the reference method calibration levels, required initial sample extraction weight/volume, and the recommended final extract volume.

20.3 Common Laboratory Contaminant - A target analyte which is present in the method blank due to environmental levels or reagent contamination which is beyond the control of the laboratory. For the purposes of this method, Octachlorodibenzodioxin is has been determined to be a common laboratory contaminant.

21. Procedure

21.1 The acceptance criteria in section 9.4 are replaced with the following;

The following criteria shall be used to evaluate the acceptability of the method blank data if project DQOs do not specify otherwise: The concentration of all target analytes shall be below the MDL check sample concentration for each target analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample results for the same analyte, whichever is greater for the MB to be acceptable. When this criterion is exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the method blank. However, sample corrective action may be limited to qualification for blank contamination (i.e., B-flag). When the concentration of any target

analytes within the MB are above the MDL check sample for the majority of the target analytes or above the MQL for target analytes known to be common laboratory contaminants, assess the effect this may have on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source of this contamination in the method blank. The case narrative should discuss this situation. If an analyte is found in the method blank and some, or all, of the other batch samples, additional corrective action is required to reanalyze the method blank, and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch would be reprepared and reanalyzed with a new method blank and batch specific QC samples. Sporadic cases of contamination may be difficult to control, however, daily contamination would not be acceptable.

22. References

22.1 US Army Corps of Engineers (USACE), EM200-1-3, Appendix I, 1 Feb 01, Shell for Analytical Chemistry Requirements.

Table 23

Method Quantitation Levels[1] for USACE NTRW Projects

Native Analyte	Water (pg/L)	Solid (pg/g)	Tissue (pg/g)	Wipe (pg)	Air (pg)	Waste (pg/g)
2,3,7,8-TCDD	20	2.0	2.0	20	20	20
Total TCDD	20	2.0	2.0	20	20	20
2,3,7,8-TCDF	20	2.0	2.0	20	20	20
Total TCDF	20	2.0	2.0	20	20	20
1,2,3,7,8-PeCDD	50	5.0	5.0	50	50	50
Total PeCDD	50	5.0	5.0	50	50	50
1,2,3,7,8-PeCDF	50	5.0	5.0	50	50	50
2,3,4,7,8-PeCDF	50	5.0	5.0	50	50	50
Total PeCDF	50	5.0	5.0	50	50	50
1,2,3,4,7,8-HxCDD	50	5.0	5.0	50	50	50
1,2,3,6,7,8-HxCDD	50	5.0	5.0	50	50	50
1,2,3,7,8,9-HxCDD	50	5.0	5.0	50	50	50
Total HxCDD	50	5.0	5.0	50	50	50
1,2,3,4,7,8-HxCDF	50	5.0	5.0	50	50	50
1,2,3,6,7,8-HxCDF	50	5.0	5.0	50	50	50
2,3,4,6,7,8-HxCDF	50	5.0	5.0	50	50	50
1,2,3,7,8,9-HxCDF	50	5.0	5.0	50	50	50
Total HxCDF	50	5.0	5.0	50	50	50
1,2,3,4,6,7,8-HpCDD	50	5.0	5.0	50	50	50
Total HpCDD	50	5.0	5.0	50	50	50
1,2,3,4,6,7,8-HpCDF	50	5.0	5.0	50	50	50
1,2,3,4,7,8,9-HpCDF	50	5.0	5.0	50	50	50
Total HpCDF	50	5.0	5.0	50	50	50
OCDD	100	10.	10.	100	100	100
OCDF	100	10.	10.	100	100	100

(1) MQLs are based on the method calibration limits specified in Table 1 of USEPA Method 8290 assuming a 20µL final extract volume as specified in section 7.8.1 of that method.

Attachment I: LRMS Dioxin Screen Strategy

LRMS Dioxin Screen Strategy

Analyte	10g LCL ppt pg/g	10g UCL ppt pg/g	5X UCL 10 g 20 uL	**5X UCL @ 1 g pg/g**	Level 4 Samp Conc pg/g	Level 4 Screen Using 1 g 20uL pg/g	Level 4 Screen Using 1 g 500 uL vs 20uL (pg/g)	Level 4 Screen Using 1.25 g 500 uL vs 20uL (pg/g)	**Level 4 Screen Using 2.5 1000 uL vs 20uL (pg/g)**
2,3,7,8-TCDD	1	400	2000	**20000**	100	1000	25000	20000	**20000**
2,3,7,8-TCDF	1	400	2000	**20000**	100	1000	25000	20000	**20000**
1,2,3,7,8-PeCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,7,8-PeCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
2,3,4,7,8-PeCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,7,8-HxCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,6,7,8-HxCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,7,8,9-HxCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,7,8-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,6,7,8-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
2,3,4,6,7,8-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,7,8,9-HxCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,6,7,8-HpCDD	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,6,7,8-HpCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
1,2,3,4,7,8,9-HpCDF	5	2000	10000	**100000**	500	5000	125000	100000	**100000**
OCDD	10	4000	20000	**200000**	1000	10000	250000	200000	**200000**
OCDF	10	4000	20000	**200000**	1000	10000	250000	200000	**200000**

If levels in screen are greater than the level 4 standard, do not prep. Send for 8280 analysis.
If peaks are observed at 1/5 to 1 time(s) the areas of the level 4 standard, prep at 1 g, 1/10 bench dilution.***
If peaks are observed at 1/50 to 1/5 time(s) the areas of the level 4 standard, prep at 1 g.***
If no peaks are observed, prep 10 grams.

*** In these cases, the glassware used is treated as contaminated. Post- Clean with solvent before washing.

Attachment II: Example Of Sample Moisture Content Worksheet

STL KNOXVILLE SPECIAL ANALYSIS GROUP SAMPLE MOISTURE CONTENT WORKSHEET

ENTERED BY: _____
QC'd BY: _____
QC BATCH #: _____

Note: EXTRACTION WEIGHT column is based upon a 10g sample adjusted for PERCENT SOLIDS

	LAB SAMPLE ID	SAMPLE NUMBER	PAN WT (g)	GROSS WET WT (g)	GROSS DRY WT (g)	SAMPLE WET WT (g)	SAMPLE DRY WT (g)	GC LAB 10/DRY FCT	DRYNESS FACTOR	PERCENT MOISTURE	PERCENT SOLIDS	EXTRACTION WEIGHT (g)	Lot #
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15													
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33													

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TESTAMERICA KNOXVILLE

ATTACHMENT TO SOP KNOX-ID-0004

TITLE: PCDD/PCDF TEQ Screening Using Modified Method 8290

(SUPERSEDES: ATTACHMENT REVISION 0)

Prepared By: _____

Reviewed By: _____
Technical Specialist

Approved By: _____
Quality Assurance Manager

Approved By: _____
Environmental, Health and Safety Coordinator

Approved By: _____
Laboratory Director

1.0 The screening method defaults to SW-846, Method 8290 as defined in the reference standard operating procedure KNOX-ID-0004, current revision, with the following modifications:

2.0 Sample Extraction/Preparation:
Ten grams of the solid sample will be weighed out and 2 mLs of internal standard solution will be spiked into the sample. The sample will then be extracted with toluene for 16 hours via soxhlet. After extraction, the sample will be concentrated to 10mLs. A 20uL portion of the sample will be removed and spiked with 1 mL of internal standard mix (Section 7.11.3 SOP KNOX-ID-0004). A screening method blank will be extracted and analyzed using the same technique. A dual column cleanup of the extract will be performed (Section 11.9.3), the extract will be concentrated to 20uL and analyzed on a HRGC/HRMS.

3.0 Instrument Performance
The mass-resolution and mass accuracy required for the HRMS instrument are the same as for the 8290 method ($\geq$10,000 resolving power, +/-5 ppm mass drift). The percent difference requirements for initial calibration is taken from Method 8290. Calibration verification requirements are listed in Table 1.

4.0 Data Deliverable
A case narrative will be provided. The screening results, as well as results for the Method Blank, and calibration standards will be provided. The results will be provided for the 17 dioxin and furan congeners, their toxic equivalency concentration, and the total toxic equivalency quotient. Qualifers are not required for the screening method.

Table 1 **Instrument Acceptance Criteria**

Performance Area	**Parameter**	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Mass Resolution	Peak width at 10 % peak height. m/z 304.98243 & 380.98756	Before initial calibration & at the beginning and end of each 12-hour shift.	≤ 100 ppm	Adjust tuning parameters, or perform instrument maintenance.
Mass Accuracy	Deviation between peak center and theoretical mass when locking on m/z 304.98243, and measuring m/z 380.98756	Before initial calibration & at the beginning and end of each 12-hour shift.	≤ 5 ppm	Perform EDAC calibration, or perform instrument maintenance.
GC Column Performance	Percent valley between 2,3,7,8-TCDD and closely eluting isomers specified in 8290	Before initial calibration & at the beginning of each 12-hour shift.	≤ 25 % valley	Replace liner, perform column maintenance. Replace inlet seal if necessary. Replace GC column if necessary
Initial Calibration – Mass Intensity	Ion Ratios for all analytes and internal standards for CS1 through CS5.	Before analyzing client samples. After major maintenance. When continuing calibration acceptance criteria cannot be achieved.	Per Method 8290 (+/- 15% of theoretical)	Adjust tuning parameters, or perform instrument maintenance.
Initial Calibration – Linearity	Response factors for CS1 through CS5	Before analyzing client samples. After major maintenance. When continuing calibration acceptance	Per Method 8290 (Percent RSD ≤ 20% for natives, 30% for labeled internal standards)	Adjust tuning parameters, or perform instrument maintenance.

		criteria cannot be achieved.		
Continuing Calibration – Mass Resolution, Mass Accuracy, GC Column Performance as shown above.				
Continuing Calibration – Response Factor Verification	Response factors for CS3	At the beginning and end of each 12-hour shift.	Beginning %D ≤ 30% of mean ICAL RF for natives, Closing verification </= 35% for natives.	Adjust tuning parameters, or perform instrument maintenance.

Table 2 Isomers Analyzed and Example Minimum Levels

Analyte	Minimum Level* ppb ng/g	TEF(1)	Minimum Level* ppb TEQ ng/g TEQ
2,3,7,8-TCDD	0.5	1	0.5
2,3,7,8-TCDF	0.5	0.1	0.05
1,2,3,7,8-PeCDD	2.5	1	2.5
1,2,3,7,8-PeCDF	2.5	0.03	0.075
2,3,4,7,8-PeCDF	2.5	0.3	0.75
1,2,3,4,7,8-HxCDD	2.5	0.1	0.25
1,2,3,6,7,8-HxCDD	2.5	0.1	0.25
1,2,3,7,8,9-HxCDD	2.5	0.1	0.25
1,2,3,4,7,8-HxCDF	2.5	0.1	0.25
1,2,3,6,7,8-HxCDF	2.5	0.1	0.25
2,3,4,6,7,8-HxCDF	2.5	0.1	025
1,2,3,7,8,9-HxCDF	2.5	0.1	0.25
1,2,3,4,6,7,8-HpCDD	2.5	0.01	0.025
1,2,3,4,6,7,8-HpCDF	2.5	0.01	0.025
1,2,3,4,7,8,9-HpCDF	2.5	0.01	0.025
OCDD	5.0	0.0003	0.0015
OCDF	5.0	0.0003	0.0015
		Total	30.45

"The authors of these TEFs caution against their inappropriate application to situations where they have limited toxicological relevance. The user is urged to consult The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds, van den Berg, et al., ToxSci Advance Access published July 7, 2006."

* Minimum Levels are subject to change based on sample size and moisture content.

Table 3 Summary of QC Measures

Performance Area	Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank/ Instrument Blank	Concentration of target analytes, using all reagents & glassware used for sample analysis.	Minimum of 1 for each 20 samples.	≤ Reporting Limit (minimum level)	If less than 5% of sample concentrations, narrate. If greater than 5% of sample concentrations, re-extract entire batch.
Laboratory Control Sample (Continuing Calibration standard)	Percent difference versus the ICAL response factors of native target analytes	Run at a frequency of once at the beginning and end of each 12 hour shift.	+/- 30%, native for open and +/- 35%, natives for close.	Re-extract entire batch.

SOP LB-3

DETERMINATION OF METHYL MERCURY BY AQUEOUS PHASE ETHYLATION, TRAP PRE-COLLECTION, ISOTHERMAL GC SEPARATION, AND CVAFS DETECTION:

BRL PROCEDURE FOR EPA METHOD 1630 (WATERS) AND EPA METHOD 1630, MODIFIED (SOLIDS)

Summary of SOP #BR-0011

Determination of Methyl Mercury by Aqueous Phase Ethylation, Trap Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630 (Waters) and EPA Method 1630, Modified (Solids)

Brooks Rand Labs

Revision 012
Written 1/90
Revised 4/1/08

Summary of BRL SOP for Determination of Methyl Mercury by Aqueous Phase Ethylation, Trap Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630 (Waters) and EPA Method 1630, Modified (Solids)

1.0 SCOPE AND APPLICATION

1.1 Method BR-0011 is the performance based procedure followed at Brooks Rand Labs (BRL) as EPA Draft Method 1630. Unless specifically stated otherwise in this document, all apparatus, materials, reagents, standards and procedures as stated in EPA Method 1630 are used at BRL.

NOTE: EPA Draft Method 1630 is for the determination of methyl mercury only in filtered and unfiltered aqueous samples. BRL Method BR-0011 is additionally for the determination of methyl mercury in sediment and biota. BRL has developed specific sample preparation methods for these matrices. With the exception of the maximum volumes analyzed, the procedures followed for the analysis of sediment and biota preparations are identical to the procedures followed for aqueous preparations.

2.0 SUMMARY OF METHOD

2.1 Prior to instrumental analysis, aqueous samples are prepared by distillation according to the procedure discussed in EPA Draft Method 1630, section 11. Additionally, aqueous and sediment samples may be prepared by dichloromethane (DCM) extraction. Biota samples are prepared by alkaline digestion.

2.2 Mono-methylmercury (MMHg) is determined by an improved method (Liang, Bloom, and Horvat 1994). The MMHg is first ethylated with sodium tetraethylborate ($NaBEt_4$) and collected by purging with dry, Hg free nitrogen onto a quartz tube filled with either Carbotrap™ or Tenax. The ethyl mercury derivatives are then thermally desorbed and transferred to a GC column held in an oven, which separates the species chromatographically by mass. The ethylated Hg compounds are pyrolized to Hg(0), then quantified by a cold vapor atomic fluorescence spectrophotometer (CVAFS). This method can be applied for the determination of MMHg in a variety of sample matrices and has been demonstrated as being very sensitive, precise, and accurate. Very good results were obtained for the determination of MMHg in standard and certified reference materials and numerous intercalibration samples (Liang, Bloom, and Horvat 1994).

3.0 INTERFERENCES

3.1 If properly applied, the distillation procedure will remove most if not all of the significant interferences. EPA Method 1630 dictates that fresh water samples must be preserved with between 0.3% to 0.5% (v/v) 11.6 M HCl (BRL preserves fresh water samples with 0.4% (v/v) 11.6 M HCl) and that salt water samples must be preserved with between 0.1% to 0.2% (v/v) 18 M sulfuric acid (H_2SO_4) (BRL preserves salt water samples with 0.2% (v/v) 18 M H_2SO_4).

3.2 Samples must not be preserved with nitric acid as it may cause partial decomposition of the analyte during distillation.

3.3 Positive artifact is possible with the distillation of samples that are high in inorganic mercury. Ambient organic matter may methylate 0.01% to 0.05% of the ambient inorganic mercury during distillation. In inorganic mercury contaminated waters this can significantly affect the results for methyl mercury. Solvent extraction may be preferable to distillation in samples that are high in divalent mercury (Hg(II)).

3.4 Refer to EPA Method 1630, Section 4.0, for a detailed account of possible contamination routes, interferences to the analysis, and how these are avoided or minimized at BRL.

4.0 APPARATUS AND MATERIALS USED AT BRL

4.1 Refer to EPA Method 1630, Section 6.0 for a list of materials used in the method employed at BRL.

4.2 Detailed instructions for the decontamination of bottles and other equipment are described in BRL SOPs BR-0400 and BR-0404.

4.3 Specific equipment used at BRL is listed below. Any modifications to EPA Method 1630 are described and explained.

4.3.1 Atomic fluorescence spectrophotometer (BRL part #AF-03): CVAFS systems are built by BRL (BRL Model III).

4.3.2 Recorder: BRL uses direct data acquisition with the BRL Guru™ integration software instead of a chart recorder or integrator as described in EPA Method 1631E, section 6.6. Use of this integration software is faster, eliminates the expense of chart recorders and/or integrators, allows for storage of data in diskette form, and eliminates possible transcription errors.

4.3.3 Reaction and purge vessels (BRL part #AF-31): A flask with a standard taper neck, fitted with a sparging stopper having a coarse glass frit that nearly extends to the flask bottom.

4.3.4 Trapping column (BRL part #AF-21): Tenax traps used for the collection of purged organomercury species.

4.3.5 Isothermal gas chromatography system: Consisting of GC column (BRL part #AF-34), GC oven (BRL part #AF-33), pyrolitic column (BRL part #AF-35), and temperature controller for GC oven (BRL part #AF-36). For a diagram of the system see Figure 2. Under a flow of high purity argon, organomercury species desorbed from a trapping column are carried by gas passing through the GC column, and eluted. Separated species are decomposed in a thermal decomposition tube and finally detected by CVAFS.

5.0 STANDARDS AND REAGENTS

5.1 Refer to EPA Method 1630, Section 7.0 for a list of standards and reagents employed at BRL.

5.2 Water: Deionized water is monitored on a daily basis during calibration of the instrument as part of the calibration blanks and the recoveries of the calibration standards.

5.3 MMHg Standard solutions

5.3.1 Standard stock solution: 1 mg/mL MMHg is purchased from a known, accredited vendor. This standard is used to prepare the calibration standards.

5.3.2 Intermediate stock solution: 1 µg/mL MMHg preserved with acetic and hydrochloric acid.

5.3.3 Working standard: 10 ng/mL MMHg preserved with acetic and hydrochloric acid.

5.3.4 Working standard: 1 ng/mL MMHg preserved with acetic and hydrochloric acid.

5.3.5 Working standard: 0.1 ng/mL MMHg preserved with acetic and hydrochloric acid.

5.3.6 Independent calibration verification solution: The independent calibration verification (ICV) solution is made up by digestion of the certified reference material DORM-2 (dogfish muscle).

5.4 Sodium tetraethylborate ($NaBEt_4$) solution: A working solution is made in a potassium hydroxide (KOH) solution that is then kept frozen. This reagent thawed prior to use. The solution expires three hours after being thawed. A new batch of the ethylating

reagent should be made as soon as there are any doubts about its quality (i.e. low recovery of matrix spikes). $NaBEt_4$ solids and solutions must not be used if they show any discoloration.

5.5 Sodium acetate buffer

5.6 Methanolic potassium hydroxide solution

5.7 Gases: High purity grade Argon and Nitrogen

5.8 potassium chloride (KCl) / L-Cysteine solution:

5.9 11.6 M hydrochloric acid (HCl)

5.10 18 M sulfuric acid (H_2SO_4)

5.11 Potassium bromide/sulfuric acid solution (KBr/H_2SO_4):

5.12 1 M copper sulfate solution ($CuSO_4$):

5.13 DCM: DCM (HPLC Grade) may be purchased from an authorized vendor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to EPA Method 1630, Section 8.0 and EPA Method 1669 (*Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels*) for a detailed description of sample collection, preservation, and storage methods.

6.2 Aqueous samples may be collected in fluoropolymer, FPE, or glass containers with fluoropolymer lined lids. Aqueous samples should be maintained at 0 – 4 ºC from the time of collection until preservation. Aqueous samples must be preserved within 2 days of collection. Freshwater samples are preserved with 4 mL/L of pre-tested concentrated HCl. Saline samples (Salinity > 10 ppt) are preserved with 2 mL/L of pre-tested 18 M H_2SO_4. Preserved samples are stable for up to 6 months if kept in the dark and cool. Brooks Rand Labs policy is to store all aqueous MMHg samples from 0 – 4 ºC.

6.3 Biota and sediment samples may be collected in glass or HDPE containers. Solid samples must be maintained at 0 – 4 ºC from the time of collection until receipt by BRL. Upon receipt, solid samples are moved to freezers for storage. Solid samples may be held for at least 1 year if kept in the dark at < -15 ºC.

NOTE: Due to uncertainty inherent in accurately measuring sample temperatures, it is understood that the measured temperature may be as much as ±2 ºC from the actual temperature. Therefore, as long as water samples remain

unfrozen, ±2 ºC are allowed beyond the above ranges without requiring qualification of the data.

7.0 SAMPLE PREPARATION

7.1 Refer to EPA Method 1630, Section 11.0 for a detailed description of the preparation of samples. Depending on the purposes and definitions of investigations of mercury biogeochemistry cycling, samples are prepared in the following methods prior to analysis.

7.2 Preparation of aqueous samples for MMHg analysis.

The following two isolation methods, distillation and solvent extraction, have been used at BRL for the determination of MMHg in aqueous samples. Good agreement was obtained in the comparison of the two methods for most water samples studied: For organic rich and/or high level sulfide containing samples, the distillation showed some advantages over the solvent extraction method with higher recoveries (85 ± 4%, Horvat, Bloom, and Liang, 1993). In addition, extraction consumes large quantities of organic solvent, which can result in environmental contamination. Therefore, distillation is the preferred preparation method for aqueous samples at BRL.

7.2.1 Distillation of aqueous samples:

Reagents: KCl in L-Cysteine, H_2SO_4

Distillation devices: Vials and caps for distillation and distillate collection are made of fluoropolymer obtained by Savillex Corporation, USA.

Distillation procedures: An aliquot of water sample, typically 50ml, is transferred into a fluoropolymer vial. All blanks including lab fortified blanks (LFBs) should be prepared by weighing out 50 mL of a 0.4%HCl solution then spiked if appropriate. Add KCl/L-Cysteine solution and H_2SO_4. Start the distillation immediately after addition of reagents with a nitrogen flow and at a heating block.

The distillate is collected in a fluoropolymer vial containing chilled DIW. The distillation is finished when the final distillate volume is correct.

7.3 Preparation of biological materials for MMHg.

7.3.1 Alkaline digestion: Weigh the biological material (wet, homogenous) into a fluoropolymer vial. Add KOH methanol solution and cap the vial tightly. Digest the sample in an oven. After digestion, dilute to the final volume with methanol. The day of analysis (if different from day of preparation), samples should be shaken thoroughly and allowed to resettle prior to analysis. Biological digestates may be stored up to seven days prior to analysis.

7.3.2 Distillation (following digestion): Distillation can significantly reduce the detection limits for the analysis of MMHg in biota samples.

Distill the alkaline digestion following the procedure outlined in section 7.2.1 for the distillation of aqueous samples.

7.4 Preparation of sediments and soils for MMHg.

7.4.1 Solvent extraction for sediments: Sediment samples should be extracted to avoid the potential for artifact formation of MMHg during distillation. An aliquot of sediment sample is accurately weighed into a clean fluoropolymer vial. The KBr/H_2SO_4 solution (Section 5.11) and $CuSO_4$ solution (Section 5.12) are added to the sample, which is then allowed to leach. After leaching, DCM is added. The sample is shaken and centrifuged. The sample phases are then separated. The organic layer is collected directly to a triple rinsed Teflon® bottle. DIW is added and the sample is then heated. Sediment extractions are stable for up to 48 hours if stored at room temperature in the dark.

The sample is then diluted to 100 mL with additional DIW. The extracted sample is analyzed following the same procedure used for the analysis of water distillations.

8.0 INSTRUMENT CALIBRATION AND SAMPLE ANALYSIS

8.1 Refer to EPA Method 1630, Sections 10.0, 11.0, and 12.0 for a detailed description of the analysis of samples and the calculation of results.

8.2 Instrument Calibration: BRL follows EPA method 1630, Section 10.0 for the instrument calibration with the same exceptions as for sample analysis. Standards, typically 2, 10, 50, 250, and 1000 pg MMHg are analyzed.

8.3 Instrumental Analysis: Refer to EPA method 1630 section 11.2 for a detailed description of the analysis. Listed in the appendix to this SOP are the modifications BRL has adopted.

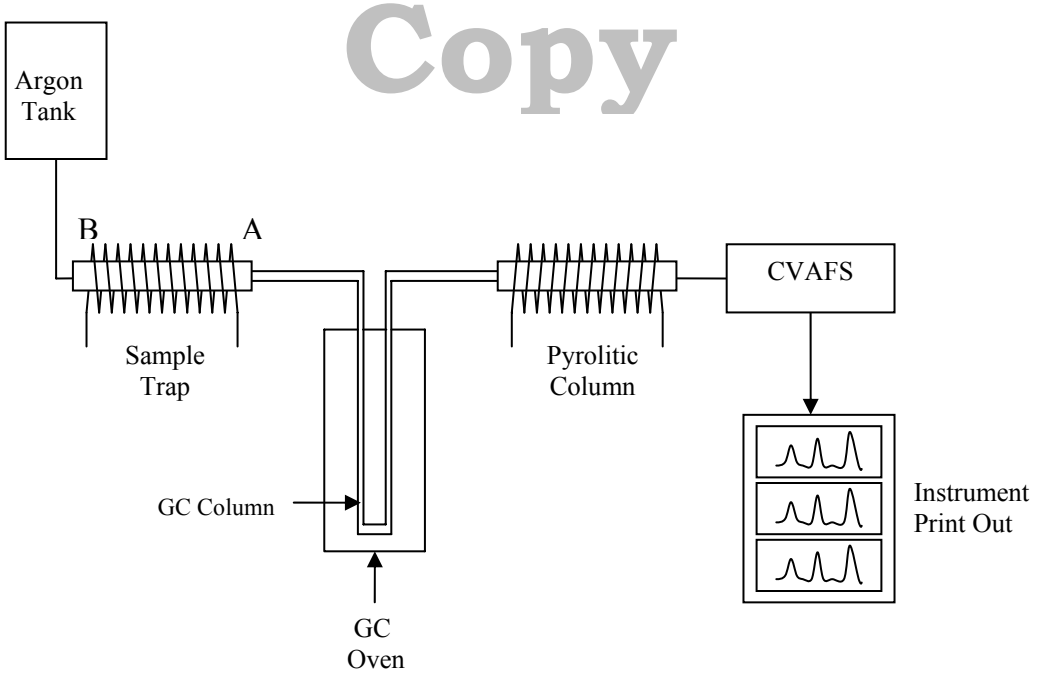

Figure 2: A schematic diagram of the isothermal Gas chromatograph system

9.0 QUALITY CONTROL

9.1 Refer to EPA Method 1630, Section 9.0 for a detailed description of the quality control procedures employed at BRL for this method.

9.2 All quality control data should be maintained and available for easy reference and/or inspection.

9.3 Each analyst must perform an initial demonstration of capability (IDOC) for the analysis of methyl mercury prior to the analysis of any client samples. The IDOC consists of an initial precision and recovery (IPR) study following the procedure in EPA Draft Method 1630, Section 9.2.2. The acceptance criteria and run sequence for the IDOC can be found in Table 3 in Section 11 of this SOP.

9.4 Calibration data must be composed of a minimum of 1 ethylation blank (BRL analyzes 4 ethylation blanks prior to analyzing the calibration standards) and a minimum of 5, preferably 6, standards (See Section 8.2 of this SOP for the standards used to calibrate instruments at BRL). Such a calibration should be run daily, prior to analysis, or whenever stock standards have been remade, conditions have changed, or initial calibration check (ICV) or ongoing precision and recovery (CCV) as defined in Section 9.5 do not yield acceptable recoveries.

9.5 The CCV solution prepared by spiking the ethylation vessel with 25 pg methyl mercury using the calibration standard and followed by an ethylation blank must be analyzed following calibration and at the end of the analysis of each analytical batch. An

independent calibration verification (ICV) is analyzed daily with the calibration. The criterion for the recovery of the CCV solution is 67-133% and the recovery criterion for the recovery of the ICV solution is 80-120%. All ethylation blanks must contain no more than the level of methyl mercury found in the low calibration standard.

9.6 Matrix spike/matrix spike duplicate (MS/MSD) analysis should be performed once per every 10 client samples or once per batch, whichever is greater. A matrix spike sample is defined as an aliquot of homogenized sample that has a known amount of analyte added to it. The matrix spike sample is then processed through the entire preparation and analytical procedure. Bias is then determined by calculating the percent recovery of the known amount using the following formula:

Percent Recovery = 100 ∗ (spiked sample result (conc.) - sample result (conc.)) / (amount spiked)

The criterion for spike recovery is determined by control charts and is different for each matrix type. The specific matrix spike recovery criteria for each matrix type and preparation procedure can be found in Tables 5 and 6 in Section 11 of this SOP.

The relative percent difference between the MS and the MSD is calculated using the following formula:

$$RPD = 200 \cdot (\left| MS\text{-}MSD \right|) / (MS + MSD)$$

The RPD for the MS/MSD pair must meet the criterion for each of the matrix types found in Tables 5 and 6 in Section 11 of this SOP.

9.7 Method duplicates are prepared and analyzed upon client request. For solid matrices method duplicates should be performed in conjunction with the MS/MSD samples and whenever the heterogeneity of a sample is deemed great enough that it may cause problems with the analysis of the sample. The relative percent difference (RPD) between duplicate samples is calculated using the same formula as used to calculate the RPD between the MS and MSD samples. The specific RPD criteria for each matrix type and preparation procedure can be found in Tables 5 and 6 in Section 11 of this SOP. If the acceptance criterion for duplicate analysis is not met for either samples or matrix spike samples, then the system performance is unacceptable. Associated samples must be qualified or the problem must be corrected and the samples reanalyzed.

9.8 Field duplicates are analyzed at the client's discretion. The acceptance criterion for field duplicate analysis is the same as that used for method duplicate analysis. The client must be notified immediately anytime that the acceptance criterion for known field duplicates is not met.

9.9 Four method blanks (MB) should be prepared and analyzed with each batch. The method blanks are prepared just using the reagents. All method blank results must meet the acceptance criteria set forth in Tables 5 and 6 of Section 11.

9.10 Laboratory fortified blanks (LFB) are prepared and analyzed with each distillation batch at a minimum frequency of one per batch. LFBs are prepared by spiking a method blank sample with the calibration standard at a concentration of approximately 2.0 ng/L. The LFB is then distilled as per an aqueous sample. The acceptance criterion for the recovery of the LFB (recovery corrected) is identical to the acceptance criterion for the recovery of CCV samples.

9.11 Appropriate certified reference materials (CRM) for MMHg are prepared for all batches containing tissue or sediment samples. It is BRL policy to prepare one CRM with every solid batch. Criteria for CRM recoveries are determined by control charts. If control charts are not available then CRM results should be within 35% of the certified value (following recovery correction) for the analysis to be considered valid. CRM accuracy results not meeting this criterion shall be reprepared and reanalyzed or qualified at the discretion of the Laboratory Director. Currently, there are not any water based CRMs available.

10.0 REFERENCES

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Horvat, M.; May, K.; Stoeppler, M.; and Byrne, A.R. (1988) *Appl. Organomet. Chem.* 2: 515.

EPA Draft Method 1630 (January 2001) "Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS."

EPA Method 1669 (April 1995) "Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels."

11.0 TABLES

Table 1 Quality Control Acceptance Criteria and Corrective Action Guidelines for the Analysis of Methyl Mercury in Aqueous Samples by Distillation

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Ethylation Blank	Contamination from bubblers	4 prior to calib.; following calib. and end of batch	≤ the PQL	Clean and test bubblers until criteria met prior to any analysis
Calibration Standards	Acceptability of the Calibration Curve	Daily, prior to analysis of samples or whenever the CCV fails	RSD of response factors ≤ 15%; Recovery of Low Standard = 65 – 135%	Reanalyze suspect calibration standard. If criteria still not met, then remake standards and recalibrate the instrument
Independent Calib. Ver. (ICV) Continuing Calib. Ver. (CCV)	Accuracy	Following Cal.; Beginning and end and 1 per 10 sample preparations	ICV Rec. = 80-120% CCV Rec. = 67-133%	Correct problem (recalibrate, remake standard, etc.) and reanalyze ICV/CCV. If criteria met, reanalyze samples backwards (if possible) until 2 consecutive results with RPD ≤ 20%
Carryover Check Ethylation Blank	Contamination due to carryover in the bubbler/trap	Following any unusually high result. Currently ≥ 2x the high standard	≤ the PQL	Clean and continue to test bubbler/trap combo until criteria met prior to further use. Reanalyze samples that were analyzed in same bubbler/trap following high result
Method Blank	Contamination from reagents, lab ware, etc.	4 per batch	Avg ≤ 0.045 ng/L StDev ≤ 0.015 ng/L or < $1/10^{th}$ of associated samples	Correct problem. All samples associated with a contaminated method blank must be reanalyzed.
Laboratory Fortified Blank (LFB)	Accuracy	1 per batch	Recovery = 70 – 130%*; RPD ≤ 30%	Reanalyze remaining volume. Correct problem prior to continuing analysis
Matrix Spike/Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Recovery = 65 – 135%*; RPD ≤ 35%	If **recoveries** similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicates	Precision	Per client request	RPD ≤ 35% or ± PQL if sample < 5x PQL	Correct problem and reanalyze all associated samples.

* Recovery Criteria for Matrix Spikes and LFB samples are based on recovery corrected results.

Table 2 Quality Control Acceptance Criteria and Corrective Action Guidelines for the Analysis of Methyl Mercury in Solid Samples by Distillation, Extraction, and/or Digestion

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Ethylation Blank	Contamination from bubblers	4 prior to calib.; following calib. and end of batch	≤ the PQL	Clean and test bubblers until criteria met prior to any analysis
Calibration Standards	Acceptability of the Calibration Curve	Daily, prior to analysis of samples or whenever the CCV fails	RSD of response factors ≤ 15%; Recovery of Low Standard = 65 – 135%	Reanalyze suspect calibration standard. If criteria still not met, then remake standards and recalibrate the instrument
Independent Calib. Ver. (ICV) Continuing Calib. Ver. (CCV)	Accuracy	Following Cal.; Beginning and end and 1 per 10 sample preparations	ICV Rec. = 80-120% CCV Rec. = 67-133%	Correct problem (recalibrate, remake standard, etc.) and reanalyze ICV/CCV. If criteria met, reanalyze samples backwards (if possible) until 2 consecutive results with RPD ≤ 20%
Carryover Check Ethylation Blank	Contamination due to carryover in the bubbler/trap	Following any unusually high result. Currently ≥ 2x the high standard	≤ the PQL	Clean and continue to test bubbler/trap combo until criteria met prior to further use. Reanalyze samples that were analyzed in same bubbler/trap following high result
Method Blank	Contamination from reagents, lab ware, etc.	4 per batch	Avg ≤ 2 x MDL StD ≤ 2/3rd MDL or < 1/10th of associated samples	Correct problem. All samples associated with a contaminated method blank must be reanalyzed.
Certified Reference Material (CRM)	Accuracy	1 per batch	Soil Rec=65-135%* Biota Rec=65-135%	Correct problem prior to continuing analysis
Matrix Spike/Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Soil Rec=65-135%*; RPD ≤ 35% Biota Rec=65-135%; RPD ≤ 35%	If **recoveries** similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicate	Precision within a given matrix	In association with MS/MSD	RPD ≤ 35% or ± 2x PQL if sample < 5x PQL	If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.

* Recovery Criteria for Distilled Matrix Spikes and CRM samples are based on recovery corrected results.

SOP LB-4

POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY (SW-846 METHOD 8082)

Title: Polychlorinated Biphenyls (PCB's) by Gas Chromatography [SW-846 Method 8082]

Approvals (Signature/Date):

William S. Cicero Laboratory Director — 12/27/07 Date	Jacob L. Bailey Current Department Manager — 12/27/07 Date
Kirstin L. McCracken Quality Assurance Manager — 12/27/07 Date	Bryce E. Stearns Technical Director — 12/27/07 Date
Bryce E. Stearns Interim Health & Safety Coordinator — 12/27/07 Date	

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-GC-8082PCB.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

STANDARD OPERATING PROCEDURE
STL BURLINGTON

POLYCHLORINATED BIPHENYLS (PCB'S) BY GAS CHROMATOGRAPHY
SW-846 METHOD 8082

Applicable Matrix: Non-Potable Water, Solid & Chemical Materials, and Tissue

APPROVAL SIGNATURES

William S. Cicero
Laboratory Director
Date: April 27, 2007

Kirstin L. McCracken
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Bryce E. Stearns
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Date: April 27, 2007

Jacob L. Bailey
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Date: April 27, 2007

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of concentrations of Polychlorinated Biphenyls (PCBs) using dual column Gas Chromatography with Electron Capture Detectors (GC/ECD) from extracts derived from non-potable water, solid and chemical materials and tissue matrices. The PCBs are identified as an Aroclor through pattern matching, Aroclors are a trade name commonly used to describe mixtures of PCB isomers. This SOP is applicable to the analytical procedure only; the extraction and extract cleanup methods referenced in this SOP are described in the following laboratory SOPs:

LM-OP-3510	Separatory Funnel Extraction
LM-OP-3540	Soxhlet Extraction
LM-OP-3541	Automated Soxhlet Extraction
LM-OP-3550	Ultrasonic Extraction
LM-OP-Cleanup	Extract Cleanup Procedures
LM-OP-GPC	Gel Permeation Chromatography (GPC)

1.2 The analytes that can be determined by this procedure and their associated Reporting Limits (RL) are listed in Table 1, Section 18.0.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate matrix-specific extraction technique. After extraction, the extract may be subject to cleanup depending on the nature of sample matrix and the target analytes. After cleanup, the extract is analyzed by injecting a 2 uL aliquot into a dual capillary column GC/ECD.

2.2 This procedure is based on SW-846 Method 8082, Revision 0, December 1996.

3.0 DEFINITIONS

3.1 A list of terms and definitions is given in Appendix C.

4.0 INTERFERENCES

4.1 Contaminated solvents, reagents or equipment can cause interferences. To reduce the occurrence of this type of interference, glassware must be cleaned thoroughly before use following the procedure given in laboratory SOP LM-OP-Glass.

4.2 Phthalate esters introduced during sample preparation can pose a problem in the determination of target analytes. Common flexible plastics contain varying amounts of phthalate esters, and these can be easily extracted or leached during extraction. To minimize this interference, avoid contact with any plastic materials.

4.3 Non-target compounds co-extracted from the sample matrix can also cause interference, the extent of which will vary considerably depending on the nature of the samples.

Elemental sulfur is often found in sediment samples and its presence will result in broad peaks. Samples are screened before analysis and those samples that contain high levels of sulfur are subject to cleanup using activated copper before analysis (SW-846 3660B). Waxes, lipids, other high molecular weight materials and co-eluting organophosphorous pesticides may be removed by extract cleanup with GPC (SW-846-3640A). Co-eluting chlorophenols can be eliminated by cleanup with silica gel (SW-846 3630C), or Florisil (SW-846 3620B), or Sulfuric acid Cleanup (SW-846 3665A) may be used to eliminate certain organochlorine pesticides and elevated baselines.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst must be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.3 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. Note: Table 2 does not include all materials used in the procedure. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used can be found in Section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 EQUIPMENT AND SUPPLIES

6.1 Autosampler Vials, National Scientific or equivalent.

6.2 Computer Hardware/Software: GC Acquisition Platform - VAX 4505 (GVAX) Multichrom V2.11. Data Processing - Hewlett-Packard 9000-series computers, an HP9000 D250 (Chemsvr4) and an HP 9000 K200 (Chemsvr5)/ HP-UX 10.20 and Target V3.5 or higher.

6.3 GC/ECD: with dual columns, dual ECDs, and auto-sampler capable of a 2-µl injection split onto two columns: HP 5890 with Leap Technology CTC A200SE and A200S Fisons autosamplers, Agilent Technologies 6890N with 7683 Series injector, or equivalent.

6.4 GC Columns: A dual fused silica capillary column system that will provide simultaneous primary and confirmation analyses.

- RTX-5, (30m x 0.25 mmID x 0.25um)
- RTX-35, (30m x 0.25 mmID x 0.25um)
- Equivalent columns may be used, provided the elution orders are documented and compound separations are maintained.

6.5 Hydrogen Generator: Whatman.

6.6 Volumetric Syringes, Class "A" (10µl, 25µl, 50µl, 100µl, 250µl and 500µl), Hamilton or equivalent.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

- Hexane, Ultra-Resi Analyzed. JT Baker or equivalent.

7.2 Standards

Purchase stock standard solutions from commercial vendors. Prepare calibration and working standards solutions by diluting a known volume of the stock standard in an appropriate solvent to a specified volume. Standard preparation formulations for this procedure are provided in Appendix A.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Sample extracts must be stored at 4°C ± 2° until the time of analysis. The analytical holding time is 40 days from date of sample extraction.

8.2 Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1 The minimum frequency requirements, acceptance criteria and recommended corrective action for all QC samples are summarized in Table 3, Section 18.0. Below is a summary of each type of QC sample that is analyzed with the method.

9.2 A Method Blank (MB) and Laboratory Control Sample (LCS) are prepared with each extraction batch. These samples show that the laboratory is in control, independent of the sample matrix.

9.3 A Matrix Spike and Matrix Spike Duplicate (MS/MSD) are prepared with each extraction batch. Project specific MS/MSD and Sample Duplicates (SD) are performed per client request. These samples show the effect of the sample matrix on the accuracy and precision of the method.

9.4 A Surrogate spike is added to all field and QC samples before extraction to assess the effect of the sample matrix on the accuracy of the method in the specific sample matrix.

9.5 Instrumental QC standards include a five-point ICAL generated for Aroclor 1016 and 1260 (referred to as AR1660) and an initial one point calibration for all other Aroclors. After the ICAL, an Initial Calibration Verification (ICV) standard, also referred to as a second source standard, containing Aroclor 1660 is analyzed to verify the ICAL standard formulation. Continuing Calibration Verification (CCV) standards are analyzed before sample analysis, every ten samples thereafter, and at the end of the run to assess instrument drift.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Operating Conditions

Install a five meter deactivated guard column to the injection port and connect the guard column to the separate analytical columns using a glass "Y". Then attach the analytical columns to the dual ECD detectors.

The recommended instrument operating conditions are as follows:

Initial Temperature:	130°C for 1 minute
Temperature Program:	20°C per minute to 190°C to 5°C per minute to 225°C to 20.0°C per minute to 300°C. Hold for 6 minutes.
Detector Temperature	310°C
Injector Temperature:	225°C
Injection volume:	2μL
Carrier Gas:	Hydrogen (supplied by hydrogen generators)

Optimize the flow rate of the carrier gas by injecting an un-retained substance onto the column at an isothermal oven state and adjusting the flow to obtain the recommended dead volume time.

10.2 Retention Time Windows

When a new GC column is installed establish RT windows for 3-5 peaks for Aroclor 1660 by analyzing three standards over a 72-hour period and calculating the mean RT and Standard Deviation (SD). Calculate the RT window as mean RT $\pm$ 3SD of the three standards. If the SD is <0.01 minutes, the laboratory may use a default SD of 0.01 minutes. If, in the professional judgment of the analyst, this procedure results in an RT window that is too tight and would favor false negatives, the laboratory may opt to use an alternate method to determine the RT windows as follows: using the RT of the midpoint initial calibration standard, calculate the RT window using $\pm$ 0.05 minutes from the midpoint of the RT in the initial calibration.

10.3 Initial Calibration

Before initial or daily calibration, inject an instrument blank (IBLK) consisting of hexane to bring the GC/ECD system online.

Perform a multi-point calibration of AR1660 at five concentrations to demonstrate linearity. AR1660 includes most of the peaks represented in the other five Aroclors. For the remaining Aroclors, analyze a mid-level standard for pattern recognition and response factor. Five point calibrations for the other Aroclors will only be performed when required by the client or when specified as a regulatory requirement. Use a minimum of three to five peaks per Aroclor for quantification.

Prepare the calibrations standards using the formulations provided in Appendix A. Inject 2-µl of each calibration standard onto the instrument using the same technique that is used for sample extracts described in Section 11.0.

The data processing system calculates the Calibration Factor (CF), mean CF and Relative Standard Deviation (%RSD) for each analyte on both columns The RSD for each target analyte must be less than or equal to 20% in order to use the mean CF or quantification. If this criterion is not met use another suitable quantification method for that analyte or correct the problem and repeat the calibration. Once a method of quantification is chosen for a specific compound, it must be consistent throughout the entire analytical sequence until a new initial calibration is performed.

Alternate Quantification Option:

Linear Regression & Weighted Linear Regression: Generate a curve of concentration vs. response for each analyte and calculate the correlation coefficient. The calibration must have a correlation coefficient (r) $\geq$ 0.995. If this criterion is not met, correct the problem and repeat the calibration. The use of linear regression requires a minimum of 5 calibration points. See SW-846 Method 8000B for linear regression calculations.

NOTE: Unless otherwise specified for the project, for DoD QSM work, the quantification option (mean CF or linear regression) must meet criteria for each target analyte otherwise the calibration must be repeated. The DoD QSM prohibits the reporting of samples against an ICAL that does not meet criteria even when associated analytical results are flagged.

10.4 Initial Calibration Verification (ICV)

Immediately after each calibration and prior to the analysis of any other QC or field samples, verify the accuracy of the initial calibration by analyzing a second source ICV.

Prepare the ICV using the formulation provided in Appendix A. Inject 2-µl of the ICV standard onto the instrument using the same technique that is used for sample extracts described in Section 11.0.

The percent recovery of each analyte must be within $\pm$ 20% of the expected value. If this criterion is not met, correct the problem and reanalyze the ICV. If the reanalysis fails,

remake the calibration standards and recalibrate. The acceptance criteria must be met on both columns.

10.5 Calibration Verification (CCV)

Analyze the continuing calibration verification standard (CCV) that contains AR1660 at a concentration at or below the mid-calibration range, each day before sample analysis, after every ten injections and at the end of each analytical batch to monitor instrument drift. The data system calculates the CF and percent difference for each analyte. The percent difference must be within ±15%. Compare the RT of each analyte in the CCV with the RT windows; the RT must be within the established window. The acceptance criteria must be met on both columns.

If the criteria are not met, the analysis of the CCV may be repeated once. If the reanalysis of the CCV fails, take corrective action. After corrective action, the sequence may be continued only if two immediate, consecutive CCVs analyzed at different concentrations are within acceptance criteria. If these CCVs do not meet the criteria, recalibrate prior to further analysis. Samples must be bracketed by passing CCVs, and samples before and after CCV failure must be reanalyzed, unless the CCV is high and there are no detects in the associated samples.

10.6 Troubleshooting: check the following items can be checked in case of calibration failures:

- ICAL Failure – Perform injection port maintenance, install new guard column, check detector ends to see if detector jet has slipped. In extreme cases, install new columns, particularly if the chromatography has degraded as evidenced by peak shapes.
- CCV Failure – Perform Injection port maintenance; if injection port maintenance does not restore CCV, install a new guard column and remove one or more loops from each analytical column.
- Needle crushed during injection - Replace the needle and check the injection port for obstructions and check the autosampler for misalignment.
- Auto-sampler failure - Reset the auto-sampler.
- Power failure - Reset run in Multichrom and re-acquire or re-initiate run sequence.

11.0 PROCEDURE

11.1 Analysis

Prepare the sample extracts for analysis by transferring ~100 uL of extract to an auto sampler vial and place the vials in the autosampler. Arrange the samples in a sequence that begins with the calibration standards followed by the analysis of QC samples, field samples and continuing calibration verification standards (CCVs).

An example analysis sequence is given below:

Injection Number	Lab Description
1	Instrument Blank
2	AR1221 (200 ppb)
3	AR1232 (200 ppb)
4	AR1242 (200 ppb)
5	AR1248 (200 ppb)
6	AR1254 (200 ppb)
7	AR1660 (50 ppb)
8	AR1660 (100 ppb)
9	AR1660 (200 ppb)
10	AR1660 (400 ppb)
11	AR1660 (800 ppb)
12	ICV
13-22	10 injections
23	CCV
	Repeat until ending with CCV

NOTE: Single point calibration standards for Aroclor 1262 and Aroclor 1268 at a concentration of 200 ppb may be analyzed as part of the calibration sequence after Aroclor 1254.

Enter the sample ID's into the data acquisition program in the order the samples were placed in the autosampler and start the analytical sequence and the autosampler.

Cleaning blanks (CBLK) consisting of hexane may be analyzed after high-level samples at the discretion of the analyst.

The data system identifies the target analytes by comparing the retention time of the peaks to the retention times of the initial calibration standards. The data system does not recognize Aroclor patterns. The analyst manually identifies Aroclors by comparing the pattern in the samples to the patterns in the initial calibration standards. When "weathered" Aroclor patterns are present, the laboratory identifies Aroclors based on the best overall pattern match. Using an average of the chosen quantification peaks per Aroclor, the data system calculates the corrected concentration for each target analyte from the calibration curve using the equations given in Appendix B. If sample interference is suspected, the laboratory may remove up to two quantification peaks per column. If the data system does not properly integrate a peak, perform manual integration. All manual integration must be performed and documented in accordance with laboratory SOP LP-QA-006 *Manual Integration.*

After analysis is complete, evaluate the results against the performance criteria given in Section 10.0 and Table 3, Section 18.0 and perform corrective action as necessary.

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the upper half of the calibration curve.

If an initial dilution is performed based on screen data, the diluted analysis should result in a determination within the upper half of the calibration curve. A more concentrated analysis is not necessary unless the result is not within the upper half of the calibration range when the project requires that all samples be analyzed undiluted or more concentrated regardless of screen results. Whenever dilutions are performed based on screen data, the screen data must be provided in the data package.

NOTE: When multiple dilutions are performed, the laboratory routinely reports the result from the appropriate diluted run (i.e. no target analyte above calibration range and the result for the analyte for which the dilution was performed is in the upper half of the calibration range). Undiluted and lesser dilutions are not routinely provided unless specifically requested by the client. For DoD work, the DoD QSM requires that the undiluted analysis or most concentrated dilution be reported along with the appropriate dilution (i.e. report multiple dilutions).

12.0 CALCULATIONS

12.1 See Appendix B.

13.0 DATA ASSESSMENT, CORRECTIVE ACTION & REPORTING

13.1 Data Review and Corrective Action

Review the samples, standards and QC samples against the acceptance criteria in Table 3, Section 18.0. If the results do not fall within the established limits, perform the recommended corrective action. If corrective action is unsuccessful, document the situation with a nonconformance report and/or qualify the data using an appropriate data qualifier (see Appendix C for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review refer to laboratory SOP LP-QA-019 *Data Review.*

In the absence of project specific control limits, use the in-house control limits specified in Table 1A, Section 18.0 for the evaluation of the LCS, MS/MSD and sample duplicate (SD).

NOTE: For DoD QSM work, unless the project specifies otherwise, if the in-house limit is outside the DoD QSM limit (identified in bold text in Table 1A), evaluate the QC samples against the DoD limit and take corrective action when recovery is outside the QSM limit but report the in-house limit in the data report. If the in-house limit is within the DoD limit, use the in-house limit for evaluation and reporting.

13.2 Data Reporting

Report quantitative results in appropriate units and significant figures and correct the results for sample volume, dilution factor, and percent solids. Unless otherwise specified for the project, report the higher result between the two columns. The data system calculated the Relative Percent Difference (RPD) between the results from each column. If the RPD is greater than 40%, qualify the result with a "P" data qualifier. If in the

analyst's judgment, the higher result is due to overlapping peaks, or interference peaks, the lower of the two results may be reported, the data qualified and the issue discussed in the project narrative.

The laboratory's routine reporting limit (RL) for each target analyte is provided in Table 1, Section 18.0. The RL is the threshold value below which results are reported as non-detected and the RL may be project-specific or laboratory routine. In either case, report sample results that have concentrations for target analytes less than the designated RL as the RL with a "U" data qualifier. Report the results for soil samples on a dry weight basis unless otherwise specified and adjust the RL for sample dilution and/or concentration.

Some projects require the reporting of positively identified target analytes less than the RL. In this case, report results to the RL but flag all results between the limit of detection (verified MDL) and the RL with a "J" data qualifier to indicate the value is estimated.

NOTE: Unless otherwise specified for a DoD project, the DoD QSM requires the reporting of estimated values.

Some projects require RLs that are less than the laboratory's routine RL. Sample results may be reported to the project RL without qualification if the project RL is greater than the limit of quantification (LOQ). In this context, the LOQ is defined as the concentration of the low calibration standard. If the project RL is less than the LOQ, all values less than the LOQ must be reported as estimated and flagged with a "J" data qualifier.

Further guidance on the application and use of the limit of detection (LOD), limit of quantitation (LOQ) and the RL, is provided in laboratory SOP LP-QA-005.

When multiple dilutions are performed, report the result from the appropriate diluted run (i.e. no target analyte above calibration range and the result for the analyte for which the dilution was performed is in the upper half of the calibration range). Undiluted and lesser dilutions are not routinely provided unless specifically requested by the client. For DoD work, the DoD QSM requires that the undiluted analysis or most concentrated dilution be reported along with the appropriate dilution (i.e. report multiple dilutions). Additionally, whenever dilutions are performed based on screen data, provide the in the data package.

Weathering of PCB's in the environment may alter the PCB's to the point that the pattern no longer matches the pattern established for that Aroclor in the initial calibration. The laboratory takes the best pattern match approach to the identification and quantification of weathered PCB's. In many cases, this entails choosing peaks such that the weathering pattern does not affect the quantification of the Aroclor.

13.3 Data Management and Records: Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP LP-QA-0014 *Laboratory Records*.

14.0 METHOD PERFORMANCE

14.1 A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP–QA-005 *Procedures for the Determination of the Limit of Detection (LOD), Limit of Quantitation (LOQ) and Reporting Limit (RL).*

14.2 Each analyst must complete an initial demonstration of proficiency (DOC) before independent analysis of client samples and demonstrate repeated proficiency annually thereafter. The procedures for employee training and demonstration of proficiency are further described in laboratory SOP LP-QA-011 *Employee Training.*

14.3 The laboratory in-house control limits used to evaluate accuracy, precision and surrogate recoveries are provided in Table 1A. The control limits for accuracy are statistically derived based on compiled data and are set at 3 standard deviations around the mean using the procedures described in laboratory SOP LP-QA-013 *Control Limits.*

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

The following waste streams are produced when this method is carried out.

- Sample Extract Vials: Satellite container-5 gallon bucket located in fume hood.
- Solvent Waste: Satellite container-4 L glass bottle located in fume hood.

Transfer the waste stream to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waster storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in the laboratory SOP LP-LB-001 *Hazardous Waste.*

16.0
16.1 REVISION HISTORY

16.2 Title Page: Updated to show current management team
16.3 Section 10.0: Changed ICV criteria to ± 20% of expected value.
16.4 Section 11.0: Added DoD QSM requirement for multiple dilution reporting and requirement to perform corrective action for DoD work, when recoveries are outside DoD QSM limits.
16.5 Section 12.0: Added DoD QSM requirement for multiple dilution reporting.
16.6 Table 1: Updated to current information and added DoD QSM limits.
16.7 Table 3: Changed ICV criteria to ± 20% of expected value.
16.8 Appendix B: Added equation for air matrix.

17.0 REFERENCES

17.1 SW-846 Method 8082 Polychlorinated Biphenyls by Gas Chromatography, Revision 0; December 1996. USEPA SW-846 Methods for Evaluating Solid Waste, Update III.

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1:Target Analyte List
18.2 Table 1A: Routine Accuracy and Precision Limits
18.3 Table 2:Primary Materials Used
18.4 Table 3:QC Summary, Acceptance Criteria and Recommended Corrective Action
18.5 Appendix A: Standard Preparation Tables
18.6 Appendix B: Equations
18.7 Appendix C: Terms & Definitions

Table 1: Routine Target Analyte List & Reporting Limit (RL)

ANALYTE	Routine Reporting Limit (RL)[1]	
	Water (ug/L)	Solid (ug/Kg)
AR1016	0.50	17
AR1221	0.50	17
AR1232	0.50	17
AR1242	0.50	17
AR1248	0.50	17
AR1254	0.50	17
AR1260	0.50	17
AR1262	0.50	17
AR1268	0.50	17

[1] The routine RL is the unadjusted value that can be achieved in a blank matrix.

Table 1A: Routine Accuracy and Precision Limits[1]

Analyte	In-House Limits[2] (%R)		Precision (RPD) (≤)	DoD QSM Limit[4]	
	Water	Solid		Water	Soil
AR1016	65-120	60-120	30	25-145	40-140
AR1260	55-120	60-125	30	30-145	60-130
Surrogate: Decachlorobiphenyl (DCB)	65-115	65-125	NA	40-135	60-125
Surrogate:TCMX (Advisory)[5]	60-115	60-125	NA		

[1] The limits in this table are those used as of the effective date of this SOP.
*[2] Any limits that appear in **bold** text are those where the in-house limit is outside of the DoD QSM limit.*
[3] Default limits were set due to an insufficient number of data points available to generate in-house control limits.
[4] Limits are taken from Appendix D of DoD QSM. If no limit listed in this table, no limit was listed in the DoD QSM.
[5] The control limits for TCMX are advisory. Corrective action is not performed when recovery is outside limits.

Table 2: Primary Materials Used

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.

[1] Always add acid to water to prevent violent reactions.
[2] Exposure limit refers to the OSHA regulatory exposure limit.

Table 3: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action[1]
ICAL	Before sample analysis, when CCVs indicate calibration is no longer valid; after major instrument maintenance	CF: RSD ≤ 20% Linear Regression: r ≥ 0.995	Correct problem, reanalyze, repeat calibration.
ICV	After each initial calibration	(% R) ± 20% from expected value	Correct problem and verify second source standard. If that fails, repeat initial calibration.
CCV	Daily before sample analysis, every 10 samples and at the end of the analytical sequence	% Difference or Drift ±15%	Re-analyze once, if still outside criteria perform corrective action, sequence can be re-started if two successive CCVs pass, otherwise repeat ICAL and all associated samples since last successful CCV, unless CCV is high and bracketed samples are non-detects.
MB	One per extraction batch of 20 or fewer samples	Target Analyte < RL DoD: ≤ ½ RL	Examine project DQO's and take appropriate corrective action, which may include re-analysis of MB, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. If there are no detects in samples, or if all detects are > 10 X MB level, re-prep and reanalysis may not be required.
LCS	One per extraction batch of 20 or fewer samples	See Table 1A	Examine project DQO's and take appropriate corrective action, which may include re-analysis of LCS, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. Flag all reported values outside of control limits.
MS/MSD SD	MS/MSD: Per extraction batch SD: Per client request	See Table 1A	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze and/or re-extract. Flag all reported values outside of control limits.
Surrogate Spike	All field and QC samples	See Table 1A	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze or re-extract. If matrix effect, review project DQOs to determine if a matrix effect must be confirmed by re-analysis. Flag all reported values outside of control limits.

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Appendix A: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in hexane using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP LP-QA-002 *Standard Preparation* for further guidance.

Intermediate Calibration Standards (10 mg/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR 1660 (1016/1260)[1]	Restek #32039	1000	0.40	40	10
AR1254	Restek #32011	1000	0.40	40	10
AR1248	Restek #32010	1000	0.40	40	10
AR1242	Restek #32009	1000	0.40	40	10
AR1232	Restek #32008	1000	0.40	40	10
AR1221	Restek #32007	1000	0.40	40	10
AR1262	Restek #32409	1000	0.40	40	10
AR1268	Restek # 32410	1000	0.40	40	10

[1] *Standard is a mix of 1016/1260. Concentration shown is the concentration of each Aroclor in the mixed standard.*

Intermediate ICV Standard (10 mg/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1660 (1016/1260)[1]	Ultra Scientific PPM8082	1000	0.40	40	10

Surrogate Solution (10 mg/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Pesticide Surrogate	Restek #3200	1000	0.40	40	10

Working ICV Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Intermediate ICV	Laboratory Prepared	10	1.0	50	200
Surrogate	Laboratory Prepared	10	0.10		20

AR1660 Calibration Standard: CAL Level 5 (800 ug/L)[1]

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1660 Intermediate	Laboratory Prepared	10	8.0	100	800
Surrogate	Laboratory Prepared	10	0.80		80

[1] *This standard is the parent standard for each level of the AR1660 calibration standards*

AR1660 Calibration Standard(s): CAL Levels 1- 4

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1660 Level 5	AR1660 CAL Level 4	800	20	40	400
AR1660 Level 5	AR1660 CAL Level 3	800	25	100	200
AR1660 Level 5	AR1660 CAL Level 2	800	5.0	40	100
AR1660 Level 5	AR1660 CAL Level 1	800	2.5	40	50

AR1254 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1254 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

AR1248 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1248 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

AR1242 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1242 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

AR1232 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1232 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

AR1221 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1221 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

AR1262 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1262 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

AR1268 Calibration Standard (200 ug/L)

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
AR1262 Intermediate	Laboratory Prepared	10	0.80	40	200
Surrogate	Laboratory Prepared	10	0.080		20

EXTRACTION STANDARDS

The following standards are used to spike field and QC samples prior to extraction. Assign an expiration date of 6 months from date prepared unless the stock standard expires sooner in which case use the earliest expiration date. Store the prepared solutions under refrigeration and protected from light at a temperature of 4ºC (±2).

8082 Spike Solution (LCS, MS/MSD)

Stock Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
AR1016/1260 Mix	Restek #32039	AR1016	1000	1.0	200	5.0
		AR1260	1000			5.0

Solvent: Hexane

Pesticide Surrogate Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Pesticide Surrogate	Restek #3200	DCB	200	1.0	1000	0.20
		TCMX	200			0.20

Solvent: Acetone

Appendix B: Equations

Calibration Factor (CF_x) = $\frac{\text{Peak area or height}_{(x)}}{\text{Standard concentration}_{(ug/L)}}$

Mean Calibration Factor ($\overline{CF}$) = $\frac{\sum_{i=1}^{n} CF_i}{n}$

where: n = number of calibration levels

Standard Deviation of the Calibration Factor (SD) = $\sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}\right)2}{n-1}}$

where: n = number of calibration levels

Percent Relative Standard Deviation (RSD) of the Calibration Factor = $\frac{SD}{\overline{CF}} \times 100\%$

Percent Difference (%D) = $\frac{CF_v - \overline{CF}}{\overline{CF}} \times 100\%$

where: CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Drift = $\frac{\text{Calculated Concentration – Theoretical Concentration}}{\text{Theoretical Concentration}}$ X 100%

Percent Recovery (%R) = $\frac{C_s}{C_n} \times 100\%$

where: C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD = $\frac{C_s - C_u}{C_n} \times 100\%$

where: C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (%RPD) = $\frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100\%$

where: C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Sample Concentration

Extract

$C_{extract}\,(ug/L) = \frac{\text{Peak Area (or Height)}}{\overline{CF}}$

Note: The concentrations of the 3-5 peaks chosen for quantificaton is calculated and the average is then taken for final calculation.

Water

$$C_{sample}(ug/L) = C_{extract}(ug/L) \times \frac{\text{extract volume (L)}}{\text{sample volume (L)}} \times DF$$

Solids

$$C_{sample}(ug/Kg) = C_{extract}(ug/L) \times \frac{\text{extract volume (L)}}{\text{sample weight (Kg)}} \times \frac{100}{\%\text{ solids}} \times DF$$

Appendix C: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration above the reporting limit.
J: Estimated Value
P: There is greater 40% difference for detected concentrations between two GC columns
C: Positive result whose identification has been confirmed by GC/MS
B: Compound is found in the sample and the associated method blank.
E: Compound whose concentration exceeds the upper limit of the calibration range.
D: Concentration identified from a dilution analysis.

X,Y,Z: Laboratory defined flags that may be used alone or combined as needed. If used, provide a description of the flag in the project narrative.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

SOP LB-5

TOTAL ORGANIC CARBON IN SOILS AND SEDIMENT (LLOYD-KAHN)

Title: Total Organic Carbon in Soils & Sediment
[Lloyd-Kahn]

Approvals (Signature/Date):

William S. Cicero — 12/27/07 Date
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Jessica A. Holzschuh — 12/27/07 Date
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Kirstin L. McCracken — 12/27/07 Date
Quality Assurance Manager

Bryce E. Stearns — 12/27/07 Date
Technical Director

Bryce E. Stearns — 12/27/07 Date
Interim Health & Safety Coordinator

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-WC-TOCLK.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

TestAmerica BURLINGTON
STANDARD OPERATING PROCEDURE

TOTAL ORGANIC CARBON IN SOILS AND SEDIMENT
Lloyd-Kahn Method

Applicable Matrix: Soils, Sediments, and Other Solids

APPROVAL SIGNATURES

William S. Cicero
Laboratory Director
Date: August 9, 2007

Kirstin L. McCracken
Quality Assurance Manager
Date: August 9, 2007

Bryce E. Stearns
Technical Director
Date: August 9, 2007

Jessica A Holzschuh
Department Manager
Date: August 9, 2007

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of total organic carbon (TOC) in soils, sediments and other solids. A procedure for the determination of TOC in marine sediment high in inorganic carbon is provided in Appendix B.

1.2 The routine reporting limit is 500 mg/kg. Additional sample may be used (up to 25 mg) to achieve as low a reporting limit as 100 mg/kg.

2.0 SUMMARY OF METHOD

2.1 A small aliquot of sample, routinely 10.0 mg, is transferred to a tin capsule and treated with phosphoric acid, then dried in an oven at 105°C for 30 minutes to one hour. This serves to separate the organic carbon from inorganic carbonates and bicarbonates. The sample is then transferred to an instrument where it is pyrolyzed in an inductive type furnace. The carbon is converted to carbon dioxide and measured by a differential thermal conductivity detector.

2.2 This procedure is based on the EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.

2.3 Dixon, Wilfrid J., and Massey, Frank J. Jr.: Introduction to Statistical Analysis (fourth edition). Edited by Wilfrid J. Dixon. McGraw-Hill Book Company, New York, 1983. P377 and P548.

3.0 DEFINITIONS

3.1 Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1 Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias. Maintaining the sample at 4°C, analyzing the sample within the specified holding time, and analyzing the wet sample, may minimize bacterial decomposition and volatilization of the organic compounds.

5.0 SAFETY

Employees must be trained on and adhere to the policies and procedures for safety in the Corporate Safety Manual and this document.

5.1 Safety Concerns or Requirements

None

5.2 Primary Materials Used

Table 1, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

Drying Oven: Capable of maintaining a temperature of 105°C.

Carlo Erba Elemental Analyzer Model EA1108 and Model NA 1500 or equivalent.

Costech Elemental Analyzer: Model 4010 or equivalent.

Analytical Balance: Capable of weighing to the nearest 0.001mg.

Aluminum Trays that hold sample capsules for use at 105°C

Tweezers

5mm X 9mm tin capsules

Quartz Columns: Costech Analytical or equivalent.

Quartz wool: for segregating and containing column materials

Copper Wire, Reduced: Costech Analytical or equivalent.

Tungsten on Alumina: Costech Analytical or equivalent.

High Temperature Gloves

Clear Plastic Sample Trays: Costech Analytical or equivalent.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagent water

Phosphoric Acid, Concentrated: Reagent Grade, J.T. Baker recommended.

Phosphoric Acid Solution (1:19): Add approximately 100 mL of reagent water to a 200 mL volumetric flask. Add 18.34 g of concentrated phosphoric acid to the volumetric flask then adjust to volume with reagent water. Mix the solution well then transfer the solution to a 250 mL polyethylene bottle. Assign an expiration date of six months from date made and store the solution at room temperature.

7.2 Standards

Acetanilide Crystals of known Carbon percentage: Purchased from Costech Analytical. Used to check instrument calibration.

Sulfanilamide Crystals (41.84% Carbon): Purchased from Costech Analytical. This material is used to calibrate the instruments.

Laboratory Control Samples (LCS) Material, Organic Material of known Carbon percentage: Purchased from LECO Corporation.

Matrix Spike Material, 1632B trace elements in coal (80.11% Carbon)

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT & STORAGE

8.1 Samples should be collected in amber glass jars. Immediately following collection, the samples should be cooled to 4°C (±2) and maintained at that temperature until time of analysis.

8.2 The holding time is 14 days from date of collection, unless otherwise specified.

8.3 Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

9.1 The following QC check samples are analyzed with each batch of 20 or less samples: Method Blank (MB) Laboratory Control Sample (LCS), Matrix Spike (MS) and a Sample Duplicate (DP). In addition to calibration (ICAL), instrument standardization is checked with acetanilide every 20 drops and at the end of the analytical sequence. The minimum frequency requirements, acceptance criteria and recommended corrective action for QC samples are summarized in Table 2, Section 18.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration Curve

Analyze a calibration curve each time the combustion column is changed (a combustion column is good for about 200 sample drops). The recommended formulations for each calibration level is provided in the following table:

Calibration Standard Sulfanimide	Weight[1] (mg)	% Carbon	Carbon (mg)
Calibration Level 1	0.100	41.84	0.0418
Calibration Level 2	0.500	41.84	0.2092
Calibration Level 3	1.00	41.84	0.4184
Calibration Level 4	1.75	41.84	0.7322
Calibration Level 5	2.50	41.84	1.046

[1]*These weights are approximate. Enter the actual weight used into the software program.*

Measure a single drop for each calibration point. The instrument software system plots peak area against mg of Carbon and calculates a correlation coefficient using standard linear regression. The correlation coefficient (r) must be $\geq$ 0.995 for the calibration to be considered acceptable. If it is not, repeat the calibration prior to further analysis.

10.2 Troubleshooting

- *Calibration passes at > 0.995 correlation, but LCS fails abnormally low*: Re-calibrate. Calibration usually needs to be > 0.999 correlation.

- *Carbon peak "maxes out" at instrument 1200mv (peak has flat top)*: Reanalyze sample at lower weight.

- *No peaks on any chromatograms, no results*: Gases to instrument may be off. Turn on all gasses at valve manifold.

- *Autosampler will not work at all*: Gasses to instrument may be off. Turn on all gasses at valve manifold.

- *Single chromatogram shows results at bottom of page, but no peak or baseline in chromatogram window*: Re-print single chromatogram.

- *Some or all chromatograms show carbon peak at same retention time as Acetanilide, but peak is not identified as carbon, or is identified as another element*: Retention time shifted. Adjust retention time in calibration window, and reprint chromatograms.

- *Upon recalibration, peaks are not being identified as carbon*: In calibration window, general tab, adjust retention time to match peaks. Starting at level 1, "Open Standard", open level1 curve pt. in calibration directory, click "Add Peak" button, click on peak itself. Increase level #, opening standard for each curve pt and add each peak. Carbon Tab should have all five calibration points on curve, if done correctly.

- *Peaks in chromatograms identified as carbon, but all results in summary table below chromatogram are zero*: Current calibration not associated with run when started. Open current calibration, copy first two columns for all points (5 rows) in small table in general tab. Then, open calibration that was associated with run (should be

empty) and paste into table in calibration tab. Reprint all chromatograms on run.

- *Software crashes during analysis*: Boot up software normally. Chromatograms already printed/analyzed are ok, but, sample that was analyzing during shutdown is lost. Restart table at next sample by un-checking "run" box for samples already run and sample that was lost.

- *Autosampler error causes few samples to remain in autosampler tray after run has finished*: Identify samples that got stuck. Create a new run and analyze stuck samples (with initial weights) with bracketing QC. No PBS/LCS needed.

- *Autosampler error causes many sequential samples to remain in autosampler tray after run has finished (usually end of run)*: Add rows onto existing table. Identify samples that did not get analyzed and repeat Ids and weights into added rows. Restart table. All analyzed samples' status should be blue(analyzed), added rows should be green (not analyzed yet).

- *Various result issues or odd peak shapes or baseline issues*: Column may be leaking or cracked. Change column, recalibrate.

11.0 PROCEDURE

11.1 Sample Preparation

Using tweezers, and working directly from the box, place a tin capsule on the analytical balance and tare. Using the small sample scoop, add approximately 10 mg (or more, if client requested) of sample to the capsule. Record the sample weight on the benchsheet. Remove the capsule from the balance and place into one of the aluminum holding trays. Weigh two separate aliquots into two separate tin capsules for each field sample. Record all weight measurements on the sample preparation log. For the method blank, set two empty tin capsules into an aluminum holding tray. For the LCS, weigh ~9 mg of LECO LCS material into two separate tin capsules and set them in sequence in an aluminum holding tray.

For the matrix spike, weigh out an additional sample aliquot and record its weight. Add 0.3 – 0.7 mg of matrix spike material and record this weight. For the sample duplicate, weigh out an additional sample aliquot. Prepare two aliquots for both the matrix spike and the sample duplicate.

Add two drops of 1:19 phosphoric acid to each tin capsule. Place the aluminum trays into a drying oven set to a temperature of 105ºC for 30-60 minutes or until all samples appear dry.

Using tweezers, pinch the top of each tin capsule closed and compress the capsule around the material inside. Work carefully so as not to tear the capsule, but crush it down to the smallest size. Set the prepared samples in line in a clear plastic sample tray for storage, or place directly into an autosampler tray for analysis. For the latter, leave positions open for the acetanilide check standards and associated calibration blanks.

Prepare the acetanilide standard and blanks as follows:

For each acetanilide spike, weigh ~0.5 mg of acetanilide material into a tin capsule. Fold the capsule up and compress down to the smallest size possible. Prepare enough acetanilde to ensure a frequency of every 20 drops and the end of the analytical sequence. For each associated calibration blank, leave an empty position in the autosampler tray.

11.2 Software Set-up and Analysis

If the column has been changed, generate a new calibration curve. If not, use the existing calibration curve for analysis. Each column will analyze approximately 200 individual sample drops. When the counter on the instrument approaches 200, watch the instrument data for signs that the column is deteriorating; poor peak resolution, trailing baselines, extraneous peaks. If a column change is necessary, refer to Appendix C for the procedure. After changing the column, generate a new calibration curve.

Select the appropriate channel: Channel 1 is the NA 1500, Channel 2 is the EA 1108, and Channel 3 is the Costech instrument, which has its own PC. At the main screen select the sample table icon. The last sample table that was run will be shown on the screen.

Open a new sample table, and select the appropriate number of sample positions for the analysis, then name the table with the date and a unique alpha designator (i.e. 061505a). In front of the %3r in the file name column of the sample table, add the sample table name to ensure that each individual chromatogram generated from this sample table has a unique filename associated with it.

If the combustion column has been changed and instrument needs to be calibrated, follow the procedure below:

Prepare a “bypass” drop to determine the retention time for carbon with the new column. The bypass is an aliquot of acetanilide. The weight is not needed. Drop the bypass into the instrument and initiate a singular analysis. Set the retention time for carbon in the software to match that of the bypass drop.

Identify the first five sample lines with the names Std1 through Std 5. Enter their respective weights in the weight column, assign them a level # in the level column (Std1 is level 1, Std2 is level 2, etc.) to alert the software the order in which to place the calibration standards. In the sample type column, use the drop down and select “standard” for each. Finally, use the drop down in the Standard name column and select “sulfanilamide” for each. Add the standards to the autosampler tray and hit “start” to run the calibration.

Sample Analysis:

Open a new sample tray and create a unique file name. When the instrument was last

calibrated, the software creates a calibration file with the same name as the sample table in which it was run. Open this file and save it with the same name as the sample table about to be run to ensure that the analysis is calculated from the most recent calibration. To do this, click on the calibration icon (looks like a little calibration curve) and use the file option to open the calibration file last performed. Save this file with the same name as your sample table. Click on the sample table icon (looks like a little sample table) to get back to your sample table.

Enter each sample ID and their respective weights and save the sample table. Enter a weight of 10 mg for the Method Blank (PBS) and instrument blanks.

An example analytical sequence follows:

Initial Calibration (calibration blank and 5 calibration standards)

Acetanilide	(1 drop)
Blank	(1 drop)
PBS	(2 individual drops)
LCS	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Sample	(2 individual drops)
Acetanilide	(1 drop)
Blank	(1 drop)

Add the samples and acetanilides to the autosampler tray and set the tray into the autosampler carriage. Turn the autosampler tray until the number 1 position is behind the post, in front of the autosampler. The tray is now set to run.

Click the “start” icon to begin the analysis

After analysis review the analytical results against the acceptance criteria given in Table 2, Section 18.0, and perform corrective action as necessary. Enter the results for all instrument blanks (including PBS) and any client sample exhibiting an area response at or lower than the lowest calibration standard into the low level Excel spreadsheet set up for this purpose. This spreadsheet calculates these low level results with a two point linear regression using the origin and the lowest calibration point. A more precise result for low level samples is determined this way. Report results in mg/kg Carbon and corrected for % solids

12.0 CALCULATIONS

12.1 Percent Carbon to mg/kg Carbon Conversion

% Carbon × 10,000 = mg/kg Carbon

12.2 LCS Percent Recovery (%R)

$$\%R = \frac{\text{LCS Result}}{\text{LCS True Value}} \times 100$$

12.3 MS Percent Recovery (%R)

$$\text{mg/Kg wet SA} = \frac{\text{Spike TV} \times \text{weight of MS added}}{\text{sample weight}} \times 1\,\text{million}$$

$$\text{mg/Kg dry SA} = \frac{\text{mg/Kg wet SA}}{\%\ \text{solid}} \times 100$$

$$\text{mg/Kg dry Carbon} = \frac{\text{mg/Kg wet Carbon (from instrument)}}{\%\ \text{solid}} \times 100$$

$$\%R = \frac{A - B}{C} \times 100$$

Where:
A= Average of three drops of MS sample result: mg/Kg dry carbon
B= Average of three drops of parent sample: mg/Kg dry carbon
C= Average of three drops of mg/Kg dry SA
SA= spike added (mg/Kg)
Spike TV= 0.8011(mg/Kg)

12.4 Relative Percent Difference (RPD)

$$RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

12.5 Dixon Test (Use 3-7 results)

1. Sort all the results in ascending order (low values to high).
2. Calculate the tau statistic for the low and high values.

3. Compare the calculated tau statistics (low and high) to critical values listed below.
4. If either calculated tau is higher than the critical value, reject that value and repeat the test.

Tau statistic for lowest value = $\tau_L = (X_2 - X_1) / (X_k - X_1)$
Tau statistic for highest value = $\tau_H = (X_k - X_{k-1}) / (X_k - X_1)$

Where:
X_2 = Second lowest value in sorted list.
X_1 = Lowest value in sorted list.
X_k = Highest value in sorted list.
X_{k-1} = Second highest value in sorted list.

Number of observations, k	Critical Values
3	0.941
4	0.765
5	0.642
6	0.560
7	0.507

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the performance criteria given in Table 2. If the results do not fall within the established limits or criteria perform corrective action. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2 An Initial Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the reference method, 40CFR, Part 136, Appendix B and laboratory SOP LP-LB-009. The MDL is verified or repeated when a significant change to the method occurs. Significant changes include the use of alternate reagents or standard reference materials, new instrumentation or the use of alternate sample preparation procedures.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2 Waste Streams generated by this method;

- Spent combustion columns

→ *Satellite Waste Container: Five Gallon Metal Bucket labeled "Glass Disposal"*

Transfer the waste stream to the appropriate hazardous waste satellite container located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite container to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 Hazardous Waste.

16.0 REVISION HISTROY

16.1 Cover Page: Changed to reflect current management team.
16.2 Section 10.2: This section was added
16.3 Section 11.0: Number of drops was changed from 4 to 2.
16.4 Section 12.5: The Dixon Test was added.
16.5 Section 18.2, Table 2: Sample precision criteria added.
16.6 Section 18.5, Appendix D: Determination of Black Carbon in Sediment Procedure added.

17.0 REFERENCES

17.1 EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.

17.2 Dixon, Wilfrid J., and Massey, Frank J. Jr.: Introduction to Statistical Analysis (fourth edition). Edited by Wilfrid J. Dixon. McGraw-Hill Book Company, New York, 1983. P377 and P548

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1: Primary Materials Used
18.2 Table 2: QC Summary
18.3 Appendix A: Definitions
18.4 Appendix B: TOC Procedure for High Concentration Marine Sediments (CITHON)
18.5 Appendix C: Column change procedure
18.6 Appendix D: Determination of Black Carbon in Sediment Procedure

Table 1: Primary Materials used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			

Table 2: QC Summary and Recommended Corrective Action

QC Sample	Frequency	Acceptance Criteria	Corrective Action
ICAL	Following each column change	r $\geq$ 0.995	Standards check, re-calibration.
Method Blank (PBS)	Once per batch of 20 samples	< RL DoD: ½ RL	Re-prepare and reanalyze batch.
LCS	Once per batch of 20 samples	%R (75-125)	Re-prepare and reanalyze batch.
Acetanilide	Every 20 drops and at the end of the analytical run	%R (85-115)	Re-prepare and reanalyze samples not surrounded by passing Acetanilides
Blank (paired with Acetanilide)	Following each Acetanilide	< RL	Re-prepare and reanalyze batch.
Matrix Spike	One per batch of 20 or less samples	%R (75-125)	Discuss outlier in project narrative
Sample duplicate	One per batch of 20 or less samples	RPD < 20	Discuss outlier in project narrative
Sample precsion	Each sample is run in duplicate	%RPD<40%	Analyze 2 more replicates and perform Dixon test for high and low outliers. If no rejects, average all 4 replicates. If 1 replicate is rejected, perform Dixon test on remaining 3 reps. Report the average of the remaining 2 or 3 replicates.

Appendix A: Definitions

Accuracy: the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above mentioned criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Blank (ICB/CCB): a volume of reagent water acidified with the same acid matrix as in the calibration standards.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration. A standard containing the analyte in question (sulphanilimide) is prepared at varying weights and analyzed. This standard is a separate source from the LCS. The sulphanilimide is used to calibrate the instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV): a prepared standard solution used to verify the stability of the instrument calibration and instrument performance during the analysis of samples.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): A prepared standard solution from a source separate from that of the calibration standards used to verify the concentration of the calibration standards and the adequacy of instrument calibration.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as samples, through all steps of the analytical procedure.

Matrix: the substrate of a test sample.

Matrix Duplicate (DP): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate; Laboratory Duplicate.

Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a replicate matrix spike.

Method Blank: a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is +100%. The MDL represents a range where qualitative detection occurs using a specific method. Quantitative results are not produced in this range.

Percent Solids (%S): the proportion of solid in a soil sample.

Appendix B: Marine Sediments High in Inorganic Carbon

Sample Preparation

Transfer approximately 10 g of a thoroughly mixed sample to an aluminum weigh dish, and dry in the 105°C oven. Grind the sample with the pink mortar and pestle to a fine powder. Record the weight of a 250 mL Teflon beaker then transfer ~ 5 g of the ground sample to this beaker.

If the sample is to be spiked, weigh the beaker to the nearest 0.1mg and record the weight. Likewise determine and record the weight of the added sample. Add 0.1g of NIST 1632b Trace Elements in Coal (80.11% Carbon) to the sample. Record the weight added. Evenly distribute the spike over the sample and use a glass stir rod to mix the spike with the sample. Do not use that stir rod with any other sample.

Use Talc-free latex gloves from this point on to minimize the risk of acid burns. Add several drops of 1:1 HCL to each sample and stir each sample with its own glass stir rod. Samples with high concentrations of inorganic carbon may effervesce to the point of overflowing the beaker, so take care to add the acid in small aliquots and stir vigorously. If the sample "boils over" it must be re-prepared. Continue to add 1:1 HCL in small aliquots until there is no further reaction, taking sample to dryness after each addition of acid with the hot plate provided.

Carefully rinse the stir rod and beaker walls with DI water using a fine-tipped squirt bottle. Use only what is needed to bring the entire sample to the bottom of the beaker. ***When adding water to acid use necessary precautions to avoid splashing!***

Dry the treated samples on the hot plate in the hood, after each acid/water addition. Do not add more than a total of 200 mL of 1:1 HCL to any sample.

NOTE*: Samples are hydroscopic and will absorb water if they are exposed to air for too long.*

Weigh beaker with residue and record the residue weight measurement. After the sample is thoroughly dry, scrape the sample residue from the beaker and grind to a powder using the pink mortar and pestle. Transfer the ground sample to a clean, dry 40-mL vial reserved for this analysis.

NOTE: *Depending on the nature of the sample, it may be difficult to completely remove the dried residue from the beaker or to grind it to a homogenous powder. Where difficulties are encountered, make a note on the preparation worksheet.*

Analysis

Perform TOC analysis on processed sample material as outlined in section 10.0 of this SOP.

Appendix C: Column Change Procedure

Turn off the helium and oxygen supplies to the instrument.

Dial the left furnace temperature to a reading of 052 (this equates to 520˚C). Wait until the temperature drops below 600˚C to remove the column.

Remove the panel covering the furnace and unscrew the autosampler connection from the top of the column.

Unscrew the fitting at the bottom of the column and remove.

Lift the column up and out of the furnace using high temperature gloves.

CAUTION: The column will still be 500-600˚C. Do not touch the center portion of the column. Place the spent column in the metal can designated for this purpose.

Lay a new quartz column on the bench top, measure and mark off for the following:

- One inch up from the bottom and add a ½ inch plug of quartz wool. Note: pack the quartz wool tightly enough for it to stay in place.
- Pour in 2 ½ inches of copper wire
- Pack another ½ inch quartz wool plug on top of the copper
- Pour in 3 inches of tungsten
- Pack a final ½ inch quartz wool plug on top of the tungsten

Place the new column into the furnace and reconnect the top and bottom fittings. Snug these up, but don't over tighten.

Replace the panel covering the furnace, dial the furnace temperature back to 102 (this equates to 1020˚C), and turn the helium and oxygen supplies back on.

When the instrument comes up to operating temperature, it is ready to calibrate.

Appendix D: Determination of Black Carbon in Sediment Procedure

1. Obtain a representative subsample of the sediment. Weight 10 grams of sample into a clean pre-tared aluminum drying pan or equivalent.

2. Dry the sample at 105^{o}C for at least 12 hours.

3. Grind the sample using a mortar and pestle.

4. Sieve the sample using a number 35 sieve (500 um).

5. Treat the sample with phosphoric acid. Add acid drop wise until effervescence is no longer observed.

6. Dry the sample at 105^{o}C for 1 hour.

7. Set aside an aliquot of the sample at this stage for direct TOC analysis, reported without correction for the IN623 percent solids. Continue with the sample for Black Carbon.

8. Place the dried sample into a clean crucible and cover the sample.

9. Bake the samples at 375^{o}C in a muffle for 24 hours.

10. Allow the samples to cool and transfer approximately 5.0 mg into each of three tin capsules.

11. Transfer the sample (in the tin capsules) to the TOC analyzer for analysis by the Lloyd Kahn Method.

12. The sample is pyrolyzed in an inductive type furnace, where the carbon is converted to carbon dioxide, which is measured using a differential thermal conductivity detector.

13. The results will be reported as mg/Kg Black Carbon.

References:

Orjan Gustafsson, Thomas D. Bucherli, Zofia Kukulska, Mette Andersson, Claude Largeau, Jean-Noel Rouzaud, Christopher M. Reddy and Timothy I. Eglinton (December 2001) Evaluation of a Protocol for the Quantification of Black Carbon in Sediments, Global Biogeochemical Cycles, Volume 15, pages 881-890.

Orjan Gustafsson, Farnaz Haghseta, Charmaine Chan, John MacFarlane & Philip M. Gschwend (1997) Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability, Environmental Science & Technology, Volume 31, pages 203-209.

SOP LB-6

PERCENT LIPID DETERMINATION

Title: Percent Lipid Determination

Approvals (Signature/Date):

William S. Cicero — 12/27/07
Laboratory Director — Date

Christopher G. Callahan — 12/27/07
Current Department Manager — Date

Kirstin L. McCracken — 12/27/07
Quality Assurance Manager — Date

Bryce E. Stearns — 12/27/07
Technical Director — Date

Bryce E. Stearns — 12/27/07
Interim Health & Safety Coordinator — Date

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-OP-Lipids.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

STANDARD OPERATING PROCEDURE
STL BURLINGTON

PERCENT LIPID DETERMINATION

Applicable Matrix: Biological Tissue

APPROVAL SIGNATURES

William S. Cicero
Laboratory Director
Date: December 20, 2006

Kirstin L. McCracken
Quality Assurance Manager
Date: December 20, 2006

Jacob L. Bailey
Department Manager
Date: December 20, 2006

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of percent lipids in biological tissue.

2.0 SUMMARY OF METHOD

2.1 A 1 mL aliquot of extract is evaporated to dryness and weighed to a constant weight. The residual weight of the dried aliquot is used to calculate percent lipids.

2.2 This procedure is based on EPA SOP ASB P100, ASB E100 for the Determination of Organics in Fish and NOAA Technical Memorandum NOS ORCA 130 Method for the Determination of Percent Lipid in Tissue, Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update.

The following exceptions to the NOAA reference method are noted:

- The laboratory does not include the dry weight determination of the tissue sample in the percent lipids calculation.
- The tissue sample may be extracted with hexane extract instead of dichloromethane when hexane is an appropriate extraction solvent for the determinative method.
- The percent lipids are determined from the extract using a gravimetric procedure without the additional filtering or concentration steps.

3.0 DEFINITIONS

3.1 Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1 Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that can cause interference and/or elevated baselines in chromatography. All reagents and solvents used during this procedure should be reagent grade or high purity in order to minimize interference. All glassware must be cleaned in accordance with laboratory SOP LP-OP-Glass and rinsed with acetone prior to use.

5.0 SAFETY

5.1 Employees must be trained on and adhere to the policies and procedures for safety in the Corporate Safety Manual and this document.

5.2 Specific Safety Concerns or Requirements

None

5.3 Primary Materials Used

Table 1, Section 18.0 lists those materials that are part of this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 Aluminum Weigh Boat(s)

6.2 Analytical Balance

6.3 Adjustable Pipette(s)

6.4 Drying Oven

6.5 Stainless Steel Tongs

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Anhydrous Sodium Sulfate- Purify for 4 hours at 400°C.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT & STORAGE

8.1 Sample extracts used for percent lipid determination must be protected from light and maintained at a temperature of 4(±2)°C.

8.2 Unless otherwise specified by client or regulatory program, after extraction samples and extracts are retained for 30 days then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1 A method blank comprised of sodium sulfate is extracted with each batch of 20 or less samples and it is taken through the percent lipids determination in the same manner as sample extracts. The calculated percent lipids in the method blank should be <0.1%.

9.2 A duplicate sample should be performed with each extraction batch or at the frequency designated by the client. The relative percent difference (RPD) in the percent lipids determination between replicate samples should be less than or equal to 25%. If it is

not, the original and duplicate sample extracts should be re-weighed. If the RPD is still not within specification, the percent lipids procedure should be repeated using new extracts.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibrate the analytical balance and mechanical pipettes on each day of use, prior to use.

11.0 PROCEDURE

11.1 Percent Lipid Determination

Weigh an aluminum boat to the nearest 0.0001 g and record the weight measurement. Tare the balance and transfer 1 mL of the 10 mL extract (pre-cleanup) to the aluminum weigh boat. The extract should be filtered using a Whatman 0.45um Autovial Filter before concentration to 10.0 mL. Using tongs transfer the weigh boat to a drying oven maintained at a temperature of 104˚C (±2°C) and allow sufficient time for the solvent to evaporate to dryness. Allow the weigh boat/sample to cool to room temperature.

Re-weigh the weigh boat to the nearest 0.0001 g and record the weight measurement.

Calculate the percent lipids using the equation given in Section 12.0.

Evaluate the results of the method blank and sample duplicate against the criteria given in Section 9.0 Quality Control and perform corrective action as necessary.

12.0 CALCULATIONS

12.1 Percent Lipid Calculation

$$\%Lipids = \frac{RW}{AV} \otimes \frac{EV}{WS} \otimes 100$$

Where RW is the residue weight *(residue + weigh boat)* minus the weight of the weigh boat, AV is the volume of the aliquot used (mL), EV is the final extract volume (mL), and WS is the original weight of sample extracted (g).

12.2 Relative Percent Difference (RPD)

$$\frac{C_1 - C_2}{\left(\frac{C_1 + C_2}{2}\right)} \otimes 100$$

Where:
C_1 = Result of Parent Sample

C_2 = Result of Duplicate Sample

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Primary Review: Review the bench sheet for correctness and completeness. Record any problems encountered during the process on the bench sheet or complete a nonconformance report, when necessary. Set aside the extracts and paperwork for secondary review.

13.2 Secondary Review: Review the bench sheet against the preparation worksheet to ensure the procedure performed is consistent with project specifications and this SOP.

13.3 For additional guidance regarding the laboratory's protocol and required elements for data review refer to laboratory SOP LP-QA -019 *Data Review*.

14.0 METHOD PERFORMANCE

14.1 This section is not applicable to this SOP.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 The following waste streams are produced when this SOP is performed:

Organic Solvents - Satellite container: 55 gallon covered and vented drum.
Solid Waste - Satellite container: 5 gallon covered bucket in fume hood.

Transfer the waste stream(s) to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 *Hazardous Waste*

16.0 REVISION HISTORY REFERENCES

16.1 Changed Title page to reflect current management team.

16.2 Section 16: Added Revision History section.

17.0 REFERENCES

17.1 *SOP for the Determination of Organics in Fish.* SOP ID: ASB P100, Mod1.0 October 1990; ASB E100, Mod1.0, October 1990. USEPA Region 4 Science and Ecosystem Support Division, Analytical Support Branch.

17.2 *Determination of Percent Lipid in Tissue.* Geochemical and Environmental Research Group, Texas A&M University College Station, TX. NOAA Technical Memorandum NOS ORCA 130 National Status and Trends Program for Marine Environmental Quality Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1: Primary Materials Used
18.2 Appendix A: Terms and Definitions

Table 1: Primary Materials Used

Material	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

[2] Exposure limit refers to the OSHA regulatory exposure limit.

Appendix A: Terms & Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

SOP LB-7

EXTRACT CLEANUP PROCEDURE
SW-846

Title: Extract Cleanup Procedure
[SW-846]

Approvals (Signature/Date):

William S. Cicero Laboratory Director	12/27/07 Date	Christopher G. Callahan Current Department Manager	12/27/07 Date
Kirstin L. McCracken Quality Assurance Manager	12/27/07 Date	Bryce E. Stearns Technical Director	12/27/07 Date
Bryce E. Stearns Interim Health & Safety Coordinator	12/27/07 Date		

This cover page documents management approval for the following changes to this SOP:

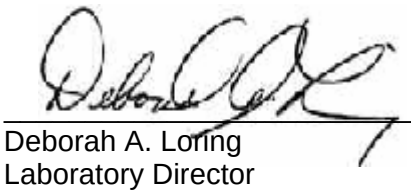
- **This SOP has been renamed and was previously identified as SOP No. LM-OP-Cleanup.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

STANDARD OPERATING PROCEDURE
STL BURLINGTON

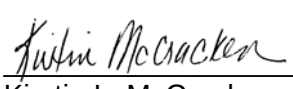
EXTRACT CLEANUP PROCEDURE
SW-846 Methods:

APPROVAL SIGNATURES



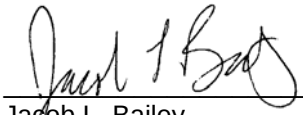
Deborah A. Loring
Laboratory Director

Date: November 3, 2006



Kirstin L. McCracken
Quality Assurance Manager

Date: November 3, 2006



Jacob L. Bailey
Department Manager

Date: November 3, 2006

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedures for cleanup applied to organic extracts. Cleanup eliminates sample interferences that may cause errors in quantitation and identification including false positive/false negative results, rapid deterioration of capillary columns, and instrument downtime. The appropriate cleanup methods that should be used for a particular group of analytes are specified in the determinative methods. The following sections give a brief description and applicability of the cleanup methods included in this SOP.

Fractionation Cleanup and Adsorption Cleanup by Florisil and Silica Gel (Source: SW-846 3620B, 3630C, and 3600C)

Fractionation is a cleanup technique that can be used to separate complex mixtures of analytes such as PCBs from organochlorine pesticides (silica gel) and fractionation of the organochlorine pesticides (florisil). Adsorption chromatography is used to separate analytes of a narrow polarity range from interfering compounds of a different polarity. This technique is most commonly used to separate relatively non-polar compounds such as organochlorine pesticides, polynuclear aromatic hydrocarbons, and nitrosamines from more polar compounds. Florisil is a trade name for magnesium silicate (Mg_2SiO_3). Silica gel, also referred to as silicic acid, is made from sodium silicate and sulfuric acid.

Copper Cleanup (Source: SW-846 3660B and 3600C)
Elemental sulfur is extracted from many sediment samples, industrial waste, some soil samples, and even aqueous samples. Sulfur is extracted along with organochlorine and organophosphorous pesticides and PCBs and sulfur interference can interfere with or completely mask target analyte peaks in the early region of the chromatogram. Organic extracts are treated with activated copper granules or powder to remove sulfur prior to analysis.

Sulfuric Acid (Source: SW-846 3665A and 3600C)
Sulfuric acid is an effective cleanup of sample extracts to be analyzed for polychlorinated biphenyls (PCBs) and should be used whenever elevated baselines or overly complex chromatograms would prevent accurate quantitation or identification of PCBs. This procedure cannot be used to cleanup extracts to be used for analysis of other target analytes as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan I and II, and Endosulfan Sulfate. It is important to note that the extract must be solvent exchanged to hexane before adding concentrated sulfuric acid as a reaction with other solvents can be violent and dangerous.

2.0 SUMMARY OF METHOD

2.1 Prior to the cleanup procedure, samples are solvent extracted following approved laboratory standard operating procedures. Following cleanup, the sample is concentrated to the appropriate volume specified in the determinative method in preparation for analysis.

2.2 This SOP is based on the following reference methods:

SW-846 3600C (Cleanup)
SW-846 3620B (Florisil)
SW-846 3630C (Silica Gel)
SW-846 3660B (Sulfur)
SW-846 3665A (Sulfuric Acid)

3.0 DEFINITIONS

3.1 This section is not applicable to this SOP.

4.0 INTERFERENCES

4.1 Florisil Cleanup

The method developer found that phthalate ester contamination was detected at levels up to 400ng/cartridge when this cleanup procedure was evaluated; complete removal may not be possible.

4.2 Silica Gel Cleanup

Phthalate ester contamination may be present when using silica gel cartridges. Use of and inert column or cartridge (made of glass or polytetrafluoroethylene (PTFE)) may reduce this contamination.

4.3 Copper Cleanup

There are no interferences that are intrinsic to the copper cleanup procedure, but an instrument blank or the preparation blank should be subjected to the cleanup procedure to ensure that the process did not introduce contamination to the extracts. Additionally, if activated copper powder is used, the acid used to activate the copper must be completely removed as the acid could degrade some target analytes.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Safety Concerns or Requirements

5.3 Primary Materials Used

Table 1, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. This table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0.

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 Florisil Cleanup

- Vacuum Manifold, Supelco 24 port.
- Valve Liners- Supelco
- Vacuum Pump

6.2 Silica Gel Cleanup

- 3 g column (10.5 ID, 13 OD 250 mm length)
- 10 g column (14.5 ID, 17 OD, 250 mm length)
- Glass Wool
- Glass Rod(s)
- 50 mL Beakers

6.3 Copper Cleanup (Copper Powder Activation)

- 8 mL/16 mL/40 mL Glass Vials with Teflon lined Caps
- Vortex Mixer
- Spatulas
- Disposable glass pipettes
- Centrifuge

6.4 Sulfuric Acid Cleanup

- Glass Vials with Teflon lined Caps
- Vortex Mixer
- Centrifuge, HN-S
- Brinkmann Dispenser
- Disposable glass pipettes

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Florisil

Acetone; J.T. Baker, Pesticide quality or equivalent.

Hexane; J.T. Baker, Pesticide quality or equivalent.

Florisil Cartridge: 6 mL/1gm Florisil Cartridge, Restek # 24034 or equivalent.

Hexane/Acetone (90:10 v/v): Measure 450 mL of hexane and 50 mL of acetone into a 500 mL labeled amber jar. Prepare the reagent fresh each day the cleanup method is performed.

7.1.2 Silica Gel

Silica Gel, 100-200 Mesh, Fisher # S679-500 or equivalent.

Reagent Water

3% Deactivated Silica Gel: Bake silica gel in an oven set at a temperature of 130°C for 8 hours. Weigh a 500 mL amber jar, add baked silica gel and weigh. Cap the jar and allow silica gel to cool. Add reagent water equal to 3% of the weight of the baked silica gel and tumble for 4 hours. Store tightly sealed in amber jar. Set expiration at 6 months from the date tumbled.

Sodium Sulfate Anhydrous, J.T.Baker Granular Cat# 3375-09

Methylene Chloride; J.T. Baker, Pesticide quality or equivalent.

Hexane; J.T. Baker, Pesticide quality or equivalent.

Reagent Water

7.1.3 Copper Cleanup

Pre-Activated Copper Granules, Restek or equivalent. Alternatively, use in-house prepared activated copper powder.

Materials Needed for Activated Copper Powder:

- Copper Powder, Spheroidal, <10 microns, 99%, Aldrich or equivalent. To activate the copper powder:
- Sulfur Sublimed Powder
- Hydrochloric Acid Concentrated, J.T. Baker Cat# 9530-33.
- Methanol, Ultra- Resi Analyzed, J. T.Baker, Cat# 9263-03
- Methylene Chloride, J.T. Baker, Pesticide Quality or Equivalent
- Hexane, J.T. Baker, Pesticide Quality or Equivalent
- Reagent Water
- Nitrogen Gas

Activation Procedure:

1) Transfer 5 to 8 g of copper powder into a clear glass 40 mL vial.

2) Add 15-20 mL of HCl to the vial. Cap and vortex the vial for 1 minute.

3) Centrifuge the vial until the HCl is separated from the copper powder. Decant and discard the HCl.

4) Repeat Steps 2-3 with another portion of HCl, then twice with reagent water followed by methanol, methylene chloride and hexane.

5) Dry the treated copper powder with nitrogen. Add approximately 0.25 g of the treated copper powder to an 8mL vial that contains a saturated sulfur solution (0.5 g sulfur/10 mL Hexane). If the copper turns black, the copper is considered activated. If the copper stays red, discard and start over with a new portion of copper powder. Care should be taken to avoid contaminating items and surfaces with sulfur powder.

7.1.4 Sulfuric Acid

Hexane; J.T. Baker, Pesticide quality or equivalent

Sulfuric Acid-concentrated. J.T.Baker

7.2 Standards

Stock standard calibration solutions are purchased from commercial vendors. Working standards are prepared from stock standards by diluting a volume of stock standards in an appropriate solvent in volumetric flasks to obtain the appropriate concentration.

7.2.1 Florisil (Method 3620B)

2,4,5-Trichlorophenol Stock Standard (100 ug/mL), Ultra Scientific Cat# PH-260 or equivalent.

2,4,5-Trichlorophenol (0.1 ug/mL): Measure 0.5 mL of the 2,4,5-Trichlorophenol stock standard solution into a 500 mL volumetric flask that contains ~ 300 mL of acetone and adjust to volume with acetone. Transfer the solution to a labeled 500 mL amber jar. Assign an expiration date of 7 days and store at 4^{o}C.

Individual Standard Mixture A (INDA): Obtain from GC laboratory.

Florisil Cartridge Performance Check Mixture: Add 0.5 mL of the 0.1 ug/mL 2,4,5-Trichlorophenol solution and 0.5 mL of INDA to 4 mL of hexane. Reduce the mixture to a final volume of 0.5 mL using nitrogen.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 This section is not applicable to this SOP.

9.0 QUALITY CONTROL

9.1 Associated quality control samples must be processed through the cleanup procedure.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Check the accuracy of the adjustable pipettes on the day of use, prior to use.

11.0 PROCEDURE

11.1 Florisil Cleanup (SW-846 Method 3620)

11.1.1 Florisil Cartridge Performance Check

Check each lot of Florisil cartridges prior to use and every 6 months with the performance check solution.

1) Place a Florisil cartridge into a valve liner on the manifold. Condition the cartridge using the procedure given in 11.1.2. Place a KD concentrator tube underneath the frit and transfer 0.5 mL of the performance check mixture to the top of a conditioned cartridge. Elute with 9 mL of hexane/acetone (9:1 v/v). Rinse the cartridge 2 more times with 1 mL of the hexane/acetone mixture.

2) Remove the concentrator tube and reduce extract to a final volume of 1.0 mL using micro-synder KD concentration or nitrogen blow-down. Forward the performance check solution and an aliquot of the 2,4,5-Trichlorophenol spike solution to the GC department.

The lot of cartridges is acceptable for use if the if the percent recovery of 2,4,5-Trichlorophenol is less than 5%, the percent recovery of all pesticides is between 80-120%, and if there are no interfering peaks present. If criteria are not met, repeat the performance check.

11.1.2 Sample Cleanup by Florisil Cartridge

Place a valve liner insert into the vacuum manifold. Tighten the valve nut to ensure the valve liners are crimped shut. Attach a Florisil cartridge to the valve liner insert for each extract. Turn on the vacuum pump and set the vacuum to 10 in (254 mm) of Hg. Gravity flow may also be used. To condition the Florisil cartridge, open the valve nut and elute ~6 mL of to acetone through each cartridge then elute ~6 mL of hexane/acetone (9:1) through each cartridge. Close the valve nut to stop flow of solvent through. Do not allow cartridges to become dry at any point during the process. If cartridges go dry, repeat the conditioning step.

Release the vacuum and place a labeled 10 mL KD concentrator tube under each frit

inside the manifold. Check to ensure the solvent line from each cartridge is placed inside the appropriate concentrator tube as the top of the manifold is replaced.

If using vacuum flow, turn on the vacuum otherwise use gravity flow. Transfer 1 mL of extract to the top of a Florisil cartridge. Elute the extract through the cartridge using 9 mL of hexane/acetone (9:1) collecting the eluent in the concentrator tube. Do not let the cartridge go dry. Concentrate the extract using nitrogen blow down or micro-synder concentration technique to the final volume listed on the bench sheet. Transfer the extract to a labeled vial. Perform additional cleanup procedures as needed or relinquish the extract to the GC department.

11.2 Silica Gel Cleanup (SW-846 Method 3630C)

11.2.1 Column Preparation

Clean the silica column prior to use following the procedure in laboratory SOP LP-OP-GLASS. Add a plug of glass wool to the column. Close the stopcock and add sufficient methylene chloride to fill the column half-full. Tap the column or use a clean glass stir rod to remove any air bubbles. Add ~4 g of granular sodium sulfate to the column and tap the column to remove air bubbles.

Weigh an appropriate amount of 3% de-activated silica gel into a 50 mL beaker and add a sufficient amount of methylene chloride to form a slurry. The amount of deactivated silica gel depends on the determinative test method. In general, use 3 grams for PCBs and 10 grams for all other methods. Refer to the bench sheet to determine the appropriate amount. Stir the slurry with a glass pipette to remove air bubbles then quantitatively transfer the slurry to the column.

Open the stopcock to let the methylene chloride drain through the column. When the level of methylene chloride is just above the level of the silica gel, add approximately 4 g of sodium sulfate to the column. Drain the methylene chloride to the top of the sodium sulfate but **do not let the column go dry.** Add 60 mL of hexane to the column allowing the solvent to drain to approximately ½ inch from the top of the sodium sulfate.

11.2.2 Extract Cleanup

Transfer the full volume of extract volume to the top of silica gel column and elute through the column. **Do not let the column go dry.** Elute the column with the appropriate solvent and collect the solvent rinse in a KD concentrator set-up using the following protocol:

- For PAHs, rinse the column with 25 mL hexane, discard the rinsate. In succession, elute 25 mL of 10% of methylene chloride/hexane then elute 60 mL of 40% methylene chloride/hexane collecting the eluate in a KD concentrator tube. Concentrate the solvent using the KD technique to the appropriate final volume.

- For PCBs, add 60 mL of hexane to the column and collect the eluate in a KD concentrator tube. Concentrate the solvent using the KD technique to the

appropriate final volume.

- For other extractions methods please refer to the extraction benchsheet for the particular procedure to be used.

11.3 Copper Cleanup (SW-846 Method 3660)

Transfer the extract to a labeled 8 mL vial. Add approximately 0.25 g of activated copper powder or granuales to each vial using a stainless steel spatula. Cap the vial and vortex for approximately 1 minute. If sulfur is present, the copper will turn blackish in color. Repeat the procedure until the activated copper does not change in color. See benchsheet for final concentration and vialing instructions.

11.4 Sulfuric Acid (SW-846 Method 3665)

Transfer the extract to a 16 mL clear glass vial. Working in a fume hood, carefully add 5 mL of concentrated sulfuric acid to the vial. Check to ensure there is no gas or heat produced. If no reaction is observed, vortex the vial for one minute. The vortex of the extract/acid mixture must be visible in the glass vial to ensure that the fluids have mixed properly. Centrifuge the vial for at least one minute then examine the solvent layer. If the solvent layer is cloudy or highly emulsified, centrifuge for a longer period of time. If repeat mixing this does not separate the layers, cool the extracts then repeat centrifugation.

If the hexane layer is still colored, remove the acid layer (lower layer) and add a fresh 5 mL portion of sulfuric acid. Repeat the previous step until the acid layer is clear. Transfer to a concentrator tube, rinse the acid interface with 1 mL of hexane, add to initial volume removed from vial used for acid cleanup, then concentrate the extract to the final volume using nitrogen blow-down or micro-snyder concentration.

Note: Acid can destroy the GC column thus, it is important not to remove any acid with the hexane phase.

12.0 CALCULATIONS

12.1 This section is not applicable to this SOP.

13.0 DATA ASSESSMENT, CRITERIA AND CORRECTIVE ACTION

13.1 Primary Review: Review the bench sheet for correctness and completeness. Record any problems encountered during the extraction process on the bench sheet or complete a nonconformance report, when necessary. Set aside the extracts and paperwork for secondary review.

13.2 Secondary Review: Review the bench sheet against the preparation worksheet to ensure the procedure performed is consistent with project specifications. Authorize release of the extracts to the appropriate analytical department.

13.3 For additional guidance regarding the laboratory's protocol and required elements for data review refer to laboratory SOP LP-QA -019 *Data Review*.

14.0 METHOD PERFORMANCE

14.1 This section is not applicable to this SOP.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 The following waste streams are produced when this method is performed:

- Hexane Waste-Satellite Container: 50 Gallon Waste Drum
- Acetone Waste-Satellite Container: 50 Gallon Waste Drum
- Mixed Solvent Waste-Satellite Container: 50 Gallon Waste Drum
- Methylene Chloride-Waste-Satellite Container: 50 Gallon Waste Drum
- Sulfuric Acid Waste-Satellite Container: 2.5L Waste Bottle Labeled with appropriate acid type (sulfuric).
- Solid Waste-Satellite Container: Solid Waste 10 Gallon Plastic Bucket (inside fume hood)

Transfer the waste stream to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in laboratory SOP LP-LB-001 *Hazardous Waste*.

16.0 REVISION HISTORY

The following changes were made in this revision:

16.1 Section 1.0: Changed references for background information about cleanup procedures and added language referencing the use of copper granules for cleanup.

16.2 Section 4.0: Changed interference information to only that concerning use of the procedures in the laboratory.

16.3 Section 6.0: Added language referencing the use of copper granules for cleanup.

16.4 Section 7.0: Added language referencing the use of copper granules for cleanup.

16.5 Section 11.0: Separated the procedures used for florisil check from florisil cleanup on

sample extracts and added the use of gravity as an alternative to vacuum for this procedure. Added procedure for the use of copper granules for cleanup.

16.6 Section 15.0: Added Acetone, Mixed solvent, and Solid Waste as addition waste streams. Removed Elemental Mercury Waste and Potassium Permananate Waste from the list of waste streams.

16.7 Section 16.0: Changed from “References” to “SOP Revision History”. Subsequent sections changed in turn.

17.0 REFERENCES

17.1 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

18.0 TABLES, DIAGRAMS, & FLOWCHARTS

18.1 Table 1: Primary Materials Used, Hazards & Exposure Limits

Table 1: Primary Materials Used, Hazards, & Exposure Limits

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

SOP LB-8

PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE, METHODS 1631E AND MCAWW 245.7

Controlled Copy
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Implementation Date: 8/12/07

SOP No. NC-MT-0001
Revision No. 5.1
Revision Date: 07/29/07
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TESTAMERICA NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE, METHODS 1631E AND MCAWW 245.7

(SUPERSEDES: REVISION 5, REVISION DATE 01/17/05)

Approved by: Roger K. Scott — Technical Specialist — 8/7/07 Date

Approved by: Dorothy J. Reeson — Quality Assurance Manager — 8/12/07 Date

Approved by: _____ — Environmental, Health and Safety Coordinator — 8/8/07 Date

Approved by: _____ — Laboratory Director — 8/8/07 Date

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LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) using Method 1631E and MCAWW Method 245.7.

1.2. The associated LIMs method codes are PR (Method 1631E) and D5 (Method 245.7). The sample preparation code for all methods is D4 (BrCl Oxidation).

1.3. CVAFS analysis provides for the determination of total mercury (organic and inorganic). The oxidant, bromine monochloride has been found to give quantitative recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method1631E (hereafter abbreviated to Method 1631 in this SOP) is applicable to the preparation and analysis of mercury in ground water, surface water, effluents and other aqueous samples. Appendix A to Method 1631 is applicable to the preparation and analysis of mercury in sediments, soils, biological media and other solid samples.All matrices require sample preparation prior to analysis.

1.5. Method 245.7 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.6. The TestAmerica North Canton reporting limit for mercury in aqueous matrices is 0.5 ng/L by Method 1631, and 5 ng/L by Method 245.7. The reporting limit for mercury by Method 1631 in solid matrices is 1.0 ug/kg.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solids and aqueous solutions. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor and fluorescence at 253.7 nm. For aqueous samples, a representative portion of the sample is digested and oxidized in bromine monochloride. For solid samples, 1 gram of sample is digested with cold aqua regia, diluted, and further oxidized with bromine monochloride Excess free halogens in the digestate are then reduced with hydroxylamine hydrochloride. The mercury (+2) is reduced to its elemental state with stannous chloride and purged from solution with argon in a gas / liquid separator. For Method 1631, the mercury vapor is collected on a gold trap and then thermally desorbed to the detector. For Method 245.7, the mercury vapor is transported directly from the gas /

liquid separator to the detector. The mercury vapor passes through a cell positioned in the light path of an atomic fluorescence spectrophotometer. Fluorescence is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample fluorescence to the calibration curve (fluorescence vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane and are oxidized by bromine monochloride. (Sample is preserved after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion and oxidation.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Gold, silver and iodide are known interferences. At mercury a concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent.

4.2. The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the chloride, sulfide and molecular absorbance interferences. No interferences have been noted for sulfide concentrations below 24 mg/L.

4.3. Water vapor may collect in the gold traps (Method 1631), and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by predrying the gold trap and by discarding those traps that tend to absorb large quantities of water.

4.4. The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause *quenching* of the excited atoms.

4.5. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. The analytical instrument and sample / standards preparation area should be protected from mercury vapor or particulates in the laboratory air. Samples, standards and

blanks should only be opened in a clean area. Gloves must be powder free and should be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to have either low level mercury contamination or interferences. Only clean gloves should touch the instrument and other equipment used to process blanks, standards and samples.

4.6. Samples known to contain mercury concentrations greater than 200 ng/L should be diluted prior to bringing them into the clean work area dedicated to processing low level mercury samples.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Bromine Monochloride	Corrosive Poison Oxidizer	0.1 (Br) ppm TWA	May be fatal if inhaled. Causes severe eye and skin burns. Causes damage to the following organs: Lungs, mucous membranes, respiratory tract, skin, central nervous system, eyes, lens or cornea.
Potassium Bromate	Oxidizer	0.1 Mg/M3 TWA	Irritates respiratory tract. May causecoughing and shortness of breath. Causes irritation to the skin. May cause redness, itching, and pain. In the presence of liquids, it is slowly absorbed in toxic amounts. Prolonged exposure may cause burns. Causes irritation to eyes with redness, pain. May cause eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as a carbon filter.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Atomic Fluorescence Spectrophotometer equipped with:

6.1.1. Fluorescence Cell with quartz ends. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.1.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.1.3. Peristaltic pump.

6.1.4. Flowmeter.

6.1.5. Recorder or Printer.

6.1.6. Gas /Liquid separator:

6.1.7. Drying devices: Nafion Dryer (used for all methods), soda lime trap (Method 1631).

6.1.8. Gold traps (2): quartz tube containing gold coated sand.

6.2. Sample bottles, 40 mL borosilicate glass VOC vials, QEC or equivalent, < 0.5 ng/L contamination when used for Method 1631 samples. In actual practice, should contribute less than 0.1 ng/L to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, 12 vials from each lot must be gravimetrically tested at the 40 mL point. Cleanliness is assessed by adding 0.2 mL BrCl (Section 7.15). Store the test vials at room temperature for at least 12 hours and analyze as samples. All vial results must be less than the reporting limit.

6.3. Argon gas supply, high purity, or equivalent. A gold trap may be used in-line to further purify the argon.

6.4. Calibrated automatic pipettes.

6.5. Disposable cups or tubes, low mercury content.

6.6. Starch / iodine paper.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a US Filter PureLab Plus deionized water system or equivalent. Reagent water must be free of mercury and interferences as demonstrated through the analysis of reagent and method blanks.

7.2. Stock (10 mg/L) mercury standards (in 5-10% HNO_3) are purchased. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 µg/L): Fill a 100 mL volumetric flask about half full with reagent water. Add 0.5 mL of BrCl solution (Section 7.15). Add 0.10 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The intermediate mercury standard should be replaced every 9 months.

7.4. Working mercury standard (1 µg/L): Fill a 40 mL vial about half full with reagent water.

Add 0.2 mL of BrCl solution (Section 7.15). Add 4.0 mL of the intermediate mercury standard (Section 7.3) and dilute to 40 mL with reagent water. The working mercury standard should be replaced every 3 months.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (Section 7.4) by transferring 0, 0.02, 0.04, 0.08, 0.2, 0.4, and 1.0 mL of a mercury standard into 40 mL vials and diluting to volume with reagent water; for Method 1631 use the working standard (Section 7.4), for 245.7 use the intermediate standard (Section 7.3). BrCl (Section 7.15) and $NH_2OH \bullet HCl$ (Section 7.13) reagent solutions are also added.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, some automated mercury systems may not require 40 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (QCS) must be made from a different manufacturer or lot than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed with all reagents that are used for sample preparation.

7.8. Hydrochloric acid (HCl), concentrated, trace metal grade and ultra trace mercury grade.

Note: Ultra trace mercury HCl (when commercially available) should be used to prepare the bromine monochloride solution. Trace metal grade HCl may be used to prepare the stannous chloride and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.9. Autosampler rinse solution (2%): 400 mL trace metal grade HC1 diluted to 20 L reagent water. Purge overnight with argon.

7.10. Stannous chloride solution concentrate: Add 500 g of $SnCl_2 \bullet 2H_2O$ to 2.4 L trace metals concentrated hydrochloric acid. Allow the $SnCl_2 \bullet 2H_2O$ to completely dissolve. ACS Reagent grade suitable for mercury determination (< 1 ppb) recommended.

7.11. Stannous chloride working solution: Fill a 2.5 L glass bottle (HCl leached) with 2.25 L of reagent water. Add sufficient stannous chloride concentrate (Section 7.10) to bring the total volume to 2.5 L. This produces a reductant solution that is 10% HCl and 2%

$SnCl_2 \bullet 2H_2O$. Purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.8).

7.12. Hydroxylamine hydrochloride solution: Dissolve 300 g of $NH_2OH \bullet HCl$ in reagent water. Dilute to 1 L. Add 1 mL of stannous chloride solution working solution and purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank made with this solution prior to analysis of samples (Section 9.8).

7.13. Potassium bromide: KBr, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.14. Potassium bromate: $KBrO_3$, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.15. Bromine monochloride preservative/oxidizing solution: In a ventilation hood, add 5.4 g KBr to 500 mL of ultra trace (low mercury) HCl. Allow the salt to dissolve. Slowly add 7.6 g $KBrO_3$. Halogen fumes will be emitted during this step. Adequate ventilation is essential to protect analyst safety. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.8)

7.16. Nitric acid, concentrated, trace metal grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Preservation and Holding Time

8.1.1. Holding time from time of collection to the time of preservation is extended to 28 days when the oxidation step is performed in the sample bottle used for collection. Preservation/oxidation is verified by the persistence of the yellow color of the BrCl. Additional BrCl must be added if the preservative/oxidizer is consumed. Record any additional BrCl used (see Section 11.1.5). Samples to be analyzed for dissolved Hg must be filtered within 48 hours of collection, then preserved as above. Once preserved, holding time is 90 days from sample collection to analysis.

8.1.2. Solid sample holding time for Hg is one year from collection. The holding time for digested and preserved solid samples is 90 days from sample preparation

8.2. Collection and Storage

8.2.1. The clean hands/dirty hands procedure should be followed for collection. Samples are stored in a mercury clean area.

8.2.2. Solid samples may be stored in fluoropolymer or borosilicate glass or polyethylene bags.

9. QUALITY CONTROL

9.1. Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.2. Initial Demonstration of Capability

9.3. Prior to the analysis of any analyte using Method 1631 or Method 245.7, the following requirements must be met.

9.3.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below both the TestAmerica North Canton reporting limit. In addition the MDL for Method 1631 must be ≤ 0.2 ng/L.

9.3.2. Initial Demonstration Study (initial precision and recovery study)- This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.3.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3.3. Carryover determination – Analyte system blanks immediately after calibration solutions containing successively larger concentrations of Hg – from this test determine the amount of Hg that will carry >0.5 ng/L of Hg into a succeeding system blank. When a sample one half or more of this determined amount is analyzed then a system blank must be analyzed to demonstrate cleanliness at the RL. Samples with detectable Hg analyzed after the high sample but before the system blank must be reanalyzed.

9.4. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must

contain a method blank, a LCS and a matrix spike/matrix spike duplicate (2 MS/MSD pairs if the batch has more than 10 samples). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.5. Sample Count - Laboratory generated QC samples (Method Blanks, LCS, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.6. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit. The sample result must be a minimum of 20 times higher than the blank contamination level.

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exceptions noted above).

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.7. If a sample requires additional BrCl beyond the normal amount (Section 11.1.5) an additional preparation blank should be prepared with the same amount of BrCl. The result of this prep blank will be added to the narrative of the associated sample if the result is ≥ the reporting limit. This prep blank does not have any specific acceptance criteria, but it should be proportional to the amount of BrCl used.

9.8. System / subtraction / reagent blank: The reagent blank consisting of all reagents used to prepare samples and standards will be used for background subtraction and system cleanliness monitoring. Three reagent blanks are prepared and analyzed with the daily initial calibration curve (ICal) . Apply the average calibration factor from the ICal to the average

raw response from these 3 reagent blanks. The calculated mercury concentration must be less than the reporting limit. The average raw response from these 3 calibration blanks will be subtracted from all raw response data from all other data prior to calculating concentration factor (for cal standards) or concentrations. Subsequent bubbler / reagent blanks are run as ICB and CCB in conjunction with the ICV (QCS) and CCV (OPR). These IC and CC blanks are used to monitor the cleanliness of the instrument and are calculated in the same manner as samples and are not used for background subtraction purposes. The absolute value of the calculated mercury concentration must be less than the reporting limit.

9.9. Laboratory Control Sample (LCS): One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur.

- In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported with qualifiers**. Such action must be addressed in the case narrative.**

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.10. Matrix Spike/Matrix Spike Duplicate (MS/MSD): One MS/MSD pair must be processed for each 10 samples in preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Method 1631 requires that each matrix be spiked at a 10% frequency. Some regulatory agencies interpret each discharge or sampling point as a separate matrix. It is the client's responsibility to determine which sample(s) is to be matrix spiked each time samples are submitted for analysis. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, control limits of 71 - 125 % recovery and 24% RPD for 1631 aqueous, 70-130% recovery and 30% RPD for 1631 solid, and 76 – 111% recovery and 18% RPD for 245.7 must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.11. Initial Calibration Verification (ICV/ICB) (QCS – quality control sample): Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution . An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.3.5) for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CCV, and CCB with the calibration curve.

9.12. Continuing Calibration Verification (CCV/CCB) (on-going precision and recovery - OPR): Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV concentration must be at 5 ng/L for 1631. The CCV result must fall within 77-123% of the true value for that solution for 1631. A CCB is analyzed immediately following each CCV. (See Section 11.3.5 for required run sequence). The CCB (system/reagent blank) must fall within +/- the reporting limit (RL) from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

- In the instance where the CCV or CCB is greater than the maximum and the sample

results are < RL, the data may be reported. Such action must be addressed in the case narrative.

9.13. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1 except that the oxidation time need does not need to be a minimum of 12 hours and can be used immediately since the mercury is already in an oxidized state in the standard.

10.2. Due to the differences in calibration ranges separate calibration and calibration verification standards must be prepared for Methods 1631 and 245.7. See Section 7.5 and Table 1.

10.3. Calibration may be performed daily (every 24 hours), but is required only when indicated by instrument and preparation QC problems. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer (Table III). Allow the instrument to become thermally stable before beginning calibration (approximately 1-2 hours of warm-up is required if the lamp has been turned off). The most stable results are obtained if the lamp is left on full time. Refer to the CVAFS instrument manual for detailed setup and operation protocols.

10.5. Run 3 deionized water blanks to ensure that the instrument, reductant solution and rinse solutions are adequately clean.

10.6. Calibrate the instrument according to instrument manufacturer's instructions, using 6 standards and 3 calibration blanks. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order beginning with the blanks. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.7. The calibration factors must have less than 15% RSD or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with

an unacceptable RSD. Also, the low standard must calculate back within ±25% of the true value.

10.8. Refer to Sections 9.11 and 9.12 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Aqueous Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed with the digestion reagents used for the field samples.

11.1.2. Open the outer sample bag, carefully dump the inner bag containing the sample bottles onto a clean bench top in the low level mercury area with a minimum of handling. Immediately discard the outer sample bag. Change gloves between each sample or work with another analyst using the clean hands-dirty hands technique.

11.1.3. Change gloves and open the remaining inner bag, remove the sample vials, label and place in the low level mercury prep area.

11.1.4. Remove ~2.7 mL from each sample vial. This will leave 40 mL in the bottle. Confirm by checking the meniscus and the 40mL calibration point. Set the cap back on the original vial. Repeat this process for all 40 mL vial aliquots of the sample. Transfer 1 mL of sample from a separate unpreserved "10X dilution" labeled tube and add 9 mL of reagent water. Reseal the original sample vial caps if it will be greater than 3 minutes before the next step of performed (Section 11.1.5)

Note: Typically two sample vials and one screening vial will be prepared per sample (six sample vials for client requested MS/MSD samples).

11.1.5. Temporarily lift the cap and add 0.20 mL of BrCl (Section 7.15) to the 40 mL sample vial, reseal and mix. If the yellow tint from the BrCl disappears add an additional aliquot of BrCl. This iterative process may be repeated until a maximum of 2 mL has been added. Record the amount of BrCl used on the bench sheet. If the 2 mL maximum was reached and the yellow BrCl color still does not persist consult supervisor to determine if sample dilution prior to preservation / oxidation is appropriate. At least one method preparation blank must be prepared for each different volume of BrCl added.

11.1.6. Add 0.05 mL BrCl to the dilution tube(s) from Section 11.1.4. Confirm the 10X

dilution tube has adequate BrCl. Add more as needed.

11.1.7. Store the sample vials at room temperature for at least 12 hours. If the yellow BrCl color disappears during the storage period, the oxidizer has been consumed. Add additional BrCl until the yellow color persists. Do not exceed a total of 2 mL. Consult laboratory Technical Director or supervisor if yellow color does not persist after 2 mL addition of BrCl. Record the total volume of BrCl added on the benchsheet. Starch / iodine paper may be used to detect excess halogens (i.e. BrCl) in colored samples where the yellow color of the BrCl can not be seen.

Note: To speed or improve oxidation, especially for samples with high organic content or known interferences, the vials may be heated at approximately 50°C. For samples requiring greater than 0.2 ml of BrCl, this can lessen preparation time.

Note: The 12 hour oxidation time is not required for the sample aliquots in the screening tubes.

11.1.8. Prepare method blank and LCS vials using the same reagents as used for the samples.

11.2. Solid sample Preparation:

11.2.1 Homogenize the sample then weigh 1 g into a 40 mL VOA vial. The VOA vial must come from a lot that has been pre-screened for Hg contamination (Sec. 6.2).

11.2.1.1 For the method blank, add approximately 1 mL of reagent water in lieu of 1 g of solid sample.

11.2.1.2 For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Sec. 7.3) in lieu of 1 g of solid sample.

11.2.1.3 For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Sec. 7.3) in addition to the 1 g of solid sample.

11.2.2 In a fume hood, add 8 ml of concentrated HCl, swirl, and add 2 mL concentrated HNO_3 to the sample in the 40 mL vial. Cap and allow the sample to digest for at least 4 hours.

11.2.3 Add 1 ml of BrCl (Sec. 7.15) to the digestate, then dilute with reagent water (Sec. 7.15) to the 40 mL calibration point. Shake, then allow to settle until supernatant is

clear. Centrifuge or filter if necessary.

11.2.4 For screening, transfer 0.1 mL of the supernatant into a "5X dilution" 10 ml culture tube and dilute to 10 mL with reagent water. For analysis, transfer 2 mL of the supernatant into a pre-screened VOA vial and dilute to the 40 mL calibration point with reagent water, then cap and shake. The "5X dilution" aliquot may be analyzed as specified in Sec. 11.3. The 40 mL VOA vial sample is ready for analysis and may be analyzed as specified in Sec. 11.4. Based on sample matrix and/or historical results, a greater dilution may be required.

11.3. Sample screening

11.3.1. Add 0.05 mL of hydroxylamine solution (Section 7.12) and analyze the 5X screening aliquot of the sample using a single point calibration (10 ng/L) and Method 245.7.

11.3.2. If the sample response exceeds that of the 10 ng/L standard (i.e. sample concentration > 2000 ng/L), then low level analysis by either 245.7 or 1631 is not technically appropriate. Remove all vials associated with this sample from the low level prep and storage areas immediately. Consult supervisor.

11.3.3. If the estimated concentration is greater than 200 ng/L, consult supervisor about analysis by 245.7. If approved, calculate the appropriate dilution and proceed with 245.7 analysis. Alternately, prepare an appropriately large dilution of the sample before bringing it into the low level preparation area. Direct low level analysis by 1631 is not technically appropriate due to the likelihood of contamination.

11.3.4. If the sample response (Note: this is a 5X dilution) exceeds that of the 5 ng/L standard then the sample concentration is beyond the normal calibration range of Method 1631. Either analyze the sample 245.7 (if allowed by the client) or prepare the appropriate dilution for 1631 analysis.

11.3.5. If the 5X dilution screen response is non-detect at 5 ng/L then the sample may be analyzed without dilution by either 245.7, or Method 1631 depending on the reporting limit needed by the client unless matrix interferences warrant dilution.

11.4. Sample Analysis

11.4.1. When ready to begin analysis, add 0.10 mL of hydroxylamine hydrochloride solution (Section 7.12) to the samples to reduce the excess BrCl (the BrCl has been reduced when no yellow color remains). Cap and shake. Add the

hydroxylamine solution in 0.10 mL increments until the BrCl is completely reduced. Record the total volume used on the benchsheet.

Note: Spiking is done before the addition of the hydroxylamine hydrochloride reagent.

11.4.2. With instrument control parameters set to appropriate values (See Table III), load samples into autosampler. Use 40 mL vials for Method 1631 and 14 mL or 40 mL tubes for 245.7.

11.4.3. Start autosampler sequence.

11.4.4. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.4.5. The following analytical sequence must be used:

Instrument Calibration
ICV (QCS)
ICB
CCV (OPR)
CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 3 and Table II (Appendix A) for the appropriate quality control criteria.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

Note: Instrument calibration need not be performed if the run QC parameters indicate that the system is in control.

11.5. To facilitate the early identification of QC failures and samples requiring rerun it is strongly

recommended that sample data are reviewed periodically throughout the run.

11.6. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.7. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by the QA Manager. The Non-Conformance Memo shall be filed in the project file.

11.8. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1.Calibration Factors are calculated according to the equation:

$$CF(x) = \left(\frac{Area(x) - Area(b)}{Conc(x)} \right)$$

Where:

CF(x) = calibration factor of standard (x)
area(x) = area of standard (x)
conc(x) = concentration of standard (x)
area(b) = average area of 3 calibration blanks

12.2. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(ICV)}{True(ICV)} \right)$$

12.3. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(CCV)}{True(CCV)} \right)$$

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.6. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.7. The final concentration for an aqueous sample is calculated as follows:

$$ng/L = \text{C x D}$$

Where:

C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8. The final concentration for a solid sample is calculated as follows:

$$ug/kg = C \times D \times W \times P$$

Where:

C = Concentration (ng/L) from instrument readout

D = Instrument dilution factor

W = Weight/volume factor = 0.040, when 1 g of sample is digested and diluted to 40 mL.

P = Preparation factor = 20, when 2 mL of digestate is diluted to 40 mL.

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.3.

13.2. Method performance is determined by the analysis of method blanks and laboratory control samples. The method blanks must meet the criteria in Section 9.6. The laboratory control sample should recover within 25% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and

Pollution Prevention."

15.2.Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Acid Waste- Aqueous waste generated by the analysis.** Samples vials are collected and taken to the waste storage building. The vials are crushed and the liquid waste and glass are separated. The liquid waste is neutralized and released to the POTW. The glass is disposed of in the trash.

16. REFERENCES

16.1. References

16.1.1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, August 2002.

16.1.2. Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, U.S. EPA, January 2001.

16.1.3. Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, U.S.EPA, January 2000.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. TestAmerica Laboratory Quality Manual (LQM), current version.

16.1.6. TestAmerica Corporate Safety Manual, M-E-0001 and TestAmerica North Canton Facility Addendum and Contingency Plan, current version.

16.2.Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-

0021

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.6. Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1 Section 9.1.7 of the method requires three method blanks per analytical batch. The section also describes an analytical sequence that includes a CCV (OPR) only at the beginning and end of the sequence, and that includes no CCBs (system blanks) after calibration. This SOP requires only one method blank per preparation batch, but requires additional stability and cleanliness checks through the analysis of a CCV/CCB pair at the beginning, end and after every ten analyses during an analytical run.

17.1.2 Section 9.2.1 of the method recommends that an MDL be determined whenever a new operator begins work. At this laboratory, a new operator receives proper, documented training and must prove competence through an initial demonstration of performance that includes the successful analysis of (4) LCSs (See Section 9.3.2).

17.1.3 Conventional MS/MSD techniques and criteria have been maintained in contrast to Section 9.3.4 of the method (See Section 17.1.2.1 of this SOP).

17.1.4 Section 9.4.3.1 of the method requires reagent blank concentrations to be <0.2 ng/L. In this laboratory, reagent blanks are analyzed as system calibration blanks and are held to the system blank criteria of <0.5 ng/L (See Section 9.8 of this SOP).

17.1.5 Section 9.4.5.1 of the method recommends that field blank analysis immediately before analyzing samples from the batch. Field blanks are analyzed as normal samples in this laboratory with no particular run order requirement.

17.1.6 Section 9.4.7 of this method recommends that 5% of the bottles in a lot be monitored. Bottle cleanliness in this laboratory is verified by the initial analysis of 5% of the bottles from three boxes of a lot of 40 mL sample vials, and then monitored through the routine analyses of system blanks (calibration blanks).

17.1.7 The volume descriptions for the equation in Section 12.3.2 of the method includes

subtraction of the volume of reagent used in the standards and the samples. Since the volume of reagents used in samples and standards is typically the same (or differs insignificantly in rare cases), this subtraction is not included in the determination of Hg concentration in this laboratory.

17.2 Performance Based Modifications from Method 245.7.

17.2.1 The preservative / oxidizer solution (Section 7.15) from Method 1631B has been used in place of the bromate/bromide oxidizer solution (Section 7.7.4 in method).

17.2.2 The autosampler is rinsed with 2% HCI solution as recommended by the manufacturer rather than deionized water (Section 11.3.2 in method).

17.3 Other Interpretations and Differences from Method 245.7.

17.3.1 Reagent blank acceptance criteria is an absolute value less than the reporting limit (Section 9.8) rather than MDL (Section 9.2.1.3 in method)

17.3.2 Conventional fixed concentration matrix spiking has been used in this SOP (Section 9.10) rather than the variable concentration spiking described in the method (Section 9.5 in method). Also, batch acceptability is determined by method blank and LCS criteria and not MS/MSD recovery and RPD.

17.3.3 All standards are prepared using the same reagents as the samples rather than only in reagent water (Section 10.1.1.2 in method). (See Section 10.1)

17.3.4 The digested sample is used for dilution since no undigested sample (Section 11.3.4 in method) is available as the BrCl solution both preserves and oxidizes the sample. Also, this form of the sample should be more homogeneous for total mercury analysis.

17.4 Interpretations and Differences from Method 1631 Appendix A

17.4.1 In the method, after digestion with aqua regia is complete, the digestate is diluted with 0.07 N BrCl for elemental carbon-containing samples. In this SOP, all samples are diluted reagent water to which 1 mL of 0.2 N BrCl has been added. This presents a BrCl concentration in the diluted digestate comparable to the concentration achieved using the method technique. Also, since it is added to all digestates (not only those known to contain elemental carbon), the analyzed digestate will always contain some BrCl, and thereby be more comparable to the calibration standards.

17.5 Documentation and Record Management

17.5.1 The following documentation comprises a complete CVAFS raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

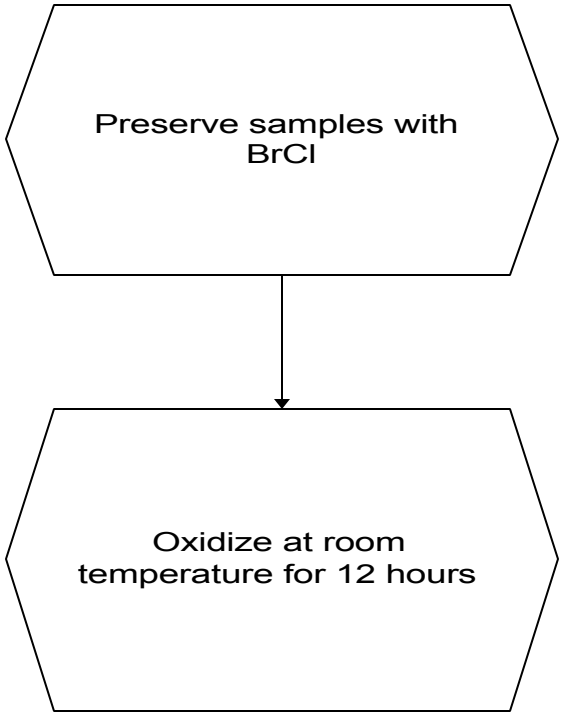
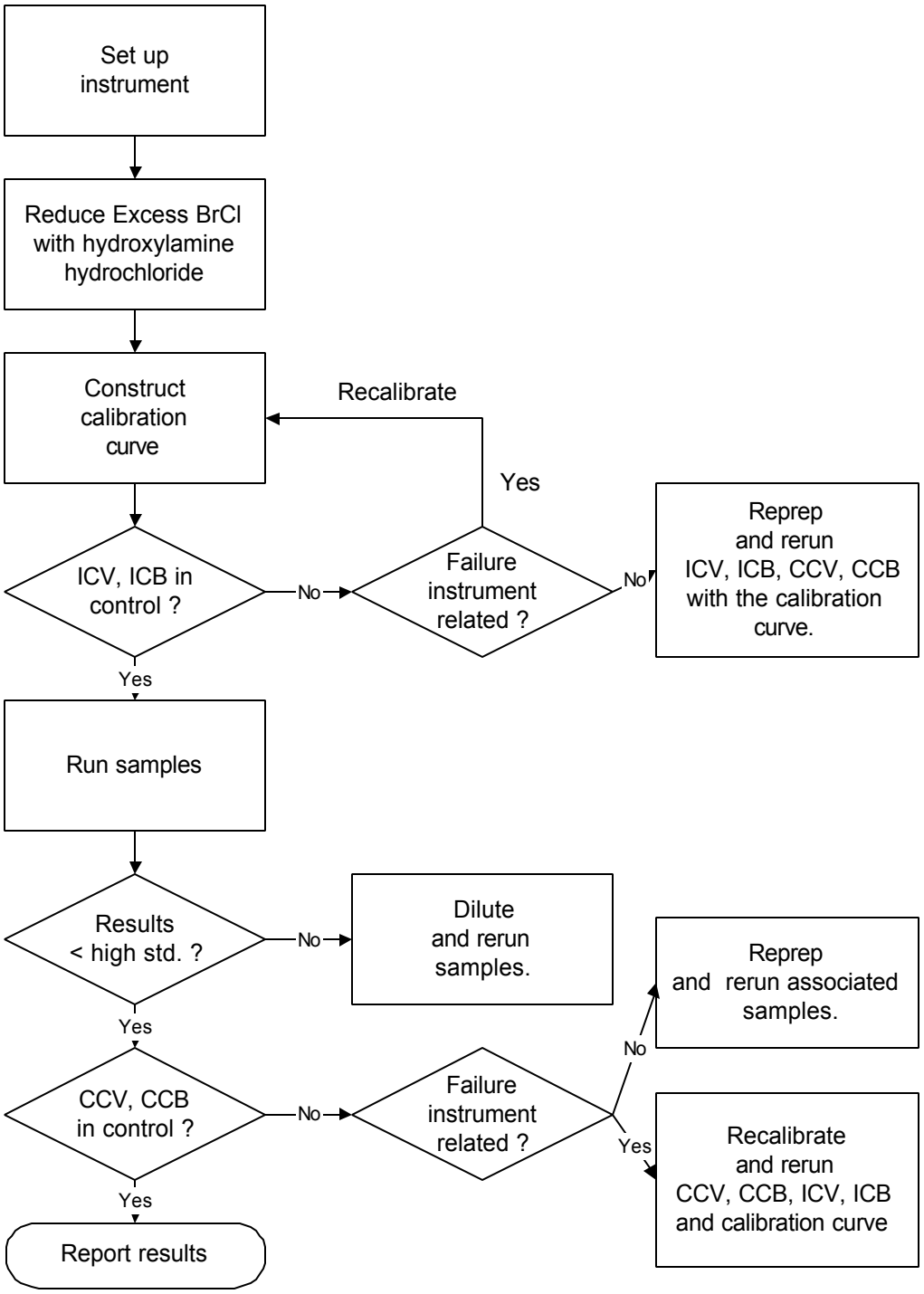


Figure 2. CVAF Mercury Analysis



APPENDIX A

TABLES

TABLE I
MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD, AND SPIKING LEVELS (ng/L)

	1631E				245.7	
	Conc ng/L	**mL Std (Sec.7.4)**	**Conc ug/kg Solid**	**mL Std (Sec.7.3) Solid**		**mL Std (Sec.7.3)**
Standard Water RL	0.5				5	
Standard Solid RL			1.0		NA	
Std 1 (in triplicate)	0	0			0	0
Std 2	0.5	20			5	20
Std 3	1	40			10	40
Std 4	2	80			20	80
Std 5	5	200			50	200
Std 6	10	400			100	400
Std 7	25	1000			250	1000
ICV (QCS)	5	200 (Sec 7.6)			10	40 (Sec 7.6)
CCV (OPR)	5	200			10	40
LCS	5	200	10	1000		
MS/MSD	5	200	10	1000	10	40

TABLE II
SUMMARY OF QUALITY CONTROL REQUIREMENTS

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA 1631	ACCEPTANCE CRITERIA 245.7	CORRECTIVE ACTION
ICV (QCS)	Beginning of every analytical sequence.	80-120 % recovery	80-120 % recovery	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (see Section 9.11)
ICB	Beginning of every analytical run, immediately following the ICV	The result must be within +/- RL (0.5 ng/L for aqueous, 1.25 ng/L for solid)	The result must be within +/- RL (5 ng/L)	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.11)
CCV (OPR)	Every 10 samples and at the end of the run	77-123 % recovery	76-111 % recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve (Note exceptions in Section 9.12)
CCB	Immediately following each CCV	The result must be within +/- RL (0.5 ng/Lfor aqueous, 1.25 ng/L for solid)	The result must be within +/- RL (5 ng/L)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve (Note exceptions in Section 9.12)
Method Blank	One per sample preparation batch of up to 20 samples. Note: additional prep blank(s) required if additional BrCl needed in some sample(s)	The result must be within +/- RL Sample results greater than 20x the blank concentration are acceptable.	The result must be within +/- RL (5 ng/L)	Redigest and reanalyze samples Note exceptions under criteria section See Section 9.6 for additional requirements.

TABLE II

SUMMARY OF QUALITY CONTROL REQUIREMENTS (Cont'd)

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA 1631	ACCEPTANCE CRITERIA 245.7	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	75-125 % recovery	75-125 % recovery	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (Note exception under Section 9.9)
Matrix Spike	Two per sample preparation batch of up to 20 samples.	71-125 % recovery for aqueous, 70-130% recovery for solid. If the MS/MSD is out for an analyte, it must be in control in the LCS	76-111 % recovery. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added (see Section 9.10)
Matrix Spike Duplicate	See Matrix Spike	Same as Matrix Spike RPD ≤ 24% for aqueous, ≤30% for solid	76-111 %; RPD ≤ 18% (see MS)	See Corrective Action for Matrix Spike

*See Section 11.3.5 for exact run sequence to be followed

TABLE III
SUMMARY OF INSTRUMENT PARAMETERS
(LEEMAN LABS HYDRA AF GOLD +)

Instrument Parameter	**1631**	**245.7**
Argon flow (L/min)	0.5	0.4
Pump flow (mL/min)	10	10
Rinse (sec)	60	120
Uptake (sec)	240	35
Sample volume (mL)	40	11
Integration (sec)	0.70 (70 sec total)	35 sec total
Method	CVAFS with trap	CVAFS
Furnace 1 temp (°C)	450	
Furnace 2 temp (°C)	450	
Dry Time (sec)	5	
Desorption Time (sec)	70	
Stabilize Time (sec)	10	

APPENDIX B

EXAMPLE
TESTAMERICA NORTH CANTON Hg DATA REVIEW CHECKLIST

Example

TestAmerica North Canton Hg Data Review Checklist

Run/Project Information

Run Date: _____ Analyst:_____ Instrument:_____
Prep Batches Run:_____
Circle Methods used: 1631E : NC-MT-0001 Rev 4 **245.7 :** NC-MT-0001 Rev 4
245.7 screen : NC-MT-0001 Rev 4

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels (including 3 initial calibration blanks)?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. Samples preserved within holding time at lab?				
2. LCS done per prep batch and within QC limits?				
3. Method blank done per prep batch and < RL?				
4. MS run at required frequency (1 per 10 samples) and within limits?				
5. MSD or DU run at required frequency (1 per 10 samples) and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately?				
2. Current MDL data on file?				
3. Calculations and Transcriptions checked for error?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct?				

Analyst: _____ Date:_____
Comments:
_____
_____

2nd Level Reviewer : _____ Date:_____
_____
_____

Standard and Reagent Numbers

ICal/CCV _____ **ICV _____**

BrCl _____ NH2OH HCl _____ SnCl2 _____

APPENDIX C

MSA GUIDANCE

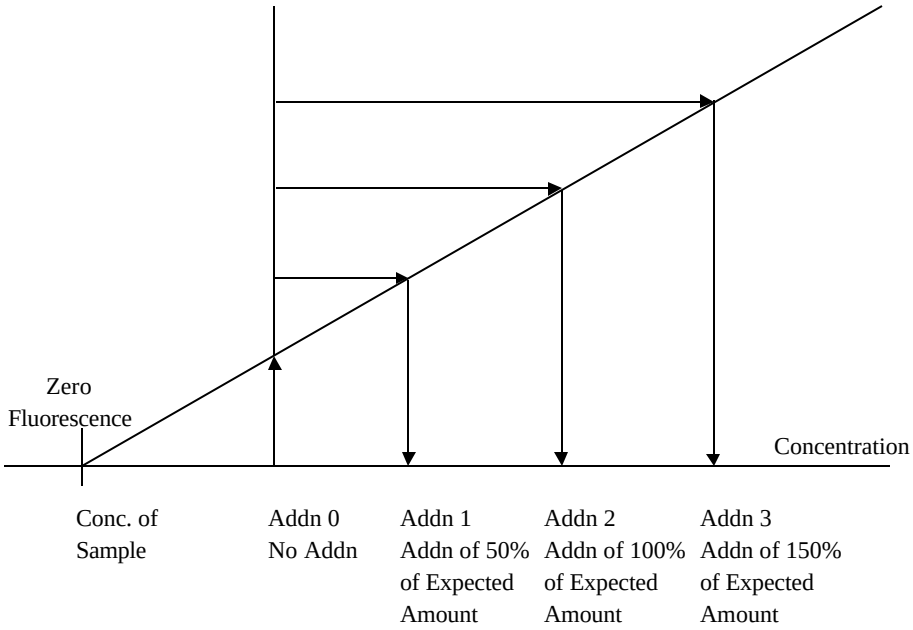
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the fluorescence (or response) of each solution is determined and a linear regression performed. On the vertical axis the fluorescence (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero fluorescence , the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D

TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Fluorescence or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal fluorescence or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 hydrochloric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the mercury laboratory since the powder contains mercury, as well as other metallic analytes. Only powder free gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and discard.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman Labs Hydra AF gold plus) (1)

Daily	Semi-annually	As Needed
Check argon flow	Check Hg lamp intensity	Change Hg lamp
Check pump tubing		Change liquid/gas separator
Check drain		Change Nafion dryer
Check soda lime drying tube		

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman Labs Hydra AF gold plus)

TO SET UP INSTRUMENT FOR ANALYSIS

1. WinHG Rack File editor

2. New Rack file

    A. Enter sample workorder # into corresponding "Sample name" (limit 8 chars, no spaces)

    B. Enter client ID into "Extended ID"

    C. Save file with Date/letter name (e.g. 0324a) (limit 8 characters, no spaces)

3. WinHg Database

    A. Select most recent calibration of appropriate method (1631 or 245.7)

    B. Save Protocol As, method / current date (e.g. 16310324) (limit 8 characters, no spaces)

    C. Clear calibration data from new protocol

    D. Apply (i.e. Save changes)

    E. Upload protocol to Runner

3. WinHg Runner

    A. Sample tab

    B. Select appropriate rack file(s), click auto sample

SOP LB-9

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY (SW-846 METHOD 8081A)

Title: Organochlorine Pesticides by Gas Chromatography
[SW-846 Method 8081A]

Approvals (Signature/Date):

William S. Cicero Laboratory Director — 12/27/07 Date	Jacob L. Bailey Current Department Manager — 12/27/07 Date
Kirstin L. McCracken Quality Assurance Manager — 12/27/07 Date	Bryce E. Stearns Technical Director — 12/27/07 Date
Bryce E. Stearns Interim Health & Safety Coordinator — 12/27/07 Date	

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LM-GC-8081A.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

TestAmerica Burlington
SOP CHANGE-IN-PROGRESS ATTACHMENT (CIPA)

SOP Number	Title	Revision	Effective Date	Change Effective Date
BR-GC-006	Organochlorine Pesticides by Gas Chromatography	8	01/01/2008	02/12/08

SOP Change Approved By:

Laboratory Director: William Cicero Date: 02/12/08

QA Manager: Kirstin McCracken Date: 02/12/08

Department Manager: Jacob Bailey Date: 02/12/08

The following revisions were made to this standard operating procedure (SOP). These changes will be incorporated into the document with the next revision.

1. Add the following text to Section 10.3, after the 5th paragraph:

NOTE: The DoD QSM requires that a five-point calibration for multi-component pesticides be performed prior to the analysis of DoD project samples. The laboratory will follow this requirement when the requirement is specified for the DoD project, otherwise the laboratory will follow its routine procedure. Exceptions to this requirement should be documented with client approval of a laboratory variance to the QSM. See the PM for further guidance if needed.

2. Add the following text to Appendix A: Standard Preparation Tables

EXTRACTION SPIKE SOLUTIONS

The following standards are used to spike field and QC samples prior to extraction. Assign an expiration date of 6 months from date prepared unless the stock standard expires sooner in which case use the earliest expiration date. Store the prepared solutions under refrigeration and protected from light at a temperature of 4ºC (±2).

Pesticide Surrogate Solution

Stock Standard	Vendor	Component	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Pesticide Surrogate	Restek #3200	DCB	200	1.0	1000	0.20
		TCMX	200			0.20

Solvent: Acetone

8081 Spike Solution (LCS, MS/MSD)

Stock Standard	Vendor	Component	Stock Standard Concentration (ug/ml)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ul/L)
Organochlorine Pest Mix AB#2	Restek #32292	Heptachlor epoxide	8	1.0	40	200
		Endosulfan sulfate	16			400
		Aldrin	8			200
		alpha-BHC	8			200
		beta-BHC	8			200
		delta-BHC	8			200
		Endosulfan II	16			400
		4,4'-DDT	16			400
		alpha-Chlordane	8			200
		gamma-Chlordane	8			200
		Endrin ketone	16			400
		gamma-BHC (Lindane)	8			200
		Dieldrin	16			400
		Endrin	16			400
		Methoxychlor	80			2000
		4,4'-DDD	16			400
		4,4'-DDE	16			400
		Endrin aldehyde	16			400
		Heptachlor	8			200
		Endosulfan I	8			200

Solvent: Methanol / Expiration Date: 2 weeks from date of preparation unless any parent component expires sooner in which case, use the earliest expiration date.

STANDARD OPERATING PROCEDURE
TestAmerica Burlington

ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY
SW-846 METHOD 8081A

Applicable Matrix: Non-Potable Water, Solid & Chemical Materials

APPROVAL SIGNATURES

William S. Cicero
Laboratory Director
Date: August 9, 2007

Kirstin L. McCracken
Quality Assurance Manager
Date: August 9, 2007

Bryce E. Stearns
Technical Director
Date: August 9, 2007

Jacob L. Bailey
Department Manager
Date: August 9, 2007

1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) describes the laboratory procedure for the determination of concentrations of organochlorine pesticides in extracts derived from non-potable water, solids, tissue, air, and chemical materials including TCLP leachates, using dual column Gas Chromatography with Electron Capture Detectors (GC/ECD). This SOP is applicable to the analytical procedure only; the extraction and extract cleanup methods referenced in this SOP are described in the following laboratory SOPs:

- LM-OP-3510 Separatory Funnel Extraction
- LM-OP-3540 Soxhlet Extraction
- LM-OP-3550 Ultrasonic Extraction
- LM-OP-Cleanup Extract Cleanup Procedures
- LM-OP-GPC Gel Permeation Chromatography (GPC)

1.2 The routine target analyte list and associated reporting limit (RL) is provided in Table 1A, Section 18.0. Non-routine target analytes that may also be analyzed by this method on a project basis are provided in Table 1B. Method performance objectives should be negotiated on a project specific basis. Provision of analytical services by this test method for any analyte not listed in these tables requires consultation with the laboratory prior to project inception. The RLs provided in Tables 1A and 1B are "wet-weight" based on a routine extraction volume of mass. RLs adjusted for percent moisture and extraction volumes are provided in the final data report.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate matrix-specific extraction technique. After extraction, the extract may be subject to cleanup depending on the nature of sample matrix and the target analytes. After cleanup, the extract is analyzed by injecting a 2 uL aliquot into a dual capillary column GC/ECD.

2.2 This procedure is based on SW-846 Method 8081A, Organochlorine Pesticides by Gas Chromatography.

3.0 DEFINITIONS

3.1 A list of terms and definitions is given in Appendix C.

4.0 INTERFERENCES

4.1 Contaminated solvents, reagents or equipment can cause interferences. To reduce the occurrence of this type of interference, glassware must be cleaned thoroughly before use following the procedure given in laboratory SOP LM-OP-Glass. Only reagent-grade solvents and reagents may be used.

4.2 Phthalate esters introduced during sample preparation can pose a problem in the determination of pesticides. Common flexible plastics contain varying amounts of

phthalate esters, and these can be easily extracted or leached during extraction. To minimize this interference, avoid contact with any plastic materials.

4.3 The presence of PCBs may interfere with the analysis of organochlorine pesticides. This interference is most severe for multi-component analytes such as Chlordane and Toxaphene.

4.4 Non-target compounds co-extracted from the sample matrix can also cause interference, the extent of which will vary considerably depending on the nature of the samples. Elemental sulfur is often found in sediment samples and its presence will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Samples are screened before analysis and those samples that contain high levels of sulfur are subject to cleanup using activated copper before analysis (SW-846 3660B). Waxes, lipids, other high molecular weight materials and co-eluting organophosphorous pesticides may be removed by extract cleanup with GPC (SW-846-3640A). Co-eluting chlorophenols can be eliminated by cleanup with silica gel (SW-846 3630C), or Florisil (SW-846 3620B).

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature before working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.3 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **Note: The table does not include all materials used in the procedure. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used can be found in Section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 EQUIPMENT AND SUPPLIES

6.1 Autosampler Vials, National Scientific or equivalent

6.2 Computer Hardware:

6.3 Computer Software: Data Acquisition: Multichrom Version 2.0, Data Processing and Report Generation: Target Version 3.5.

6.4 Data system capable of handling a minimum of 200 chromatographic peaks per detector.

6.5 GC/ECD: with dual columns, dual ECDs, and auto-sampler capable of a 2-µl injection split onto two columns: Hewlett Packard 6890 or equivalent.

6.6 GC Columns:

- RTX-CLPesticides (30m x 0.32 mmID x 0.25um), Restek or equivalent.
- RTX-CLPesticides II, (30m x 0.32 mm ID x 0.25um), Restek or equivalent.

6.7 Hydrogen Generator

6.8 Volumetric Syringes, Class "A" (10µl, 25µl, 50µl, 100µl, 250µl and 500µl), Hamilton or equivalent.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

- Acetone, Ultra-Resi Analyzed. JT Baker or equivalent.
- Hexane, Ultra-Resi Analyzed. JT Baker or equivalent.
- Methanol, Ultra-Resi Analyzed. JT Baker or equivalent.

7.2 Standards

Purchase stock standard solutions from commercial vendors. Prepare calibration and working standards solutions by diluting a known volume of the stock standard in an appropriate solvent to a specified volume. Standard preparation formulations for this procedure are provided in Appendix A.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Sample extracts must be stored at 4°C ± 2° until the time of analysis. The analytical holding time is 40 days from date of sample extraction.

8.2 Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

The minimum frequency requirements, acceptance criteria and recommended corrective action for all QC samples are summarized in Table 3, Section 18.0. The following sections summarize each type of QC sample analyzed with this method.

9.1 A Method Blank (MB) and Laboratory Control Sample (LCS) is prepared with each extraction batch. These samples show that the laboratory is in control, independent of the sample matrix.

9.2 A Matrix Spike and Matrix Spike Duplicate (MS/MSD) are prepared with each extraction batch. Project specific MS/MSD and/or Sample Duplicates (SD) are performed per client request. These samples show the effect of the sample matrix on the accuracy and precision of the method.

9.3 Surrogate spike is added to all field and QC samples before extraction to assess the ability of the method to successfully recover the target analytes from the sample matrix.

9.4 Instrument QC standards include a Breakdown Check Standard (BCS) before each Initial Calibration (ICAL), at the beginning of any daily run, and every 10 samples within a sequence. A five-point ICAL is generated for each individual single component pesticide and each qualitatively identified multi-component pesticide. After the ICAL, an Initial Calibration Verification (ICV) standard, also referred to as a second source standard, is analyzed to verify the ICAL standard formulation. Continuing Calibration Verification (CCV) standards are analyzed before sample analysis, every ten samples thereafter, and at the end of the run to assess instrument drift.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Operating Conditions

Install a 5-m deactivated guard column to the injection port and connect the guard column to the separate analytical columns attached to dual ECD detectors using a glass "Y". Set the instrument operating conditions. The recommended instrument operating conditions are as follows:

Initial Temperature:	120°C for 1 minute
Temperature Program:	16°C per minute to 210°C to 6°C per minute to 245°C to 12.5°C per minute to 300°C. Hold for 4 minutes.
Detector Temperature	300°C
Injector Temperature:	225°C
Injection volume:	2-μL
Carrier Gas:	Hydrogen (supplied by hydrogen generators)

Optimize the flow rate of the carrier gas by injecting an un-retained substance onto the column at an isothermal oven state and adjusting the flow to obtain the recommended dead volume time.

The GC conditions listed above may be changed provided the elution orders are documented and compound separations are maintained but once the operating conditions are established, use the same conditions for analysis of calibration standards, QC and field samples.

10.2 Retention Time (RT) Windows

When a new GC column is installed establish RT windows by analyzing three standards over a 72-hour period and calculating the mean RT and Standard Deviation (SD). Calculate the RT window as mean RT $\pm$ 3SD of the three standards. If the SD is <0.01 minutes, the laboratory may use a default SD of 0.01 minutes. If, in the professional judgment of the analyst, this procedure results in an RT window that is too tight and would favor false negatives, the laboratory may opt to use an alternate method to determine the RT windows as follows: using the RT of the midpoint initial calibration standard, calculate the RT window using $\pm$ 0.05 minutes from the midpoint of the RT in the initial calibration.

10.3 Initial Calibration (ICAL)

Perform initial calibration of the instrument during initial method set-up, whenever a new column is installed, when significant instrument maintenance has been performed and when the result of continuing calibration verification (CCV) indicate the calibration is no longer valid. Significant instrument maintenance includes changing the lengths of the analytical columns and baking or installing detectors.

Before calibration, if the instrument has been idle for longer than 8 hours, prepare and analyze a Column Prime Standard. The formulation for the preparation of the standard is provided in Appendix A.

To initiate the calibration, prepare and analyze the breakdown check standard (BCS). The formulation for the preparation of the BCS is provided in Appendix A. Evaluate the results. The break down values for DDT and Endrin must be $\leq$ 15%. If the breakdown criteria are not met, correct the problem and reanalyze the BCS. Repeat the analysis of the BCS at the start of each sequence, every 10 samples, and at the end of the sequence.

Prepare the calibration standards using the formulation provided in Appendix A. Inject 2-µl of each calibration standard onto the instrument using the same technique used for sample extracts as described in Section 11.0. Unless otherwise specified for a specific project, the calibration for single component pesticides is established with a minimum of five calibration points. Multi-component pesticides use a single-point calibration at or near the low-point of the calibration range for pattern recognition.

When a multi-component pesticide is detected in a field sample, a five-point curve is established for the analyte and the extract is re-analyzed and quantified from the five-point calibration.

The data processing system calculates the Calibration Factor (CF), mean CF and Percent Relative Standard Deviation (% RSD) for each analyte on both columns. The equations used are provided in Appendix B. The RSD for each target analyte must be less than or equal to 20% in order to use the mean CF or quantification. If this criterion is not met use another suitable quantification method for that analyte or correct the problem and repeat the calibration. Once a method of quantification is chosen for a specific compound, it must be consistently used throughout the entire analytical sequence until a new initial calibration is performed.

Alternate Quantification Option:

Linear Regression & Weighted Linear Regression: Generate a curve of concentration vs. response for each analyte and calculate the correlation coefficient. The calibration must have a correlation coefficient (r) $\geq$ 0.995. If this criterion is not met, correct the problem and repeat the calibration. The use of linear regression requires a minimum of 5 calibration points. See SW-846 Method 8000B for linear regression calculations.

NOTE: Unless otherwise specified for the project, for DoD QSM work, the quantification option (mean CF or linear regression) must meet criteria for each target analyte otherwise the calibration must be repeated. The DoD QSM prohibits the reporting of samples against an ICAL that does not meet criteria even when associated analytical results are flagged.

10.3.1 Initial Calibration Verification (ICV)

Immediately after each calibration and prior to the analysis of any other QC or field samples, verify the accuracy of the initial calibration by analyzing a second source ICV.

Prepare the ICV using the formulation provided in Appendix A. Inject 2-µl of the ICV standard onto the instrument using the same technique that is used for sample extracts described in Section 11.0.

The percent recovery of each analyte must be within $\pm$ 20% of the expected value. If this criterion is not met, correct the problem and reanalyze the ICV. If the reanalysis fails, remake the calibration standards and recalibrate. The acceptance criteria must be met on both columns.

10.4 Continuing Calibration

Analyze a CCV each day before sample analysis (after analysis of the BCS) after every ten samples and at the end of each analytical batch to monitor instrument drift. The CCV should include all single component analytes and the concentration of the CCV standard should be varied within the calibration range. When a multi-component analyte is detected in a field sample, analyze a multi-component CCV varying the concentration within the analytical batch.

The data system calculates the percent difference for each analyte on both columns. The percent difference must be within ±15% of the expected value from the ICAL for each analyte and the retention time (RT) for each analyte must be within the established RT window. The acceptance criteria must be met on both columns, with the exception of Technical Chlordane and Toxaphene, which require pattern recognition rather than second column confirmation.

If the CCV fails, it may be repeated once. If it still fails, corrective action must be taken. The sequence may be continued only if two immediate, consecutive CCVs are within acceptance criteria. If the two CCVs do not meet the criteria, recalibration is required prior to running samples. Samples must be bracketed by passing CCVs, and samples before and after CCV failure must be reanalyzed unless the CCV is high and there are no detects in the associated samples.

10.5 Troubleshooting

Check the following items in case of calibration failures:

- ICAL Failure – Perform injection port maintenance, install new guard column, check detector ends to see if detector jet has slipped. In extreme cases, install new columns, particularly if the chromatography has degraded as evidenced by peak shapes.
- CCV Failure – Perform Injection port maintenance; if injection port maintenance does not restore CCV, install a new guard column and remove one or more loops from each analytical column.
- Needle crushed during injection - Replace the needle and check the injection port for obstructions and check the autosampler for misalignment.
- Auto-sampler failure - Reset the auto-sampler.
- Power failure - Reset run in Multichrom and re-acquire or re-initiate run sequence.

11.0 PROCEDURE

11.1 Extract Screen Procedure

At the discretion of the laboratory samples may be screened prior to analysis. If the results of the screen indicate that the sample should be analyzed at a primary dilution, prepare the dilution in hexane using a Hamilton syringe or other appropriate Class A glassware. When required by client or regulatory program, include the screen data in the final data report.

11.2 Analysis

Prepare the sample extracts, QC samples, calibration and instrument performance check standards for analysis by transferring ~100 uL of extract to an auto sampler vial and place the vials in the autosampler. Arrange the samples in a sequence that begins with the calibration standards followed by the analysis of QC samples, field samples and

continuing calibration verification standards (CCVs). Cleaning blanks (CBLK) consisting of hexane may be analyzed after high-level samples at the discretion of the analyst.

An example analytical sequence that includes initial calibration is given below:

Injection Number	Lab Description	
1	Column Priming Standard	Column Prime
2	Breakdown Check Standard	BCS
3	Single Component Level 1	INDAB-1
4	Single Component Level 2	INDAB-2
5	Single Component Level 3	INDAB-3
6	Single Component Level 4	INDAB-4
7	Single Component Level 5	INDAB-5
8	Technical Chlordane -50 ppb	TOX50
9	Toxaphene - 500 ppb	T.CHLOR500
10	ICV – Second Source Standard	ICV
11-20	10 injections	QC and Field Samples
21	Breakdown Check Standard	BCS
22	Continuing Calibration Verification Standard	CCV
23-32	10 injections	QC and Field Samples
33	Breakdown Check Standard	BCS
34	Continuing Calibration Verification Standard	CCV
Repeat until ending with BCS and CCV		

Enter the sample ID's into the data acquisition program in the same order that the samples were placed in the auto-sampler. Start the analytical sequence and acquire the data.

The data system tentatively identifies single component pesticides by comparing the retention time of the peaks to the established RT windows and quantifies analytical results using the equations given in Appendix B. Detects are confirmed if the peak is within the retention time window on both columns. If the data system does not properly integrate a peak, perform manual integration. All manual integration must be performed and documented in accordance with laboratory SOP LP-QA-006 *Manual Integration.*

Multi-component pesticides are identified by pattern recognition and quantified using 3-5 major peaks. The data system calculates a calibration factor for each of the 3-5 major peaks for each calibration level using height or area. The average CF is used to calculate the concentration for each of the 3-5 major peaks, and the resulting concentrations are averaged to provided the final result in sample.

After analysis is complete, evaluate the results against the performance criteria given in Section 10.0 and Table 3, Section 18.0 and perform corrective action as necessary.

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should result in a determination within the upper half of the calibration curve.

If an initial dilution is performed based on screen data, the diluted analysis should result in a determination within the upper half of the calibration curve. A more concentrated analysis is not necessary unless the result is not within the upper half of the calibration range or when the project requires that all samples be analyzed undiluted or more concentrated regardless of screen results.

NOTE: When multiple dilutions are performed, the laboratory routinely reports the result from the appropriate diluted run (i.e. no target analyte above calibration range and the result for the analyte for which the dilution was performed is in the upper half of the calibration range). Undiluted and lesser dilutions are not routinely provided unless specifically requested by the client. For DoD work, the DoD QSM requires that the undiluted analysis or most concentrated dilution be reported along with the appropriate dilution (i.e. report multiple dilutions).

12.0 CALCULATIONS

12.1 See Appendix B.

13.0 DATA ASSESSMENT, CORRECTIVE ACTION & REPORTING

13.1 Data Review and Corrective Action

Review the samples, standards and QC samples against the acceptance criteria in Table 3, Section 18.0. If the results do not fall within the established limits, perform the recommended corrective action. If corrective action is unsuccessful, document the situation with a nonconformance report and/or qualify the data using an appropriate data qualifier (see Appendix C for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review refer to laboratory SOP LP-QA-019 *Data Review.*

13.1.1 LCS/MS/MSD/SD Evaluation

In the absence of project specific control limits, use the in-house control limits specified in Table 1A, Section 18.0 for the evaluation of the LCS, MS/MSD and sample duplicate (SD). For DoD QSM work, unless the project specifies otherwise, if the in-house limit is outside the DoD QSM limit (identified in bold text in Table 1A), evaluate the QC samples against the DoD limit and take corrective action when recovery is outside the QSM limit but report the in-house limit in the data report. If the in-house limit is within the DoD limit, use the in-house limit for evaluation and reporting.

Based on the number of analytes spiked into the LCS it is statistically likely that at least some analytes will sporadically exceed the control limit and these outages may be a marginal exceedance (ME). A ME is defined as a sporadic recovery of an analyte that is outside the established control limit but within a control limit that is + 4 SD around the mean. Sporadic outages do not require corrective action so long as the outage is random and the recovery of the analyte is within the ME limit. However, if the same

analyte consecutively recovers outside the in-house limit, the outage is no longer considered random and the ME evaluation does not apply, corrective action must be taken.

For this test method, 1 marginal exceedance is allowed based on the number of analytes (20) spiked into the LCS. In other words: if the recovery of up to 1 analyte is not within the in-house limits but the recovery of the analyte is within the ME limit, corrective action is not required unless the recovery of those same analytes were not within control limits in the LCS analyzed immediately prior to the LCS under evaluation.

To evaluate for Marginal Exceedances:

When the recovery of a spiked analyte is outside the in-house limit, calculate the ME limit as follows:

$$\text{ME (Lower Limit)} = \text{Lower Limit} - \frac{(\text{Upper Limit} - \text{Lower Limit})}{6}$$

$$\text{ME (Upper Limit)} = \text{Upper Limit} + \frac{(\text{Upper Limit} - \text{Lower Limit})}{6}$$

If the recovery is within the calculated ME limit, corrective action is not required so long as the recovery of that same compound was within limits in the previous LCS analyzed. If the recovery of the same analyte was not within limits in the previous LCS or if the recovery of the spiked compound is not within the ME limit, the recommended corrective action must be taken.

13.2 Data Reporting

Report quantitative results in appropriate units and significant figures and correct the results for sample volume, dilution factor, and percent solids. Unless otherwise specified for the project, report the higher result between the two columns. If in the analyst's judgment, the higher result is due to overlapping peaks, or interference peaks, the lower of the two results may be reported, the data qualified and the issue discussed in the project narrative. If the calculated Relative Percent Difference (RPD) between the results from each column is greater than 40%, qualify the result with a "P" data qualifier.

The laboratory's routine reporting limit (RL) for each target analyte is provided in Table 1, Section 18.0. The RL is the threshold value below which results are reported as non-detected and the RL may be project-specific or laboratory routine. In either case, report sample results that have concentrations for target analytes less than the designated RL as the RL with a "U" data qualifier. Report the results for soil samples on a dry weight basis unless otherwise specified and adjust the RL for sample dilution and/or concentration.

Some projects require the reporting of positively identified target analytes less than the RL. In this case, report results to the RL but flag all results between the limit of detection (verified MDL) and the RL with a "J" data qualifier to indicate the value is estimated.

NOTE: Unless otherwise specified for a DoD project, the DoD QSM requires the reporting of estimated values.

Some projects require RLs that are less than the laboratory's routine RL. Sample results may be reported to the project RL without qualification if the project RL is greater than the limit of quantification (LOQ). In this context, the LOQ is defined as the concentration of the low calibration standard. If the project RL is less than the LOQ, all values less than the LOQ must be reported as estimated and flagged with a "J" data qualifier.

Further guidance on the application and use of the limit of detection (LOD), limit of quantitation (LOQ) and the RL, is provided in laboratory SOP LP-QA-005.

When multiple dilutions are performed, report the result from the appropriate diluted run (i.e. no target analyte above calibration range and the result for the analyte for which the dilution was performed is in the upper half of the calibration range). Undiluted and lesser dilutions are not routinely provided unless specifically requested by the client. For DoD work, the DoD QSM requires that the undiluted analysis or most concentrated dilution be reported along with the appropriate dilution (i.e. report multiple dilutions). Additionally, whenever dilutions are performed based on screen data, the DoD requires that the screen data be provided in the data package.

13.3 Data Management and Records

All electronic and hardcopy data is managed, retained, and archived as specified in laboratory SOP LP-QA-0014 *Laboratory Records*.

14.0 METHOD PERFORMANCE

14.1 A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP–QA-005 *Procedures for the Determination of the Limit of Detection (LOD), Limit of Quantitation (LOQ) and Reporting Limit (RL).*

14.2 Each analyst must complete an initial demonstration of proficiency (DOC) before independent analysis of client samples and demonstrate repeated proficiency annually thereafter. The procedures for employee training and demonstration of proficiency are further described in laboratory SOP LP-QA-011 *Employee Training.*

14.3 The laboratory in-house control limits used to evaluate accuracy, precision and surrogate recoveries are provided in Table 1A. The control limits for accuracy are statistically derived based on compiled data and are set at 3 standard deviations around the mean using the procedures described in laboratory SOP LP-QA-013 *Control Limits.*

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

The following waste streams are produced when this method is carried out.

- Sample Extract Vials: Satellite container-: 5 gallon bucket located in fume hood.
- Solvent Waste: Satellite container-: 4 L glass bottle located in fume hood.

Transfer the waste stream to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waster storage room for future disposal in accordance with Federal, State and Local regulations. The procedures for waste management are further given in the laboratory SOP LP-LB-001 *Hazardous Waste.*

16.0 SOP REVISION HISTORY

The following changes were made in this revision:

16.1 Title Page: Updated to show current management team
16.2 Section 10.0: Changed ICV criteria to ± 20% of expected value.
16.3 Section 11.0: Added DoD QSM requirement for multiple dilution reporting and requirement to perform corrective action for DoD work, when recoveries are outside DoD QSM limits.
16.4 Section 12.0: Added DoD QSM requirement for multiple dilution reporting.
16.5 Table 1A: Updated to current Control Chart Information.
16.6 Table 2: Changed to Primary Materials Used Table
16.7 Table 3: Changed ICV criteria to ± 20% of expected value.

17.0 REFERENCES

17.1 SW-846 Method 8081A, Organochlorine Pesticides by Gas Chromatography, Test Methods for the Chemical Analysis of Water and Wastes, Revision 1, December 1996.

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1: Target Compound List, Reporting Limits
18.2 Table 1A: Routine and DoD QSM Control Limits
18.3 Table 2: Primary Materials Used
18.4 Table 4: QC Summary and Recommended Corrective Action
18.5 Appendix A: Standard Preparation Tables
18.6 Appendix B: Equations
18.7 Appendix C: Terms and Definitions

Table 1: Routine Target Compound List and Reporting Limit (RL)

Analyte	Water (ug/L)	Solid (ug/Kg)
alpha-BHC	0.05	1.7
beta-BHC	0.05	1.7
delta-BHC	0.05	1.7
gamma-BHC (Lindane)	0.05	1.7
Heptachlor	0.05	1.7
Aldrin	0.05	1.7
Heptachlor Epoxide	0.05	1.7
Endosulfan I	0.05	1.7
Dieldrin	0.10	3.3
4,4-DDE	0.10	3.3
Endrin	0.10	3.3
4,4-DDD	0.10	3.3
Endosulfan II	0.10	3.3
Endosulfan sulfate	0.10	3.3
4,4-DDT	0.10	3.3
Methoxychlor	0.50	17
Endrin ketone	0.10	3.3
Endrin aldehyde	0.10	3.3
alpha-Chlordane	0.05	1.7
gamma-Chlordane	0.05	1.7
Technical Chlordane	0.50	17
Toxaphene	5.0	170

Table 1A: Added Compound List and Reporting Limit (RL)

Analyte	Water (ug/L)	Solid (ug/Kg)
Mirex	0.10	3.3
2,4-DDE	0.10	3.3
2,4-DDD	0.10	3.3
2,4-DDT	0.10	3.3

Table 2: Routine Accuracy and Precision Limits[1]

Analyte	In-House Limits[2] (%R)		Precision (RPD)	DoD QSM Limit[3]	
	Water	Solid	(≤)	Water	Soil
alpha-BHC	70-135	**55-130**	30	25-140	60-125
beta-BHC	70-135	60-**130**	30	65-125	60-125
delta-BHC	70-135	**50-135**	30	45-135	55-130
gamma-BHC (Lindane)	70-135	55-**135**	30	25-135	60-125
Heptachlor	60-125	60-135	30	40-130	50-140
Aldrin	60-125	55-135	30	25-140	45-140
Heptachlor Epoxide	70-135	60-130	30	60-130	65-130
Endosulfan I	60-125	55-125	30	50-110	15-135
Dieldrin	70-**135**	**60-145**	30	60-130	65-125
4,4-DDE	70-135	**60-145**	30	35-140	70-125
Endrin	70-135	60-**145**	30	55-135	60-135
4,4-DDD	70-135	60-**145**	30	25-150	30-135
Endosulfan II	60-125	55-125	30	30-130	35-140
Endosulfan sulfate	70-135	**40-140**	30	55-135	60-135
4,4-DDT	70-135	60-**155**	30	45-140	45-140

Methoxychlor	75-140	65-145	30	55-150	55-145
Endrin ketone	70-135	65-**145**	30	75-125	65-135
Endrin aldehyde	70-135	**15**-110	30	55-135	35-145
alpha-Chlordane	70-135	**60-140**	30	65-125	65-120
gamma-Chlordane	70-135	**60**-140	30	60-125	65-125
Surrogates:					
Tetrachloro-m-xylene (TCMX)	55-120	**55-130**	NA	25-140	70-125
Decachlorobiphenyl (DCB)	40-130	60-**135**	NA	30-135	55-130

[1] *The limits in this table are those used as of the effective date of this SOP.*
[2] *Any limits that appear in **bold** text are those where the in-house limit is outside of the DoD QSM limit.*
[3] *Limits are taken from Appendix D of DoD QSM. If no limit listed in this table, no limit was listed in the DoD QSM.*

Table 3: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 4: QC Summary and Recommended Corrective Action

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[1]
Breakdown Check Standard	Before initial calibration and each CCV.	Degradation ≤15% for Endrin and DDT each	Correct problem, reanalyze, repeat calibration.
Initial Calibration	Before sample analysis, when calibration verification standards indicate calibration relationship is no longer valid; after major instrument maintenance	See Section 10.2	Correct problem and repeat initial calibration.
ICV	After each initial calibration	%Difference ±20% from expected value for each analyte	Correct problem and verify second source standard. If that fails, repeat initial calibration.
CCV	Daily before sample analysis, every 10 samples and at the end of the analytical sequence	% Difference ±15%	Correct problem, reanalyze CCV and all associated samples since last successful CCV.
Method Blank	One per extraction batch	< RL DoD: If analyte in sample > RL blank value ≤ ½ RL	Correct problem, re-extract and reanalyze. Examine project DQO's with PM, if there are no detects in the associated samples re-prep and reanalysis may not be required.
LCS	One per extraction batch	%R within control limits given in Table 1	Correct problem, re-extract, reanalyze along with associated samples Examine project DQO's, flag data if corrective action fails.
MS/MSD	Batch: one pair per extraction batch Client Specific: per client request	Evaluated against control limits in Table 1	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze or re-extract, if matrix effect, report data with qualifier.
Sample Duplicate	Per client request	Evaluated against RPD control limits in Table 1	Same as above.
Surrogate Spike	All field and QC samples	%R within control limits given in Table 1	Evaluate data and determine if a matrix effect or analytical error is indicated. If analytical error, re-analyze or re-extract. If matrix effect, review project DQOs to determine if a matrix effect must be confirmed by re-analysis; report data with qualifier.

[1]*The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.*

Appendix A: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in hexane using Class A volumetric glassware and Hamilton syringes. Unless otherwise specified for a standard solution, assign an expiration date of 6 months from date of preparation unless the parent standard expires sooner in which case use the earliest expiration date. See laboratory SOP LP-QA-002 *Standard Preparation* for further guidance.

INTERMEDIATE STANDARDS – in hexane

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Toxaphene	Restek #32005	1000	1.0	20	50
Technical Chlordane	Restek #32021	1000	0.40	40	10

Surrogate Solution (10 mg/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Pesticide Surrogate	Restek #3200	1000	0.40	40	10

ICV – Second Source Standard – Varied Concentrations – Stock Solution

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Pesticide Mix A	Ultra # CLP-216	5-50	1.0	10	500-5000
Pesticide Mix B	Ultra # CLP-226B	5-10	1.0	10	500-1000

Mirex (10mg/L)

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Mirex	Ultra # PST-720S	100	1.0	10	10

WORKING STANDARDS - in hexane

Column Prime Standard – Varied Concentrations

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Organochlorine Pesticide Mix AB #2	Restek #32292	8-80	1.0	20	400-4000
Surrogate	Laboratory Prepared	10	0.80		400

Breakdown Check Standard (BCS) – Varied Concentrations

Parent Standard	Vendor	Stock Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (mg/L)
Pesticide Performance Evaluation Mix	Ultra #CLP-250	10-250	0.30	30	10-250

ICV – Second Source Standard – Varied Concentrations – Working Standard

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Pesticide Mix A	Ultra # CLP-216-1	0.5-5.0	2.0	50	200-2000
Pesticide Mix B	Ultra # CLP-226B-1	0.5-1.0	2.0		

CALIBRATION STANDARDS – in hexane

INDAB-5: Pesticide Calibration Level 5 – Varied Concentrations

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Organochlorine Pesticide Mix AB #2	Restek #32292	8-80	1.0	100	80-800
Mirex Stock Standard	Laboratory Prepared	10	1.6		160
Surrogate Stock Standard	Laboratory Prepared	10	0.80		80

INDAB Calibration Standard(s): CAL Levels 1- 4 - Varied Concentrations

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
INDAB-5	INDAB-4	80-800	20	40	40-400
INDAB-5	INDAB-3	80-800	10	40	20-200
INDAB-5	INDAB-2	80-800	5.0	40	10-100
INDAB-5	INDAB-1	80-800	2.5	40	5-50

Toxaphene Working Standard - Calibration Level 5

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Toxaphene Intermediate Standard	Laboratory Prepared	50	16	100	8000
Surrogate	Laboratory Prepared	10	0.80		80

Toxaphene Calibration Standard(s): CAL Levels 1- 4

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Toxaphene Calibration Level 5	Toxaphene Level 4	8000	20	40	4000
Toxaphene Calibration Level 5	Toxaphene Level 3	8000	10	40	2000
Toxaphene Calibration Level 5	Toxaphene Level 2	8000	5.0	40	1000
Toxaphene Calibration Level 5	Toxaphene Level 1	8000	2.5	40	500

Technical Chlordane Working Standard - Calibration Level 5

Parent Standard	Vendor	Parent Standard Concentration (mg/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Technical Chlordane Intermediate Standard	Laboratory Prepared	10	8.0	100	800
Surrogate	Laboratory Prepared	10	0.80		80

Technical Chlordane Calibration Standard(s): CAL Levels 1- 4

Parent Standard	Calibration Standard	Parent Standard Concentration (ug/L)	Volume Added (mL)	Final Volume (mL)	Final Concentration (ug/L)
Technical Chlordane Calibration Level 5	Technical Chlordane Level 4	800	20	40	400
Technical Chlordane Calibration Level 5	Technical Chlordane Level 3	800	10	40	200
Technical Chlordane Calibration Level 5	Technical Chlordane Level 2	800	5.0	40	100
Technical Chlordane Calibration Level 5	Technical Chlordane Level 1	800	2.5	40	50

Final Concentration of INDAB Curve in Extract

Analyte*	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)
TCX (surrogate)	5	10	20	40	80
DCB (surrogate)	5	10	20	40	80
Alpha-BHC	5	10	20	40	80
Beta-BHC	5	10	20	40	80
Delta-BHC	5	10	20	40	80
Gamma-BHC	5	10	20	40	80
Heptachlor	5	10	20	40	80
Aldrin	5	10	20	40	80
Heptachlor Epoxide	5	10	20	40	80
Endosulfan I	5	10	20	40	80
Dieldrin	10	20	40	80	160
4-4'-DDE	10	20	40	80	160
Endrin	10	20	40	80	160
Endosulfan II	10	20	40	80	160
4-4'-DDD	10	20	40	80	160
Endosulfan Sulfate	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
Endrin Ketone	10	20	40	80	160
Endrin Aldehyde	10	20	40	80	160
gamma-chlordane	5	10	20	40	80
alpha-chlordane	5	10	20	40	80
Technical Chlordane	50	100	200	400	800
Toxaphene	500	1000	2000	4000	8000

APPENDIX B: EQUATIONS

% DDT Breakdown = $\frac{\text{Sum of peak area or height (DDE+DDD)}}{\text{Sum of peak area or height (DDE+DDD+DDT)}}$ x 100%

% Endrin Breakdown = $\frac{\text{Sum of peak area or height (Endrin aldehyde + Endrin ketone)}}{\text{Sum of peak area or height (Endrin aldehyde+Endrin ketone+Endrin)}}$ x 100%

Calibration Factor (CF_x) = $\frac{\text{Peak area or height}_{(x)}}{\text{Extract concentration}_{(ug/L)}}$

Mean Calibration Factor ($\overline{CF}$) = $\frac{\sum_{i=1}^{n} CF_i}{n}$

where: n = number of calibration levels

Standard Deviation of the Calibration Factor (SD) = $\sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}\right)2}{n-1}}$

where: n = number of calibration levels

Percent Relative Standard Deviation (RSD) of the Calibration Factor = $\frac{SD}{\overline{CF}} \times 100\%$

Percent Difference (%D) = $\frac{CF_v - \overline{CF}}{\overline{CF}} \times 100\%$

where: CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

Percent Drift = $\frac{\text{Calculated Concentration – Theoretical Concentration}}{\text{Theoretical Concentration}}$ X 100%

Percent Recovery (%R) = $\frac{C_s}{C_n} \times 100\%$

where: C_s = Concentration of the Spiked Field or QC Sample

C_n = Nominal Concentration of Spike Added

Percent Recovery (%R) for MS/MSD = $\frac{C_s - C_u}{C_n} \times 100\%$

where: C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

Relative Percent Difference (%RPD) = $\frac{C_1 - C_2}{\left(\frac{C_1 + C_2}{2}\right)} \times 100\%$

where: C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

Sample Concentration

Extract

$C_{extract}\,(ug/L) = \frac{\text{Peak Area (or Height)}}{\overline{CF}}$

Water

$C_{sample}\,(ug/L) = C_{extract}\,(ug/L) \times \frac{\text{extract volume (L)}}{\text{sample volume (L)}} \times DF$

Solids

$C_{sample}\,(ug/Kg) = C_{extract}\,(ug/L) \times \frac{\text{extract volume (L)}}{\text{sample weight (Kg)}} \times \frac{100}{\%\,\text{solids}} \times DF$

where: DF = Extract Dilution Factor. If no dilution was made, DF=1.

Appendix C: Terms & Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The EPA-defined qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration above the reporting limit.

J: Estimated Value

P: There is greater 40 % difference for detected concentrations between two GC columns

C: Postive result whose identification has been confirmed by GC/MS

B: Compound is found in the sample and the associated method blank.

E: Compound whose concentration exceeds the upper limit of the calibration range.

D: Concentration identified from a dilution analysis.

X,Y,Z: Laboratory defined flags that may be used alone or combined as needed. If used, provide a description of the flag in the project narrative.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

SOP LB-10

HOMOGENIZATIONOF BIOTA/TISSUE

Title: HOMOGENIZATION OF BIOTA/TISSUE

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1.0 Scope and Application

This SOP describes the laboratory procedure for the extraction of biota and tissue samples by tissuemizer in preparation for analysis by a variety of chromatographic procedures.

1.1 Analytes, Matrix(s), and Reporting Limits

Refer to analytical methods for analyte lists and reporting limits.

2.0 Summary of Method

2.1 Homogenization

Tissue samples are homogenized using a titanium blade homogenizer. Biota samples are homogenized using stainless steel knives. The homogenized sample(s) are transferred to labeled glass jars and stored in a freezer maintained at a temperature of -15ºC (±5ºC) in preparation for extraction.

This procedure was derived from the Comprehensive Descriptions of Trace Organic Analytical Methods given in the Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Volume IV, National Status and Trends Program for Marine Environmental Quality.

2.2 Extraction

A portion of homogenized sample is mixed with anhydrous sodium sulfate. The mixture is then macerated for 3 minutes in an appropriate extraction solvent using the Tissumizer. The solvent layer is then poured into a sodium sulfate filled funnel attached to a collection vessel. The extraction is repeated two more times with fresh portions of extraction solvent. After extraction, the combined extracts are concentrated to an appropriate final volume using K-D Technique. Percent lipids are determined following procedures given in laboratory SOP BR-EX-016 *Percent Lipid Determination* and extract cleanup is performed when necessary.

This procedure is based on method GERG Trace Organic Contaminant Analytical Techniques published in NOAA Technical Memorandum NOS Orca 71, Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Volume IV, Comprehensive Descriptions of Trace Organic Analytical Methods, July 1993.

3.0 Definitions

Biota: flora and fauna. For this SOP, all reference to “biota” refers to plant material.

Tissue: an aggregate of cells usually of a particular kind together with their intercellular substance that form one of the structural materials of a plant or animal. For this SOP, all reference to “tissue” refers to structural materials from an animal.

A list of general terms and definitions are provided in Appendix A.

4.0 Interferences

Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing equipment that can cause interference and/or elevated baselines in chromatography. All reagents and solvents used during this procedure should be reagent grade or high purity in order to minimize interference. All glassware must be cleaned in accordance with laboratory SOP BR-EX-017 *Glassware Cleaning*, and rinsed with acetone and methylene chloride prior to use.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP, and should not be used.

During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard.

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Homogenization Equipment

- Cutting Board- High density polyethylene 16X23”
- Homogenizer equipped with 55 mm Titanium Blade Omni International or equivalent.
- Food Processor Cuisinart or equivalent
- Stainless steel knives
- Glass Jars, wide mouth; 125 mL-1000 mL. ESS or equivalent.

6.2 Extraction Equipment

- Tissuemizer equipped with a 20 mm x 195 Generator probe. Omni International PowerGen 700 or equivalent.
- Filter Funnels – 100 mm diameter for filtration/drying. Fisher Scientific or equivalent.
- No. 54 Filter paper. Whatman 18.5 cm, or equivalent.
- Beakers – 400 mL. Fisher Scientific or equivalent.

6.3 Extract Concentration (KD Apparatus)

- Concentrator Tube, 10 mL Graduated: ChemGlass Catalog # CG-1316-11 or equivalent
- Snyder Column: Three ball macro, AMK Catalog # SC2-01 or equivalent
- Snyder Column: Two ball micro, AMK Catalog # SC3-01 or equivalent
- Evaporation Flask: 500 mL attached to concentrator tube with clip, AMK Catalog Number KDF-500 or equivalent.
- Boiling Chips: Silicon carbide, approximately 10/40 mesh, solvent extracted in methylene chloride, Troemner Catalog # 133B or equivalent.
- Heating Mantle: Rheostat controlled for water bath capable of temperature control (±5°C). ChemGlass Catalog # PL3122 or equivalent.
- Water Bath, capable of temperature control to ±5°C. Barnstead Corporation Catalog # HM0500-HS1 or equivalent.
- Solvent Vapor Recovery System, Kontes K-54000-1006, K-547300-000, Ace Glass Catalog # 6614-30 or equivalent.

6.4 Miscellaneous

- Disposable Glass Pasteur Pipette and bulb: Fisher Scientific or equivalent.
- Top Loading balance: Capable of measuring to 0.01 gram accuracy, Mettler Model # PM4800 or equivalent.
- Vials and caps: 2, 4, 8, and 16 mL with Teflon lined septa and screw caps, Fisher Scientific or equivalent.
- Teflon and Stainless Steel Spatulas, Fisher Scientific or equivalent.
- Adjustable Pipette: Finnpipette or equivalent
- 0.5 mL – 2.0 mL Hamilton Gastight® syringes or equivalent.
- Paper towels

7.0 Reagents and Standards

7.1 Reagents

- Sodium Sulfate (Na_2SO_4), Granular Anhydrous: J.T. Baker or equivalent. Purify by heating at 400°C for at least 4 hours.
- Methylene Chloride (CH_2C_{12}): Pesticide Quality, J.T Baker or equivalent.
- Hexane, (C_6H_{14}): Pesticide Quality, J.T. Baker or equivalent.
- Acetone, ($(CH_3)_2CO$): Pesticide Quality, J.T. Baker or equivalent.
- Reagent Water: RO water filtered through a Nanopure System.
- Alkaline Liquid Detergent: Contrex or equivalent.

7.2 Prepared Reagents

- Methylene Chloride/Acetone (1:1): In a 4 L amber glass bottle mix 2 L methylene chloride with 2 L acetone. Store the solution in a fume hood. Assign an expiration date of 6 months from date of preparation unless the parent material expires earlier, in which case, use the earliest expiration date.

- Hexane /Acetone (1:1): In a 4 L amber glass bottle mix 2 L hexane with 2 L acetone. Store the solution in a fume hood. Assign an expiration date of 6 months from date of preparation unless the parent material expires earlier, in which case, use the earliest expiration date.

7.3 Standards

Stock standards are purchased as certified solutions from commercial vendors. Surrogate and spiking solutions are prepared in the laboratory by diluting a known volume of the stock standard solutions in an appropriate solvent. The name and concentration of the surrogate and/or spike standard solution is recorded on the extraction log along with the volume used. Standard preparation is documented in logbooks designated for this purpose.

Prepared standard solutions are stored in glass containers at 4°C or below. Unless otherwise specified, prepared surrogate and LCS/matrix spike standards are assigned an expiration date of 6 months from the date of preparation or in accordance with the expiration date of the parent standard, whichever is sooner. The recommended formulation for each standard used in this procedure is provided in the analytical method along with the recommended source materials, expiration dates and storage conditions.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Tissue	Glass or Sealable Bags (Ziploc)	50g	-15°C (±5°C).	Extraction: *14 days Extraction: **6 months Analytical: 40 days	NA

[1]Extraction holding time is determined from sampling date; analytical holding time is determined from date of initiation of extraction.
* Extract within 14 days after the sample was thawed or removed from frozen storage.
** Extract within 6 months as long as the samples are frozen.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

Tissue and biota samples should be collected in glass jars or sealable bags (Ziploc). Immediately following collection, biota samples should be iced to a temperature of 4°C (±2°C) and tissue samples should be frozen and maintained at a temperature of -15°C (±5°C) until the time of homogenization. After homogenization is complete, all samples must be stored in a freezer maintained at a temperature of -15°C (±5°C).

Tissue and biota samples should be extracted within 14 days after the sample was thawed or removed from frozen storage. The remaining sample should be returned immediately to the freezer after extraction. As long as the samples are frozen, a six-month holding time will apply.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	See Analytical SOP
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Analytical SOP
Matrix Spike(s) MS/MSD	With every batch if sufficient volume is available	See Analytical SOP
Sample Duplicate (SD)	Client Request	See Analytical SOP

9.2 Instrument QC

For information regarding instrument QC refer to the analytical SOP for the determinative test method.

10.0 Procedure

10.1 Instrument Calibration

Check the calibration of the balance each day of use prior to use.

Check the calibration of the adjustable pipettes each day of use prior to use.

Perform periodic maintenance on the tissuemizer's generator probe as necessary. Maintenance may include but is not limited to the replacement of Teflon bearings and rotor shafts when a loud squealing noise is heard. Refer to the PowerGen 700 Homogenizer Instruction Manual for further guidance and for the manufacturer's recommended maintenance program.

10.2 Homogenization of Tissue Samples

Prior to use and between each sample, wash all equipment with detergent and hot water. Rinse the equipment with DI water and allow to air dry prior to use. After each sample, disassemble the blender, wash thoroughly, and rinse the homogenizer blade with reagent water, acetone and methylene chloride prior to use.

To ensure the equipment is clean, prepare an equipment blank by transferring 50 mL of reagent water to the piece of equipment that will be used for homogenization. Blend the reagent water for two minutes and transfer to a labeled glass jar for future preparation for analysis. This process should be done randomly during homogenization to verify the cleaning process.

Remove the samples from storage and allow sufficient time for them to completely thaw.

If possible, select a glass jar large enough to accommodate the entire sample. Label the jar with the sample's lab ID and place the jar on the analytical balance. Tare the balance. Put on a pair of nitrile gloves, and using your hands, remove the tissue sample from the storage container and place in the labeled jar. Record the initial weight of the sample on the bench sheet.

Remove the sample and place on a pre-cleaned cutting board. Cut the sample into 1-3" sections using a stainless steel knife (for samples designated for organic analyses) or a ceramic knife (for samples designated for metals analyses). Re-tare the balance and place the sectioned sample in the labeled jar. Insert the titanium blade into the jar and homogenize the sample at 2000-4000 RPM for 2 minutes or until the sample becomes a slurry. Manual mixing with a stainless steel or Teflon spatula (stainless steel for organic analyses and Teflon for metals) may be required to insure complete homogenization. Remove the blade from the sample jar and scrape any remaining sample from the blade into the labeled jar. Record the final weight measurement on the bench sheet.

Note: Samples that are greater than 12 inches or samples with weight measurements that exceed 1-2 pounds should be homogenized in a stainless steel meat grinder or food processor prior to blade homogenization. If the sample is very large there may be a need to perform rough homogenization using a knife prior to full homogenization. After full homogenization the entire sample shall be recombined and homogenized to create a uniform sample.

10.3 Homogenization of Biota Samples

Prior to use and between each sample, wash all equipment with detergent and hot water. Rinse the equipment with DI water and allow to air dry prior to use.

To ensure the equipment is clean, prepare an equipment blank by transferring 50 mL of reagent water to the piece of equipment that will be used for homogenization. Blend the reagent water for two minutes and transfer to a labeled glass jar for future preparation for analysis. This process should be done randomly during homogenization to verify the cleaning process.

Remove the samples from storage. Select a glass jar large enough to accommodate the entire sample. Label the jar with the sample's lab ID and place the jar on the analytical balance. Tare the balance. Remove the biota sample from the storage container and place in the labeled jar. Record the initial weight of the sample on the bench sheet.

Remove the sample and place on a pre-cleaned cutting board. Slice the material into very fine sections using a stainless steel knife or a food processor. Re-tare the balance and transfer the sample to the labeled jar. Record the final weight measurement on the bench sheet.

10.4 Extraction

Clean glassware prior to use following the procedure given in laboratory SOP BR-EX-017 *Glassware Cleaning*. Label all glassware with field and QC samples ID numbers clearly and unambiguously during each step of the extraction procedure. Solvents will erase grease pens and "sharpie ink", so caution must be taken to ensure that the labels are not obliterated during the procedure.

Assemble a KD apparatus set-up and prepare a glass funnel for each sample to be extracted. Fold a 185 mm Whatman® 54 filter into quarters and place a filter in each funnel. Fill each funnel ~3/4 full with purified granular anhydrous sodium sulfate. Rinse the funnel with ~30 mL acetone

and methylene chloride each and discard the solvent rinse. Place a prepared funnel onto each K-D setup.

Assemble the Tissuemizer by attaching the 20 mm x 195 mm-generator probe to the Tissumizer motor. Place the Tissuemizer in the fume hood and attach to the aluminum staging using clamps. Clean the Tissuemizer prior to use by running the generator probe for 10 seconds in a 400 mL beaker filled with ~ 200 mL of reagent water. Discard the reagent water and repeat with another aliquot of reagent water. Repeat the cleaning step two more times each with ~250 mL of acetone.

Mix the sample using a stainless steel or Teflon spatula. Place a labeled 400 mL beaker onto the top-loading balance and depress the "tare" button. Referring to the extraction log, weigh out the appropriate amount of sample and record sample weight to the nearest 0.01 g in the extraction log. Repeat for all samples. Transfer two additional aliquots of the sample selected for the MS and MSD into labeled 400 mL beakers. Transfer the same weight of sodium sulfate each into labeled 400 mL beakers to serve as the method blank (MB) and laboratory control sample (LCS).

Add a sufficient volume of granular sodium sulfate to each sample and mix thoroughly with a stainless steel spatula until a free-flowing mixture is formed.

Add the appropriate volume of surrogate spike to each field sample and QC sample. Add the appropriate volume of spike solution to the laboratory control samples and the MS/MSD. Refer to extraction log for details.

Add 100 mL of the appropriate extraction solvent to each beaker. Use 1:1 $MeCl_2$/Acetone for samples to be analyzed by GC/MS and 1:1 Hexane/Acetone for GC/ECD.

Immerse the generator probe in the first sample beaker so that it is approximately ½" into the extraction solvent. Turn on the Tissuemizer. Adjust the speed on the motor until the solvent begins to vortex in the beaker, but does not splash out of the beaker. Extract the sample for 3 minutes. During extraction move the beaker in a circular motion to ensure that the entire sample is subject to extraction. Remove the beaker and decant the extraction solvent into the sample's corresponding funnel and K-D apparatus. Repeat the extraction 2 more times with ~100 mL of extraction solvent. After the 3rd extraction, pour the entire contents of the beaker into the funnel, rinse the beaker with more of the extraction solvent, and pour this into the funnel as well.

Rinse the funnel with ~30 mL of extraction solvent and allow the solvent to completely drain into the K-D apparatus. Remove the funnel from the K-D apparatus and discard the contents of the funnel. Clean the generator probe and repeat the extraction for each sample.

Concentrate the extracts following the procedure given in section 10.5 in preparation for percent lipids determination and extract cleanup. After concentration and prior to extract cleanup, set aside a 1 mL aliquot of the concentrated extract and determine the percent lipids following procedures given in laboratory SOP BR-EX-016 *Percent Lipids Determination.*

Perform extract cleanup as appropriate following procedures given in laboratory SOPs BR-EX-002 *Extract Cleanup Procedure* and BR-EX-011 *Gel-Permeation Cleanup.* Refer to extraction log for details. After cleanup, concentrate the extracts following the procedure given in section 10.5.

Enter the extraction data into the Organic Extraction Module in LIMS. Assemble the extraction log and any associated paperwork and submit the extracts to the supervisor for a final project

check. After review is complete, relinquish the extracts to the appropriate analytical department and place in the refrigerated storage area.

Note: Immediately following concentration, all sample extracts must be stored in a refrigerator maintained at a temperature of 4ºC (±2°C) in order to maintain thermal preservation.

10.5 Extract Concentration (KD Apparatus)

10.5.1 Macro Concentration

Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder column to the flask. Place the concentrator tube so that it is partially immersed in a hot water and the entire lower rounded surface of the flask is bathed with hot vapor. The boiling point and recommended water bath temperatures for the extraction solvents are listed in the following table:

Solvent	Boiling Point	Water Bath Temperature
Hexane	69°C	84 – 89°C
Methylene Chloride	39.8°C	54.8 – 74.8°C
Ether	34.6°C	49.6 – 69.6°C

NOTE: Higher water bath temperatures than those given in the above table may be used for macro distillation so long as the recovery of target analytes is not impacted.

Attach the solvent vapor recovery glassware to the Snyder column of the KD apparatus following manufacturer's instructions. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with solvent. When the apparent volume reaches <10 mL, remove the KD apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

If a solvent change is required for cleanup or analysis, when the apparent volume of extract is approximately <10 mL, add ~60 mL of exchange solvent to the top of the Synder column. Continue to concentrate the extract to an apparent volume of less than <10mL. Remove the Synder column and rinse the flask and the lower joints into the concentrator tube with ~1 mL of methylene chloride or the exchange solvent. Adjust the extract to final volume. If the final extract volume should be less than 10 mL, concentrate the extract further using a micro-Synder column. Refer to the bench sheet to determine final extract volumes and whether solvent exchange is necessary.

10.5.2 Micro Concentration

Attach a two ball micro-Snyder column to the KD setup. Place the concentrator tube in the water bath so that the concentrator tube is partially immersed in a hot water bath set to the appropriate temperature based on extract solvent (See Table in Section 10.4.1) At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with solvent. Continuously monitor the distillation process to ensure sample extracts do not evaporate too quickly. When the apparent volume reaches 0.5-1.0 mL, remove the KD apparatus from the hot water bath and allow it to drain and cool for at least 10 minutes. Remove the Synder column and rinse the flask and the lower joints into the concentrator tube with 0.2 mL of methylene chloride or

the exchange solvent. Adjust to final extract volume. Refer to the bench sheet to determine final extract volumes.

10.5.3 Nitrogen Blowdown

Place the concentrator tube in a warm water bath maintained at a temperature of 35°C. Apply a steady stream of nitrogen until the desired final extract volume is achieved. Rinse the internal wall of the concentrator tube several times with the appropriate solvent during the evaporation and ensure the solvent level in the concentrator is positioned such to prevent water condensations. Monitor the concentration carefully and do not allow the extract to evaporate to dryness.

10.6 Extract Preparation & Handling

Transfer the extract to a labeled Teflon lined screw vial. If extract cleanup is not required, complete the extraction bench sheet and enter the extraction data into the Organic Extraction Module in LIMS. Assemble the paperwork and notify the department supervisor(s) that the extraction batch is ready for their review. If this review will not be performed immediately, place the extracts into refrigerated storage. When supervisory review is complete, relinquish the extracts to the appropriate analytical department.

If extract cleanup is required, complete the extraction bench sheet and place the paperwork in the location designated for work scheduling of extract cleanup procedures. If cleanup will not be performed immediately, place the extracts in refrigerated storage. Refer to SOP BR-EX-002 *Extract Cleanup Procedure* for cleanup step instructions.

11.0 Calculations / Data Reduction

11.1 Data Review

11.1.1 Primary Review

Review the bench sheet for correctness and completeness. Record any problems encountered during the extraction process on the bench sheet or complete a nonconformance report, when necessary. Set aside the extracts and paperwork for secondary review.

11.1.2 Secondary Review

Review the bench sheet against the preparation worksheet to ensure the extraction performed is consistent with project specifications. Authorize release of the extracts to the appropriate analytical department.

For additional guidance regarding the laboratory's protocol and required elements for data review refer to laboratory SOP BR-QA -019 *Data Review*.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A Method Detection Limit (MDL) Study must be determined for each test method associated with this extraction procedure during initial method set-up or prior to the analysis of field samples. The

MDLs are verified annually or after major instrument maintenance. The procedure for the determination of MDLs is described in laboratory SOP BR-QA-005 *Determination of LOD, LOQ, & RLs.*

12.2 Demonstration of Capabilities (DOC)

Each analyst must complete an Initial Demonstration of Capability prior to unsupervised performance of this method.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001 *Hazardous Waste*. The following waste streams are produced when this method is carried out.

- Organic Solvents - Satellite container: 55 gallon covered and vented drum.
- Vials containing extracts - Satellite container: 5 gallon covered bucket in fume hood.
- Methylene Chloride-Waste-Satellite Container: 55 Gallon Waste Drum
- Sulfuric Acid Waste-Satellite Container: 2.5L Waste Bottle Labeled with appropriate acid type (sulfuric).
- Solid Waste-Satellite Container: Solid Waste 5 Gallon Plastic Bucket (inside fume hood)

15.0 References / Cross-References

- Comprehensive Descriptions of Trace Organic Analytical Methods given in the Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Volume IV, National Status and Trends Program for Marine Environmental Quality.

- GERG Trace Organic Contaminant Analytical Techniques published in NOAA Technical Memorandum NOS Orca 71, Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984-1992, Volume IV, Comprehensive Descriptions of Trace Organic Analytical Methods, July 1993.

- CW-E-M-001 *Corporate Environmental Health and Safety Manual*
- BR-EX-016 *Percent Lipid Determination*

- BR-EX-017 *Glassware Cleaning*
- BR-EX-002 *Extract Cleanup Procedure*
- BR-EX-011 *Gel-Permiation Cleanup*
- BR-QA -019 *Data Review*
- BR-QA-005 *Determination of LOD, LOQ, & RLs*
- BR-EH-001 *Hazardous Waste*

16.0 Method Modifications

There are no modifications from referenced method.

17.0 Attachments

- Table 1: Primary Materials Used
- Appendix A: Terms and Definitions

18.0 Revision History

Revision 5:
- Title Page: Updated approval signatures.
- Section 6.0: Inserted vendor information
- Section 8.0: Inserted table
- Section 15.0: Added cross referenced methods with the SOP
- All Sections: Fixed typographical errors

Table 1: Primary Materials Used

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

[1] *Always add acid to water to prevent violent reactions.*
[2] *Exposure limit refers to the OSHA regulatory exposure limit.*

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Surrogate: a substance with properties that mimic the analyte of interest but that are unlikely to be found in environmental samples.

SOP LB-11

DETERMINATION OF LIMITS OF DETECTION (LOD), LIMITS OF QUANTITATION (LOQ), AND REPORTING LIMITS (RL)

Title: Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ), and Reporting Limits (RL)

Approvals (Signature/Date):

William S. Cicero — 12/27/07 Date
Laboratory Director

Kirstin L. McCracken — 12/27/07 Date
Current Department Manager

Kirstin L. McCracken — 12/27/07 Date
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Bryce E. Stearns — 12/27/07 Date
Technical Director

Bryce E. Stearns — 12/27/07 Date
Interim Health & Safety Coordinator

This cover page documents management approval for the following changes to this SOP:

- **This SOP has been renamed and was previously identified as SOP No. LP-QA-005.**
- **Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)**
- **The effective date of this SOP has been changed to January 1, 2008.**

Facility Distribution No. Electronic **Distributed To: Electronic SOP Directory**

STANDARD OPERATING PROCEDURE
STL BURLINGTON

DETERMINATION OF LIMITS OF DETECTION (LOD), LIMITS OF QUANTITATION (LOQ) AND REPORTING LIMITS (RL)

APPROVAL SIGNATURES

William S. Cicero
Laboratory Director

Date: April 26, 2007

Kirstin L. McCracken
Quality Assurance Manager

Date: April 26, 2007

Bryce E. Stearns
Technical Director

Date: April 26, 2007

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory's policy and procedure(s) for the determination of limit of detection (LOD), limit of quantitation (LOQ), and reporting limit(s) (RL) for each test method.

2.0 SUMMARY OF METHOD

2.1 General Requirements

The laboratory establishes a LOQ and RL for each test method for each analyte in each matrix (water, soil, air). An LOD is not required for test methods for which spike solutions or quality control (QC) samples are not available, such as temperature or when test results are never reported outside the range of calibration. However, some federal programs, such as the Department of Defense (DoD), require that results between the LOD and the LOQ always be reported, thus an LOD study will always be required for test methods performed for those programs. Additionally, some state programs require that an LOD be established when possible even when results are not reported outside calibration range. Lastly, other federal programs, such as CLP, specify program requirements for the LOD. In each situation, the laboratory should follow the most stringent requirement for the LOD to ensure that all programs are supported.

2.2 Limit of Detection (LOD) & Method Detection Limit (MDL).

The Limit of Detection (LOD) is an estimate of the minimum amount of substance that an analytical system can reliably detect. The LOD is initially determined for each compound of interest for each test method in each matrix during method validation and verification (initial method set-up). Once the LOD is established, the LOD is verified annually to ensure that the LOD is still appropriate and relevant to the performance of the method and its application. In the absence of regulatory or mandated method requirements, the laboratory uses method detection limit (MDL) studies to establish the LOD.

The MDL study is performed following the protocol given in 40CFR, Part 136, Appendix B, the DoD Quality System Manual (DoD QSM) and the NELAC standard or using an equivalent statistical approach that provides a detection limit relevant for the intended use of the data. Any alternate approach used must be based on specified regulatory, method or client requirements and must be approved by the laboratory's QA Manager.

An MDL verification check (MDLV) is performed with or immediately after each MDL study to verify the statistical MDL is technically sound. The MDLV samples are spiked at a concentration 2-3 times the statistical MDL for single test analytes and 1-4 times the statistical MDL for multiple analytes tests. If any of the analytes are not qualitatively identified in the MDLV, the concentration of the MDLV is increased and the MDLV analysis repeated until the analytes are qualitatively detected. The lowest detectable concentration is then used in lieu of the statistical MDL to set the verified MDL (vMDL). The verified MDL is considered the limit of detection (LOD).

When multiple instruments with identical configurations are used, the MDL study is performed on the least sensitive instrument and the attainability of the MDL is checked on each instrument with the MDL verification check sample. The LOD is set to the highest verified MDL value obtained from the set of instruments. The laboratory does not perform instrument specific MDLs unless the test method requires instrument specific MDLs.

2.3 Limit of Quantitation Limit (LOQ) and Reporting Limit (RL)

The quantitation limit (QL), is the value at which an instrument can measure an analyte at a specified level of accuracy. The quantitation limits are established by the upper and lower limits of the calibration range with the limit of quantitation (LOQ) set at the value of the lowest calibration standard. In the absence of method or other regulatory requirements for the LOQ, the LOQ is set minimally three times higher than the LOD in order to minimize the error (~±100%) associated with results near the LOD. Results reported between the LOD and the LOQ are reported as estimated values. If an LOD is not required for a test method, the LOQ should be verified, when possible.

The reporting limit (RL) is a threshold value for which the laboratory reports results as non-detected. Unless the RL is specified in the test method, such as with CLP SOW, the laboratory sets the RL to the same value as the LOQ or a value higher than the LOQ. When a project requires the RL to be below the laboratory's established LOQ but above the LOD, the laboratory will support the project RL but all results reported to the project RL will be qualified as estimated values (Data Qualifier:"UJ"). Additionally, laboratory or project RLs may never be less than the LOD.

If a project requires very low levels of quantification and data cannot be flagged as estimated due to a risk assessment or compliance issue, upon client request, the laboratory may analyze an RL check standard at the project RL needed as a way to assess the accuracy of quantitation at this level or the laboratory may modify the method as needed to meet performance criteria. Any method modifications required to achieve project RLs must be documented, approved and determined in conjunction with the client.

The procedures in this SOP are intended to meet the requirements of the NELAC Quality Systems Standard, July 2003 and the Department of Defense (DoD) Quality Systems Manual (QSM), Version 3, January 2006. The MDL study procedure is based on 40 CFR Part 136, Appendix B and supplemented by the MDLV verification procedures described in the DoD QSM and the NELAC standard.

3.0 DEFINITIONS

3.1 Limit of Detection (LOD): An estimate of the minimum amount of substance that an analytical system can be reliably detect.

3.2 Method Detection Limit (MDL): The minimum concentration of a substance (analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix

containing that analyte.

3.3 Limit of Quantitation (LOQ): The value at which an instrument can accurately measure an analyte at a specific concentration.

3.4 Reporting Limit (RL): A data value specified by the client or promulgated test method that is based on the sensitivity requirements from project specific or program required action levels.

4.0 RESPONSIBILITIES

4.1 It is the responsibility of the Department Manager (DM) to schedule, perform, and complete MDL studies in accordance with the procedures specified in this SOP. Additionally, the DM must ensure that results reported are evaluated and reported in a manner consistent with the LOD, LOQ and the established RL for each test method.

4.2 It is the responsibility of all laboratory staff to comply with the procedures given in this SOP.

4.3 It is the responsibility of the laboratory's Technical Director to ensure that any initial method development procedures include determinations for the LOD and LOQ that comply with the procedures in this SOP.

4.4 It is the responsibility of the laboratory's Project Manager(s) to ensure that any project specific RLs or any other project specification for the LOD, LOQ or RL complies with the procedures in this SOP.

5.0 SAFETY

5.1 Safety procedures are described in the test method SOPs and are not applicable to this procedure.

6.0 PROCEDURE

6.1 Reporting Limit (RL)

Unless the RL is specified in the test method, such as with CLP SOW, the laboratory routinely sets the RL to the same value as the LOQ or a value higher than the LOQ. The laboratory RL is published in each test method SOP.

A project RL may be specified by the client when the laboratory's RL does not meet project-specific requirements. Results do not need to be qualified if the project RL is set above the laboratory RL. In this instance, non-detected results are reported to the project RL. When the project RL is set below the laboratory's established LOQ, the laboratory may support the project RL but all results must be qualified as estimated values. If a project requires very low levels of quantification and data cannot be flagged as estimated due to a risk assessment or compliance issue, upon client request, the laboratory may analyze an RL check standard at the required project RL as a way to

assess the accuracy of quantitation at this level or the laboratory may modify the method as needed to meet performance criteria. Any method modifications required to achieve project RLs must be documented, approved and determined in conjunction as with the client.

Lastly, laboratory or project RLs may never be less than the established LOD.

6.2 Limit of Quantitation (LOQ) & LOQ Verification Procedure

Quantitation limits are established by the upper and lower limits of the calibration range with the LOQ set at the value of the lowest calibration standard for multi-point calibrations and no lower than the low-level calibration check sample for single point calibrations.

For all test methods with a limit of detection (LOD) and in the absence of method or other regulatory requirements for the LOQ, the laboratory sets the LOQ minimally three times higher than the LOD in order to minimize the error (~±100%) associated with results near the LOD. Results reported between the LOD and the LOQ are reported as estimated values. The on-going validity of the LOQ is verified with the LOD determination (See Section 6.3).

For test methods for which an LOD is not required because spike solutions are not available, such as temperature, the LOQ is set at a value appropriate for the use of the data.

For test methods for which an LOD is not performed because results are never reported outside the calibration range, the LOQ is verified annually and the results are maintained by the QA Department.

6.2.1 LOQ Verification Procedure

Prepare an LOQ spike solution that includes each target analyte at approximately 1-2 times the LOQ. Record the preparation of this standard in the logbook designated for this purpose.

Prepare a QC sample for each matrix and spike the sample with an appropriate volume of the LOQ spike solution. Extract, digest or analyze the sample in the same manner as used with field samples.

The percent recovery of each target analyte in the LOQ verification sample must be within the established control limits. If it is not, the LOQ verification was not successful. Troubleshoot the problem and repeat the verification process. If necessary, adjust the LOQ until the verification is successful.

Prepare an LOQ Verification Package and forward the package to the QA Department. The LOQ Verification Package must include the following information assembled in the following format:

Organics LOQ Verification Package Format

Item	Deliverable
1	Form 3 for the LOQ Sample(s)
2	Sample Preparation Log(s)
3	Instrument Run Log(s)
4	Form 5 for each Tune Standard Report(s) {GC/MS Only}
5	Form 6 for each ICAL
6	Form 7 for each CCV
7	Quantitation Report & Chromatogram(s) for ICAL, CCV, & LOQ Sample

Metals & Wet Chemistry LOQ Verification Package Format

Item	Deliverable
1	Level 4 Data Package minus DWS Report for WC

6.3 Limit of Detection (LOD)

An LOD must be determined and verified annually for each test method for which results are reported outside the calibration range and when an LOD determination is required by the test method or any applicable regulatory program, such as the DoD, state certification programs or EPA CLP SOW. An LOD determination is not required for any test method for which spike solutions are not available, such as temperature or when an LOD determination is not required by the test method, such as with CLP SOW OLC2.1.

For dual column test methods in which results may be reported from either column, the LOD will be set for the least sensitive column. For dual columns test methods in which a primary and confirmation column are assigned, the LOD is set to the value that is achieved on the primary column.

When multiple instruments with the same configuration are used to perform the same test method, the LOD is set for the least sensitive instrument and the LOD is verified on each instrument to ensure that the instrument can achieve that level of sensitivity.

As routine practice and where appropriate, the laboratory will use an MDL study determination to establish the LOD and the LOD is set to the value of the verified MDL. Alternate procedures to establish the LOD may be used with approval by the QA Manager. Any alternate procedure must be documented and verified to show that the approach used provides an LOD that is technically sound and appropriate for the intended use of the data.

6.3.1 Method Detection Limit (MDL) Study Procedure

<u>MDL Scheduling and Log-In Requirements:</u>

The Department Manager (DM) should initiate the request for an MDL study at least 45 days prior to the expiration date of the current MDL. For this purpose, the expiration date of the MDL is 365 days from the date of analysis of any replicate in the previous MDL study.

To initiate the request, the DM should submit a log-in request to the sample management supervisor. The log-in request should include the following information:

- BITLAB Test Method Code
- Matrix
- Turn Around Time (TAT). The maximum TAT for any MDL study should 28 days.

The Log-In Environmental Test Request (ETR) should be forwarded to report management and the sample preparation and analytical worksheets given to the DM who initiated the MDL request. Prior to release of the worksheets to laboratory staff, the DM must establish the MDL study design specifications. It is recommended that the DM review the previous MDL to set the appropriate spike concentrations for the MDL and the MDLV.

MDL Spike Solutions:

The MDL study must include all target analyte(s) but the formulation of multiple spike solutions may be necessary when target analytes are incompatible in the sample solution. The parent materials used to prepare the MDL spike solution may be from the same source used for instrument calibration (primary), initial calibration verification (secondary), or any other suitable standard.

The spike concentration for the MDL replicates should be based on prior experience and knowledge of the analytical system but the recommended concentration for the spike solution is ½ the value of the LOQ (concentration of the low calibration standard).

The appropriateness of the MDL spike concentration(s) is evaluated from the ratio between the statistical MDL and the mean recovered concentration. This ratio, referred to as “X” within the laboratory, should be between 1-5 for water matrices and 1-10 for other matrices.

When the calculated ratio exceeds the range given, the MDL spike concentration used was likely too high or too low, and the MDL spike concentration should be adjusted and the MDL study repeated. However- failure to meet ratio criteria does not necessarily mean that the statistical MDL is invalid due to the spike concentration and that the study should be repeated. The ratio may be difficult to achieve when the analytes exhibit good precision and accuracy at the limit of qualitative identification or when the analyte is a known poor performer. Additionally for test methods with a large number of spiked analytes it is statistically likely that some will be outside criteria. For these reasons, the “X” factor is not the sole criteria used by the laboratory to determine if the spike concentration was appropriate. The laboratory instead uses the MDL verification procedure. When the results of the MDL verification are successful and the statistical or verified MDL is adequate to support the LOQ, the laboratory will not repeat of the MDL study based on failure to meet the ratio criteria except when more than 10% of the spike analytes exceed the ratio. When greater than 10% of the spiked analytes exceed 1-5 for waters or 1-10 for soils it is likely that the spike concentrations used were not appropriate and the MDL study should be repeated (See MDL Evaluation).

MDL Preparation & Analysis:

Use reagent water to simulate the water matrix. For soils, the interference free matrix depends on the test method but reagent water may not be used. For organic test methods, use reagent sand or anhydrous granular sodium sulfate. Reagent sand may be purchased commercially (Ottawa Sand) or prepared by heating or solvent rinsing "sandbox" sand prior to use. For metals and wet chemistry methods, glass beads or Teflon chips are recommended.

Prepare the MDL spike solution at the appropriate concentration and document the preparation of this standard in the standard preparation logbook designated for this purpose.

Prepare a minimum of seven replicates and a blank. If more than seven replicates are prepared, all replicates must be included in the MDL calculation.

Add an appropriate volume of MDL spike solution to each MDL replicate. Extract and analyze the study samples using the same extraction, concentration and extract clean-up procedures normally used for field samples. Unless otherwise specified by the test method, the replicates may be extracted on the same day or over a number of days.

Analyze the samples using the same instrument conditions normally used for field samples. Unless otherwise specified by the test method, the replicates may be analyzed on the same day or over a number of days on the same instrument or on several instruments.

Acquire and process the data. Set the data system to report the analytical results to 4 significant figures.

NOTE: The MDL verification check samples may be extracted and analyzed at the same time as the MDL replicates. However, if the MDLV sample do not meet criteria for spike concentration (See MDL Spike Solutions) after the MDL study is complete, additional MDLV samples may need to be performed.

MDL Evaluation:

Review the results of the method blank. If no analyte is detected in the blank, proceed to the next step. If any analyte is detected in the method blank, review the result of each MDL replicate and the mean percent recovery for that analyte to assess for potential contamination. If contamination is evident, stop work and notify the Department Manager (DM). The DM must troubleshoot to determine if the contamination is an isolated instance or inherent background contamination. If the contamination is an isolated instance, the MDL study must be repeated after the source for contamination has been eliminated. If the analyte is a lab contaminant that frequently produces positive blank results, then the verified MDL should be elevated above the 95% upper confidence limit of the long-term blank concentration. Additionally, in order to meet DoD QSM requirements for ICB and CCB evaluation for metals analyses, the long-term blank

concentration should always be determined and the MDL adjusted as needed. The procedure for the long-term blank study is provided in Appendix A.

Import the data into the laboratory's LIMS MDL generator program and create the Statistical MDL Study Summary. The Statistical MDL Study Summary provides the following information:

- MDL Spike Concentration
- Analytical Result for each MDL Replicate
- Mean Recovered Value
- Mean Percent Recovery
- Standard Deviation
- Statistical MDL
- Reporting Limit
- Ratio of the MDL to the Mean Recovered Value ("X ")
- Test Method(s)
- Analysis Date
- Analyst(s)
- Instrument ID
- Column Description

The statistical MDL values in this report are derived using laboratory created software that calculates the replicate average and standard deviation for each analyte by the appropriate Student's $t_{0.99}$ value for the number of replicates used. An example calculation is provided in Table 2, Section 8.0 along with the Student's t values for 7-11 replicates.

The values in the Statistical MDL Summary Report adhere to the following reporting rules: The analytical result for each replicate, the mean value, and the standard deviation are reported with 4 significant figures. The MDL spike concentration is reported with 3 significant figures. The statistical MDL is reported with 2 significant figures. The "X" ratio is reported with 1 significant figure.

Print the Statistical MDL Study Summary and check the following items. If criteria are not met, perform the required corrective action.

- The analyte must be detected in each MDL replicate. If an analyte is not detected in any one of the replicates, repeat the MDL study for the analyte.

- The ratio between the calculated MDL and the mean recovered concentration ("X") should be between 1-5 for waters and 1-10 for other matrices. If there are exceptions, count the number of analytes spiked against the number of exceptions. Up to 10% of the spiked analytes may exceed the ratio criteria. If greater than 10% of analytes exceed criteria, repeat the MDL study with adjusted spike concentrations. Stop work and see the Department Manger, QA Manager or the Technical Director for further guidance.

- Evaluate each analyte for outliers or obvious error. A replicate result may be

identified as an outlier only with verification by a statistical test such as the Grubbs Test or when there is obvious and observed error such as a spike or data transfer error, otherwise the data point must be included in the calculation. Since a minimum of seven replicates is required to calculate the MDL, removal of an MDL replicate that would result in less than seven replicates is not allowed. If you suspect an outlier, consult with the QA Manager for further instruction. The reason for rejecting any data point must be clearly documented in the MDL study.

- For metals, the statistical MDL should be less than the established IDL. If it is not, note the exception and consult with the DM for further guidance.

- Compare the list of analytes included in the MDL study against the test method SOP to ensure that an MDL was performed for every analyte. If any analyte is missing, stop work and initiate an MDL study for those analyte(s).

6.3.2 MDL Verification (MDLV) Procedure

Prepare the MDLV spike solution at the appropriate concentration for each target analyte. Document the preparation of this solution in the logbook designated for this purpose. The spike concentration of the MDLV for single test analytes should be between 2-3 times the statistical MDL. For multi-analyte tests, the spike solution should be ~2 times the statistical MDL for each analyte, but this can not always be achieved due to multi-component spike solutions so for multi-analyte tests the MDLV spike solution should be between the between 1-4 times the statistical MDL for each analyte. The spike concentration of the MDLV should never be less than the statistical MDL and when this occurs, the MDLV must be repeated at a higher concentration.

Analyze the MDLV samples on the same instrument(s) used to analyze the MDL replicates and on each instrument used for the test method.

Acquire and process the data. Set the data system to report the analytical results to 4 significant figures. The target analyte must be qualitatively identified in the MDLV samples in order for the MDLV to be successful. Qualitative identification for GC/MS includes existence of the characteristic primary ion and a response at least 3 times above the instrument's noise level. For GC, qualitative identification includes pattern recognition for multi-component analytes, second column confirmation, or an instrument response at least 3 times above the instrument's noise level. For metals, qualitative identification includes a response above the IDL and for wet chemistry methods qualitative identification includes a response above the statistical MDL. For all test methods, the analytical result of the MDLV must be above the statistical MDL.

Import the data into the LIMS MDL generator program and generate a Method Detection Limit Verification (MDLV) Study Summary for each MDLV sample analyzed for each instrument on which the MDLV samples were analyzed and generate the MDL Verification Study Summary Report.

The software used to generate the MDL Verification Study Report pulls into the report the results of each MDLV sample analyzed on each instrument and calculates the ratio

between the MDLV spike concentration and the statistical MDL and sets the verified MDL value (vMDL) using the following logic:

- If the ratio of the MDLV spike concentration to the statistical MDL for any one of the MDLV samples analyzed is within 2-3 times the statistical MDL for single-analyte tests and 1-4 times the statistical MDL for multi-analyte tests and if the analyte has been qualitatively identified in one of those MDLV samples and the analytical result of the analyte in that MDLV is greater than the statistical MDL, the MDL verification is considered successful and the LOD is set to the value of the statistical MDL.

- When the ratio of the MDLV spike concentration to the statistical MDL exceeds 3 for single-analyte tests and 4 for multi-analyte tests, the verified MDL is raised to the concentration of the MDLV sample.

- If the ratio of the MDLV spike concentration to the statistical MDL is less than 1, the verification procedure was not successful and the MDLV must be repeated at a higher spike concentration.

Print the MDL Verification Study Summary and check the following items. If criteria are not met, perform corrective action.

- The analyte must be qualitatively identified in at least one of the MDLV samples analyzed. If this criterion is not met, repeat the MDLV at successively higher concentrations until the analyte is qualitatively identified.

- The MDLV spike to MDL ratio is greater than 1 for each analyte in at least one of the MDLV samples analyzed. If this criterion is not met, prepare and analyze additional MDLV sample(s) spiked at a higher concentration until the required ratio is met.

- The MDLV spike concentration to statistical MDL ratio does not exceed 3 for single-analyte tests and 4 for multi-analytes tests in at least one of the MDLV samples analyzed for which the target analyte was qualitatively detected. If this criterion is not met, prepare and analyze an additional MDLV sample(s) at a lower concentration unless the spike concentration of the MDLV analyzed reflects the lowest detectable concentration for that analyte or if the raised MDL is adequate to support the existing LOQ.

6.3.3 MDL Study & MDLV Verification Package

When the MDL study is complete for all target analytes, assemble the Verified MDL Study package in the format specified for your section and forward the complete packet to the QA department. A complete MDL study is one in which all criteria are met for every analyte performed using the test method and the MDL verification procedures are complete on each instrument used for the test method. If criteria are not met for any analyte, provide a written summary of technical justification for each exception taken with the MDL study package.

Organics Verified MDL Study Package

Item	Deliverable
1	Technical Justification Write-Up (for all criteria exceptions)
2	MDL Verification Summary Report
3	MDL Verification Study Summaries in Alpha Order
4	Statistical MDL Summary Report
5	Analytical Worksheets
6	Sample Preparation Log(s)
7	Instrument Run Logs(s)
8	Tune Standard Reports (GC/MS Only)
9	ICAL Summary Report
10	CCV Summary Reports
11	Quantitation Report & Chromatogram for blank & each MDL replicate
12	Quantiation Report, Chromatogram and Spectra (GC/MS) for each MDLV

Metals Verified MDL Study Package

Item	Deliverable
1	Technical Justification Write-Up (for all criteria exceptions)
2	MDL Verification Summary Report
3	MDL Verification Study Summaries in Alpha Order
4	Statistical MDL Summary Report
5	Analytical Worksheets
6	Level 4 Data Package (Raw Data)

Wet Chemistry Verified MDL Study Package

Item	Deliverable
1	Technical Justification Write-Up (for all criteria exceptions)
2	MDL Verification Summary Report
3	MDL Verification Study Summaries in Alpha Order
4	Statistical MDL Summary Report
5	Analytical Worksheets
6	Level 4 Data Package minus DWS Report

6.3.4 QA Review & Approval of Verified MDL

Generate the Verified MDL Summary Report from the LIMS program and confirm that the verified MDL (LOD) to quantitation limit (QL) for each target analyte meets the following criteria:

- In the absence of mandated method or other program requirements, the LOD must be minimally 3 times less than the LOQ. If this criterion is not met, either the MDL study must be repeated to achieve a lower limit of detection or the LOQ must be raised to minimally 3 times higher than the LOQ.
- For CLP SOM01.1: The verified MDL (LOD) must be less than the contract required quantiation limit (CRQL).

- For Drinking Water: The verified MDL must meet the required detection limits given

in 40CFR Part 141 and/or the EPA Office of Water Manual for the Certification of Laboratories Analyzing Drinking Water.

When any of the above criteria are not met, consult with the Department Manager and the Technical Director to determine next steps. Corrective actions may include but are not limited to raising the LOQ as needed, method development to improve method performance, repetition of the MDL study if it is believed the MDL is biased high or the study specifications were incorrect.

In any instance where the LOQ is changed, make arrangements with the DM to update the SOP as needed.

When the MDL study is complete and criteria are met, approve the MDL study, scan the MDL Report to PDF and post the MDL Report to a central directory located on a server accessible to all employees. After approval, forward the hardcopy package to report management for archival.

7.0 REFERENCES

7.1 Title 40, Code of Federal Regulations Part 136, Appendix B. USEPA

7.2 Quality System Manual for Environmental Laboratories, DoD Environmental Data Quality Workgroup, Department of Navy, Version 3, January 2006.

7.3 Chapter 5, Constitution, Bylaws, and Standards, NELAC, Current Version.

7.4 Chemical Engineers Handbook, 4th Edition, Perry, Chilton, and Kirkpatrick, 1963

7.5 STL Corporate SOP S-Q-003 Method Detection Limit Studies, Current Version.

8.0 REVISION HISTORY

8.1 Title Page: Updated to current management structure

8.2 All Sections: The entire SOP was re-written to incorporate use of the terms LOD & LOQ.

8.3 Section 6.3.1: Procedures for the evaluation of the method blank and long-term blank monitoring were added.

8.4 Section 6.3.1, 6.3.2 & 6.3.4. Detailed instructions for corrective action were added.

8.5 Appendix A: Procedure for determination of long-term blank concentration was added.

9.0 TABLES, DIAGRAMS & FLOWCHARTS

9.1 Table 1:Student's $t_{0.99}$ Values & Example MDL Calculation

9.2 Appendix A: Long-Term Blank Study Procedure

Table 1: Student't $t_{0.99}$ Values

Number of Aliquots (n)	Degrees of Freedom (n-1)	$t_{0.99}$*
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764

***** Students t –value for n-1 degrees of freedom taken from the "Chemical Engineers Handbook", 4th Edition, Perry, Chilton, and Kirkpatrick, 1963 and 40CFR Part 136, Appendix B, Revision 1.11.

Example MDL Calculation

Seven replicates of reagent water are spiked with an MDL solution at a concentration of 0.20mg/L. The results from analysis are:

Replicate	Concentration (mg/L)
1	0.1694
2	0.1476
3	0.1953
4	0.1804
5	0.2037
6	0.1871
7	0.1708

Calculate the average result= 0.1792
Calculate the standard deviation=0.01866
Multiply the standard deviation by the Student's t value for the number of replicates performed= 0.01866 X 3.143=0.059mg/L

Appendix A: Long-Term Blank Concentration

Pool at least 6 months of blank data and generate a graph that shows the concentration of the blank plotted over the 6 month time-frame. Calculate the mean concentration (m) and the standard deviation (s). Determine the 95% upper confidence limit using the following equation:

$95\%UCL = m + (t \otimes s)$ t = the student's t value

Student's t, Single-tail, 95% Upper Confidence Limit

Number of Replicates	Degress of Freedon (n-1)	Students t value
21	20	1.725
31	30	1.697
41	40	1.684
51	50	1.676
61	60	1.671
71	70	1.667
81	80	1.664
91	90	1.662
101	100	1.660
121	120	1.658
∞	∞	1.645

Example: An MDL study was performed for aluminum on each of 4 instruments and the following MDLs were obtained.

Instrument	MDL (ug/L)
1	10.9
2	6.5
3	4.4
4	0.71

Using these results, the laboratory would set the LOD to the highest verified MDL for the instrument set, in this example, 10.9 ug/L. To determine if this value was above the long-term blank concentration,

6 months of blank data (62 points) from the instruments above were plotted over a time period of May-November 2006. The calculated mean is 0.005922 mg/L, the standard deviation is 0.00444 mg/L and the student's t value for this number of points is 1.671. Using the calculation above the 95% UCL calculates to 0.0133 mg/L, which equals 13 ug/L.

The long-term blank is greater than the verified MDL, 10.9 ug/L, thus the LOD should be raised to 13 ug/L.

APPENDIX B

QUALITY ASSURANCE PROJECT PLAN (QAPP)

APPENDIX B
QUALITY ASSURANCE PROJECT PLAN

Based on the Intergovernmental Data Quality Task Force
Uniform Federal Policy for Quality Assurance Project Plans

September 2008

TABLE OF CONTENTS

QAPP Worksheet #1
(UFP-QAPP Manual Section 2.1)
Title and Approval Page

Site Name/Project Name: Onondaga Lake Baseline Monitoring
Site Location: Syracuse, New York

Title: Book 2 – Fish and Invertebrate Sampling for 2008
Revision Number: 2
Revision Date: September 5, 2008

Quality Assurance Project Plan, Book 2 – Fish and Invertebrate Sampling
Document Title

Parsons
Lead Organization

Margaret H. Murphy Quantitative Environmental Analysis, LLC (QEA)
Preparer's Name and Organizational Affiliation

290 Elwood Davis Road, Suite 215 Liverpool, NY 315 453 9009 mmurphy@qeallc.com
Preparer's Address, Telephone Number, and E-mail Address

July 2, 2008
Preparation Date (Day/Month/Year)

Investigative Organization's Project Manager: _____
Signature

_____
Printed Name/Organization/Date

Project QA Officer: _____
Signature
Maryanne Kosciewicz, Parsons

Lead Organization's Project Manager: _____
Signature

Ed Glaza, Parsons
Printed Name/Organization/Date

Approval Signatures: _____
Signature

_____
Printed Name/Title/Date

_____
Approval Authority

QAPP Worksheet #2
(UFP-QAPP Manual Section 2.2.4)
QAPP Identifying Information

Site Name/Project Name: Onondaga Lake Baseline Monitoring
Site Location: Syracuse, New York
Operable Unit: N/A
Contractor Name: QEA, Exponent, and Parsons
Contractor Number: N/A
Contract Title: N/A
Work Assignment Number: N/A

Title: Book 2 – Fish Invertebrate and Littoral Water Monitoring for 2008
Revision Number: 1
Revision Date: September 5, 2008

1. Identify guidance used to prepare QAPP:
Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) Manual (505-B-04-900A) (Version 1)

2. Identify regulatory program: CERCLA

3. Identify approval entity: New York State Department of Environmental Conservation (NYSDEC) and U.S. EPA Region 2

4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one)

5. List dates of scoping sessions that were held:

June 6, 2007, October 25, 2007, and January 17, 2008

6. List dates and titles of QAPP documents written for previous site work, if applicable:

Title	Approval Date
2007 Onondaga Lake Nitrate Evaluation QAPP	February 11, 2008

7. List organizational partners (stakeholders) and connection with lead organization:
NYSDEC, Earth Tech (consultant to NYSDEC), USEPA, Honeywell, Parsons (consultant to Honeywell), Exponent (consultant to Parsons/Honeywell) and SU (consultant to Honeywell), and UFI (consultants to SU/Honeywell)

8. List data users: Exponent, Parsons, NYSDEC, U.S. EPA, EarthTech, Honeywell

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below.

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	QAPP Worksheet #1
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	QAPP Worksheet #2
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	QAPP Worksheet #3 & #4
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	QAPP Worksheet #5, #6, #7 & #8
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	QAPP Worksheet #9 & #10
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	QAPP Worksheet #11 & #12
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	QAPP Worksheet #13

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	QAPP Worksheet #14, #15, & #16
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/ SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	QAPP Worksheet #17, #18, #19, #20, #21, & #22 and SOPs in Appendix A
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	QAPP Worksheet #23, #24, #25 and SOPs in Appendix A
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	QAPP Worksheet #19, #26, #27 and SOPs in Appendix A

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Related Documents
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	QAPP Worksheet #28
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	QAPP Worksheet #29, #30
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4.2 QA Management Reports	- QA Management Reports Table	QAPP Worksheet #33
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5.1 Overview		
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5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		

Distribution List

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Ed Glaza	Project Manager	Parsons	315-451-9560	315-451-9570	edward.glaza@ parsons.com	
Betsy Henry	Technical Oversight	Exponent	518-370-5132	518-381-4115	henryb@exponent.com	
Margaret H. Murphy	Program Oversight	QEA	315-453-9009	315-453-9010	mmurphy@qeallc.com	
John McAuliffe	Project Manager	Honeywell	315-431-4443	315-431-4777	john.mcauliffe@ honeywell.com	
Tim Larson	Project Manager	NYSDEC	518-402-9767	518-402-9020	tjlarson@gw.dec.state.ny.us	
Robert Nunes	Project Manager	U.S. EPA Region 2	212-637-4254	212-637-3966	nunes.robert@epa.gov	
Neil Ringler	Field Staff Oversight	SUNY-ESF	315-470-6609	315-470-6779	neilringler@esf.edu	
Joe Mastriano	Field Staff Oversight	OCDWEP	315-435-2260	315-435-5023	joemastriano@ongov.net	
Kirk Young	Project Manager	Test America	802-923-1017	802-660-1919	kirk.young@testamericainc.com	

Organization: QEA

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Margaret H. Murphy	Program Oversight	315-453-9009		

Organization: Parsons

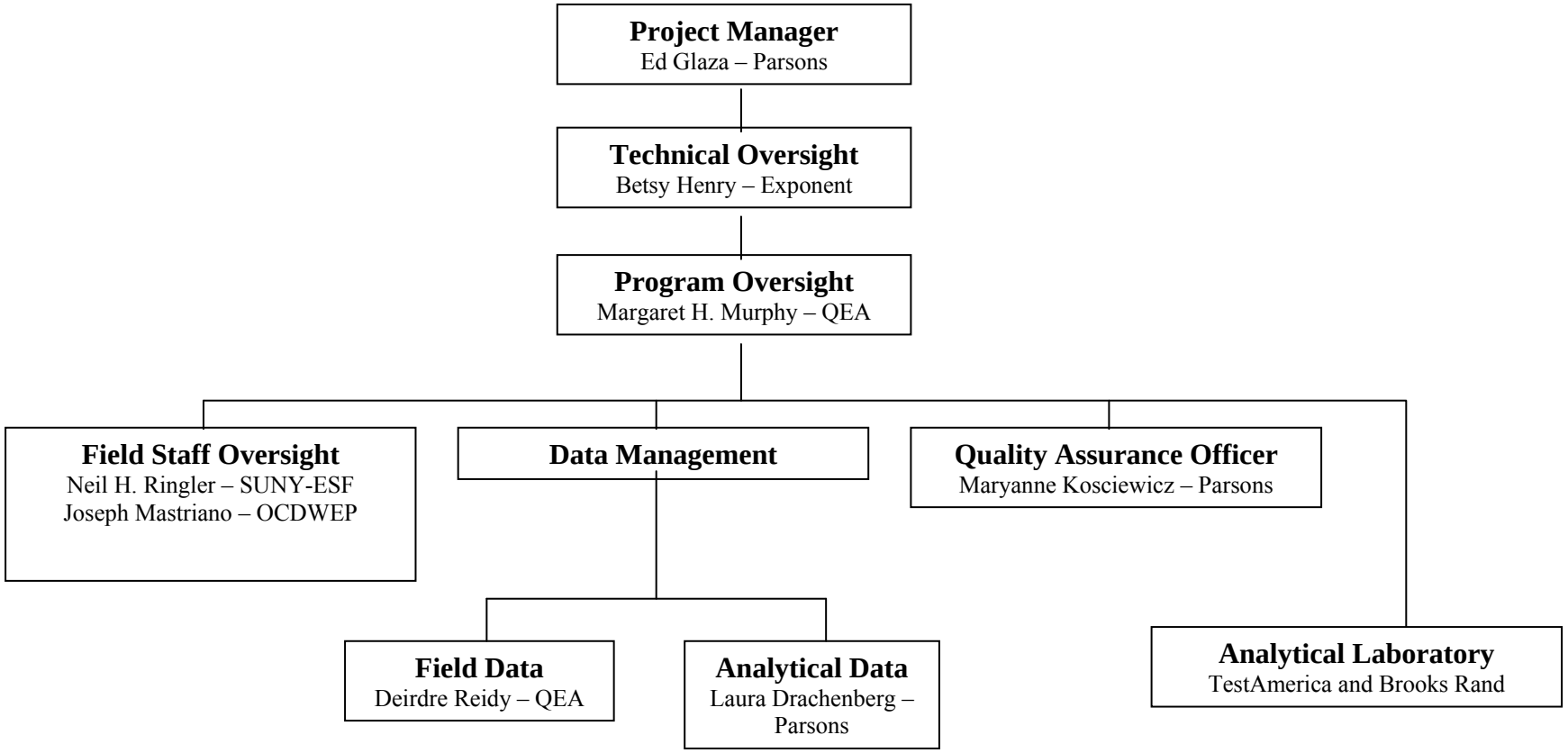
Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Maryanne Kosciewicz	Quality Assurance Officer	315-451-9560		

Organization: TestAmerica

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Kirk Young	Lab Project Manager	802-923-1017		
Kirstin McCracken	Lab Quality Assurance Officer	802-923-1019		
William Cicero	Lab Director	802-923-1014		

Organization: Brooks Rand Labs

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Michelle Briscoe	VP of Analytical Services, Laboratory Director	206-632-6206		
Misty Kennard-Mayer	Project Manager	206-632-6206		
Frank McFarland	Quality Assurance Manager	206-632-6206		


Project Manager
Ed Glaza – Parsons
Technical Oversight
Betsy Henry – Exponent
Program Oversight
Margaret H. Murphy – QEA
Field Staff Oversight
Neil H. Ringler – SUNY-ESF
Joseph Mastriano – OCDWEP
Data Management
Quality Assurance Officer
Maryanne Kosciewicz – Parsons
Field Data
Deirdre Reidy – QEA
Analytical Data
Laura Drachenberg – Parsons
Analytical Laboratory
TestAmerica and Brooks Rand

Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Point of contact with data users	Lead Organization and Project Manager	Ed Glaza	315-451-9560	All materials and information about the project will be forwarded to the data users by Ed Glaza or his designee.
Manage all project phases	Lead Organization and Project Manager	Ed Glaza	315-451-9560	Ed Glaza will be the liaison with data users.
Manage field collection	Program Oversight Manager	Margaret H. Murphy	315-453-9009 ext. 29	Notify Ed Glaza of field-related problems by phone, email, or fax by COB the next business day.
QAPP changes in the field	Program Oversight Manager	Margaret H. Murphy	315-453-9009 ext. 29	Notify Maryanne Kosciewicz by phone or email of changes to QAPP made in the field and the reasons within one business day. Any major changes to the QAPP must be approved by Maryanne Kosciewicz.
Daily field progress reports	Field Team Leader	Neil Ringler Joseph Mastriano	315-470-6609 315-435-2260	Notify Margaret Murphy of any problems or issues.
Field corrective actions	Program Oversight Manager/Quality Assurance Officer	Margaret H. Murphy	315-453-9009	The need for corrective action for field issues will be determined by Margaret Murphy.
Reporting lab data quality issues to Parsons	Laboratory Project Manager – TestAmerica	Kirk Young	802-923-1017	Notify Kirk Young when problems occur, report data and supporting quality assurance information as specified in this QAPP.
Laboratory analytical corrective actions	Laboratory Quality Assurance Manager – TestAmerica	Kirstin McCracken	802-923-1019	The need for corrective action for TestAmerica analytical issues will be determined by the Project Manager and the Quality Assurance Manager.
Release of laboratory analytical data to Parsons	Laboratory Project Manager – TestAmerica	Kirk Young	802-923-1017	No laboratory analytical data can be released until Kirk Young has approved the release.

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Reporting lab data quality issues to Parsons	Laboratory Quality Assurance Lead – Brooks Rand	Frank McFarland	206-632-6206	Notify Misty Kennard-Mayer when problems occur, report data and supporting quality assurance information as specified in this QAPP.
Laboratory analytical corrective actions	Laboratory Quality Assurance Officer – Brooks Rand	Frank McFarland	206-632-6206	The need for corrective action for Brooks Rand analytical issues will be determined by Frank McFarland
Release of laboratory analytical data to Parsons	Laboratory Quality Assurance Officer – Brooks Rand	Frank McFarland	206-632-6206	No laboratory analytical data can be released until validation is completed and Frank McFarland has approved the release.
Release of laboratory analytical data to project team	Parsons Quality Assurance Officer	Maryanne Kosciewicz	315-451-9560	No laboratory analytical data can be released until Maryanne Kosciewicz has approved the release.
QAPP amendments	Parsons Quality Assurance Officer	Maryanne Kosciewicz	315-451-9560	Any major changes to the QAPP must be approved by Maryanne Kosciewicz before changes can be implemented.

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Margaret H. Murphy	Program Oversight Manager	QEA, LLC	Oversight of daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues, and oversight of field progress. Authorize and document minor adjustments to the field program in response to changing field conditions.	Ph.D Fisheries Biology/Aquatic Ecology, 15 years experience
Neil H. Ringler	Field Staff Coordination	SUNY-ESF	Coordinate and supervise SUNY-ESF field activities; ensure that field procedures are completed in accordance with the work plan and QAPP.	Ph.D Fisheries Biology, 33 years experience
Joseph Mastriano	Field Staff Coordination	OCDWEP	Coordinate and supervise OCDWEP field activities; ensure that field procedures are completed in accordance with the work plan and QAPP.	30 years experience
Maryanne Kosciewicz	Quality Assurance Officer	Parsons	Provide technical quality assurance assistance, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required, supervise data validation. Maintain the official, approved QAPP.	B.S. Mathematics and Chemistry, 19 years experience

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
William Cicero	Laboratory Director	TestAmerica	Oversee all TestAmerica's laboratory personnel at the Burlington facility, the activities, equipment, and records; track submittal and receipt of samples to the laboratory; retain all chain-of-custody records; ensure that samples receipt and custody records are properly handled and data are reported within the specified turnaround times. Ensure that laboratory staff maintain and calibrate instruments as necessary, perform internal quality control measures and analytical methods as required, take appropriate corrective actions as necessary, notify QA/QC officer when problems occur, and report data and supporting quality assurance information as specified in this QAPP.	B.S. in Biology, 15 years experience
Kirk Young	Laboratory Project Manager	TestAmerica	Primary point of contact for TestAmerica, Burlington. Oversee daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues; oversee field and laboratory progress; deliver data to project participants; organize and maintain project database. Authorize and document minor adjustments to the field/laboratory program in response to changing field conditions.	B.S. in Civil Engineering, 34 years experience

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Kirstin McCracken	Quality Assurance Officer	TestAmerica	Provide technical quality assurance assistance, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required. Maintain the official, approved QAPP.	B.A. in Geography, 13 years of experience
Michelle Briscoe	VP of Analytical Services, Laboratory Director	Brooks Rand	Oversee all Brooks Rand laboratory personnel, activities, equipment, and records; track submittal and receipt of samples to the laboratory; retain all chain-of-custody records; ensure that samples receipt and custody records are properly handled and data are reported within the specified turnaround times. Ensure that laboratory staff maintain and calibrate instruments as necessary, perform internal quality control measures and analytical methods as required, take appropriate corrective actions as necessary, notify QA/QC officer when problems occur, and report data and supporting quality assurance information as specified in this QAPP.	B.S. in Chemistry and Physics; 16 years environmental laboratory experience; 13 years trace metals specialty laboratory experience (including 9 years in management positions).
Misty Kennard-Mayer	Client Services Manager, Project Manager	Brooks Rand	Oversee daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues; oversee field and laboratory progress; deliver data to project participants; organize and maintain project database. Authorize and document minor adjustments to the field/laboratory program in response to changing field conditions.	B.S. in Environmental Science 7 years project management in trace level analytical chemistry 1000 hours in sample collection of groundwater, freshwater, and surface and sub-surface soil samples

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Frank McFarland	Quality Assurance Manager	Brooks Rand	Provide technical quality assurance assistance, develop and review QAPP, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required, supervise data validation.	B.S. in Ecology; 13 years environmental laboratory experience; 10 years laboratory quality assurance experience (including 7 years in management positions).

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates[1]
Water sampling for low-level mercury analysis	Clean hands – dirty hands sampling protocol	Margaret Murphy	Prior to water sampling	Field staff	QEA	QEA

[1]If training records and/or certificates are on file elsewhere, document their location in this column. If training records and/or certificates do not exist or are not available, then this should be noted.

Project Name Onondaga Lake Baseline Monitoring Projected Date(s) of Sampling May to November, 2008 annually Project Manager_Ed Glaza, Parsons	Site Name Onondaga Lake Site Location Syracuse, NY

Date of Session: several (see comments below)
Scoping Session Purpose: to discuss baseline monitoring needs

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Margaret H. Murphy	Scientist	QEA	315-453-9009	mmurphy@qeallc.com	Technical Support to Honeywell
Mark LaRue	Scientist	QEA	315-453-9009	mlarue@qeallc.com	Technical Support to Honeywell
John McAuliffe	Project Manager	Honeywell	315-431-4443	John.mcauliffe@ honeywell.com	Overall Project Manager
Betsy Henry	Technical Oversight	Exponent	518-370-5132	henryb@ exponent.com	Technical support to Honeywell
Ed Glaza	Project Manager	Parsons	315-451-9560	edward.glaza@ parsons.com	Technical support to Honeywell
Tim Larson	Project Manager	NYSDEC	518-402-9767	tjlarson@ gw.dec.state.ny.us	NYSDEC Project Manager
Robert Montione	Senior Scientist	Earth Tech	518-951-2226	robert.montione@ earthtech.com	Technical support to NYSDEC
Michael Spera	Senior Project Director	Earth Tech	212-798-8577	michael.spera@ earthtech.com	Technical support to NYSDEC

Comments/Decisions: The Baseline and Long-Term Monitoring Technical Work Group met on June 6 and October 25, 2007 and on January 17, 2008 to discuss baseline monitoring needs. Participants varied, but included representatives from Syracuse University, Upstate Freshwater Institute, Exponent, Parsons, NYSDEC, USEPA, EarthTech, and USFWS. Minutes of these meetings are on file. Margaret Murphy presented the work scope to NYSDEC by conference call on April 23, 2008.

Action Items: Revised and finalized work plan to address NYSDEC's May 16, 2008 and June 27, 2008 comments on the draft Book 2 Work Plan.

Consensus Decisions: _____

_____

Problem Definition and Background

The purpose and background for the remediation of the Onondaga Lake Bottom Subsite are summarized in the ROD (NYSDEC and USEPA, 2005) and presented in detail in the Feasibility Study Report (Parsons, 2004).

The overall goal of baseline monitoring is to document the condition of the lake prior to remedial action. This monitoring will permit evaluation of changes that result from remedial action and verification of remedy effectiveness in achieving the remedial action objectives and preliminary remedial goals. As described in the Baseline Monitoring Scoping Document (Parsons 2008), the Baseline Monitoring Program for Onondaga Lake has three program objectives:

- Establish a comprehensive description of baseline chemical and physical conditions prior to remediation to assess remedy effectiveness and to facilitate remedy design;
- Provide additional data for future understanding of remedy effectiveness in achieving preliminary remediation goals (PRGs); and
- Provide habitat-related information.

Specific objectives for the biota baseline monitoring include:

- Provide basis to measure achievement of PRG 2 (fish tissue target concentrations); and
- Assess biological factors that may contribute to variability in fish mercury concentrations.

Project Description

The monitoring program described in this QAPP was developed to establish baseline chemical concentrations in fish and invertebrates, and provide a basis to measure achievement of fish tissue target concentrations (PRG 2). The primary task will be to collect sport fish fillets (and tissue plugs) and whole body composites of prey fish to assess human health and ecological exposure. In addition, the monitoring program will include an assessment of biological factors that contribute to variability in fish mercury concentrations to assist in understanding the future effectiveness of the remedy in achieving fish tissue target concentrations. Toward this end, benthic macroinvertebrates and zebra mussels will be collected for mercury concentration and community analysis and phytophilous macroinvertebrates will be collected for community analysis. Sediment and littoral water will also be sampled for mercury analysis to assess exposure. Finally, baseline biota monitoring will include analysis of the food web and an assessment of fish population and community composition. See Figures 1 and 2 in the Book 2 work plan for fish and invertebrate sampling locations, respectively. Collection and analysis of zooplankton is described in Book 1 (UFI and SU, 2008).

UFI and SU. 2008. Onondaga Lake Baseline Monitoring Book 1: Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell, Morristown, NJ. Upstate Freshwater Institute and Syracuse University, Syracuse, NY.

Who will use the data?
Data collected through the Biota Baseline Monitoring Program will be used by the Baseline/Long-Term Monitoring Technical Working Group, NYSDEC, USEPA, and OCDWEP.

What will the data be used for?
The primary data uses for biota monitoring are:

- to provide a basis to measure achievement of PRG2 (fish tissue concentrations); and
- to assess biological factors that may contribute to variability in fish mercury concentrations.

What type of data are needed?
Biota monitoring includes fish and invertebrate samples collected for laboratory analysis and measurements made for community assessments. The target analytes for laboratory analysis of tissue are as follows:

- Total mercury (USEPA Method 7471A)
- Methylmercury (invertebrates only)
- Polychlorinated biphenyls (PCBs) (Aroclors) (subset of adult sport fish and prey fish only)
- DDT and metabolites (subset of adult sport fish and prey fish only)
- Hexachlorobenzene (subset of adult sport fish and prey fish only)
- Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs) (subset of adult sport fish only)
- Lipid content (subset of adult sport fish and prey fish only).

Additional parameters measured on fish include:

- Age
- Sex
- Weight (in grams)
- Total length (in mm).

Benthic invertebrates will consist of a composite sample and the entire sample will be weighed to the nearest 0.1 gram. If sample mass is limited, sample will be analyzed for methylmercury only.
Additional parameters measured on zebra mussels include:

- Weight (in 0.1 grams)
- Shell length (in mm).

The target analytes for laboratory analysis of sediment are as follows:

- Total mercury
- Methylmercury
- Total organic carbon.

The target analytes for laboratory analysis of water are as follows:

- Total mercury
- Methylmercury.

Field measurements for water quality will also be made for:

- Temperature
- Dissolved oxygen
- Conductivity
- pH.

Concentration levels (i.e., project action and quantitation limits, analytical and achievable laboratory method detection and quantitation limits) for the laboratory analytes are documented in Worksheet #15, field sampling techniques are referenced in Worksheet #21, and laboratory analytical techniques are referenced in Worksheet #23.

How "good" do the data need to be in order to support the environmental decision?
The data must support a long-term trend analysis for chemical concentrations in fish and invertebrates. The key analytes in terms of decision-making are total mercury and methylmercury. All analytes will be subject to Level III validation as described in the Pre-Design Investigation QAPP (Parsons 2005) and procedures described in Worksheet #36. In addition, ten percent of the total mercury, methylmercury, PCBs, DDT and metabolites, hexachlorobenzene, and PCDD/PCDF data will be validated based on Level IV protocols as described in Worksheet #36.

How much data are needed? (number of samples for each analytical group, matrix, and concentration)
See Worksheet #18

Where, when, and how should the data be collected/generated?
Samples for chemical analyses will be collected from Onondaga Lake from August through November using field sampling techniques summarized in Worksheet #21 and provided in Appendix A to the work plan.

Who will collect and generate the data?
Samples will be collected by QEA, SUNY-ESF, and Onondaga County Department of Water Environment Protection (OCDWEP)

QEA activities are as follows:

- Provide program oversight
- Collect littoral water samples
- Collect littoral sediment samples
- Collect, sieve, and sort macroinvertebrates for tissue analysis
- Collect adult sport fish and prey fish for tissue analysis

SUNY-ESF activities are as follows:

- Conduct adult sport fish population surveys
- Assess juvenile fish abundance and distribution
- Gut content analysis
- Assess community composition of phytophilous macroinvertebrates
- Assist with adult sport fish collection for tissue analysis
- Conduct juvenile seining for prey fish tissue collection/analysis

OCDWEP activities are as follows:

- Collect, sieve, and sort benthic macroinvertebrates for invertebrate community composition.
- Conduct juvenile seining for prey fish tissue collection/analysis during the summer.

Laboratory analyses will be performed by TestAmerica and Brooks Rand. Identification of invertebrates to lowest taxonomic level will done by Aquatic Resources Center, Inc.

How will the data be reported?
The data will be presented in the Data Summary and Usability Report referenced in the Work Plan.

How will the data be archived?
All field and laboratory data and chain of custody information will be stored in Parsons LocusFocus EIM (Locus Technologies) data management system. Additionally, field databases developed using Microsoft Access VBA used during sample collection will be archived by Parsons or QEA. The electronic data management systems will be implemented to process the information effectively without loss or alteration. Brooks Rand stores chain-of-custody forms and laboratory data in hard copy, and the electronic data are stored on the Brooks Rand server. Data are protected through daily backups via computer and secure storage of data in hardcopy. All hardcopy forms (COC, preparation logs, analytical

bench sheets, etc.) are scanned and stored as electronic PDF files as well as in hardcopy form. The Brooks Rand server runs SuSE Linux Professional (v. 9.1) on a Dell PowerEdge 700 computer. All hardcopy and electronic data are stored for a minimum of 7 years from the date of reporting.

TestAmerica stores sample handling, laboratory data, and administrative records in a secure fashion. All records are stored in archived storage, and electronic records consist of hard copies, write-protected backup copies, or an electronic audit trail controlling access. All electronic records are backed up on the TestAmerica archive server on the local area network. All records are removed from the archive and disposed after 5 years, unless otherwise specified by a client or regulatory requirement.

Matrix	Fish and Invertebrate Tissue
Analytical Group	Total mercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-1, SB-2, SB-3	LB-1, LB-10	Precision	RPD 30%	Matrix spike and matrix spike duplicates	A
		Accuracy/Bias	Five standards with the correlation coefficient≥0.995 and low standard recovery 70-130%	Initial calibration standards	A
			Control limit recovery 85-115%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 85-115%	Laboratory control samples	A
			90-110% of expected value for ICV; 80-120% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	0.034 µg/g wet	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

Matrix	Fish Tissue
Analytical Group[1]	Percent Lipids
Concentration Level	Low to High

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-1, SB-3	LB-6, LB-10	Accuracy	<RL, or associated samples >5x blank values	Laboratory blank	A
		Precision	The RPD for lab duplicates should be ≤20%	Laboratory duplicates	S&A
		Sensitivity	0.1 %	Reporting limits	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Completeness	95%	Comparison of number of confident quantifications to total quantifications	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #21 (see Section 3.1.2).
[3]Reference number from QAPP Worksheet #23 (see Section 3.2).

Matrix	Invertebrate Tissue and Water
Analytical Group	Methylmercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-2 (invertebrates) SB-9 (water)	LB-3, LB-10 (tissue)	Precision	RPD 35%	Laboratory duplicate samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 65–135%	Initial calibration standards	A
			Control limit recovery 65-135%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 65-135%	Laboratory control samples	A
			80-120% of expected value for ICV; 67-133% of expected value for CCV[3] samples	Initial and continuing calibration verification samples	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	9.0 ng/g wet (tissue): 0.05 ng/L (water)	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
[3]Referred to as OPR in SOP.

Matrix	Fish Tissue
Analytical Group	PCBs (Aroclor)
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-1, SB-3	LB-4, LB-7, LB-10	Precision	RPD ≤40%	Matrix spike and matrix spike duplicates	A
		Accuracy/Bias	Five standards with the RSD ≤20%	Initial calibration standards	A
			<½ RL or associated samples >5X blank values	Laboratory blank	A
			Control limit recovery 30–130% for Aroclor 1016 and 1260	Matrix spike and matrix spike duplicates	A
			Control limit recovery 60-120% for Aroclor 1016 and 1260	Laboratory control samples	A
			Surrogate control recovery 30-130% for TMX and DCB[4]	All samples and associated quality controls	A
			80-120% of expected value for ICV; 85-115% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	13 µg/kg wet	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

Matrix	Adult Sport Fish Tissue
Analytical Group	Dioxins/Furans
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-1, SB-3	LB-2[3], LB-10	Precision	On-going recovery within limits: Native analyte recovery limits 70-130%, internal standard recovery limits 40-135%	Laboratory Control Sample/On-going Precision Recovery (OPR) Sample	A
		Accuracy/Bias	Five standards with the % RSD for native analytes ≤ +/- 35% with the exception of OCDF and 1,2,3,7,8,9-HxCDD which are +/-35%, internal standards +/-35%	Initial calibration standards	A
			<RL or associated samples >20X blank values	Laboratory blank	A
			Native analyte recovery limits 70-130%, internal standard recovery limits 40-135%	Laboratory Control Sample/On-going Precision Recovery (OPR) Sample	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	1-10 pg/g wet	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.
[3]The referenced laboratory SOP provides procedures and QA/QC for two similar, but not identical, methods (1613B and 8290). Method 8290 will be used.

Matrix	Sediment
Analytical Group	Total mercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-7	LB-1	Accuracy	< sample-specific RL, or associated samples >5× blank values	Laboratory or equipment blank	A
			Control limit recovery 85-115%	Laboratory control sample	A
			Control limit recovery 85-115%	Matrix spike	A
			80-120% of expected value for ICV; 67-133% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Precision – Field	RSD 30%	Field duplicate	S&A
		Precision – Lab	RPD 30%	Matrix spike duplicate	A
		Sensitivity	0.034 μg/g	Reporting limits	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Completeness	95%	Comparison of number of confident quantifications to total quantifications	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

Matrix	Sediment
Analytical Group	Methylmercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-7	LB-3	Accuracy	< sample-specific RL, or associated samples >5× blank values	Laboratory or equipment blank	A
			65-135%	Laboratory control sample	A
			65-135%	Matrix spike	A
		Precision – Field	RSD 35%	Field duplicates	S&A
		Precision – Lab	RPD 35%	Laboratory duplicates	A
		Sensitivity	0.025 ng/g wet	Reporting limits	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Completeness	95%	Comparison of number of confident quantifications to total quantifications	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

Matrix	Sediment
Analytical Group	Total organic carbon
Concentration Level	Medium

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-7	LB-5	Accuracy	< sample-specific RL, or associated samples >5× blank values	Laboratory or equipment blank	A
			75-125%	Laboratory control sample	A
			75-125%	Matrix spike	A
			85-115% of expected value for ICV; 85-115% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Precision – Field	RSD 20%	Field duplicates	S&A
		Precision – Lab	RPD 20%	Laboratory duplicates	A
		Sensitivity	500 mg/kg	Reporting limits	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Completeness	95%	Comparison of number of confident quantifications to total quantifications	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group	Total mercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-9	LB-8	Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 75–125%	Initial calibration standards	A
			Control limit recovery 71-125%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 75-125%	Laboratory control samples	A
			85-115% of expected value for ICV; 77-123% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 24%	Laboratory duplicate samples	A
			77-123%	Ongoing precision and recovery samples	A
		Contamination	Less than reporting limit (0.4 ng/L)	Field, method, and instrument blanks	A
		Sensitivity	0.5 ng/L	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

Matrix	Fish Tissue
Analytical Group	Pesticides[1]
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
SB-1, SB-3	LB-4, LB-7, LB-10	Precision	RPD ≤40%	Matrix spike and matrix spike duplicates	A
		Accuracy/Bias	Five standards with the RSD ≤20%	Initial calibration standards	A
			<½ RL or associated samples >5X blank values	Laboratory Blank	A
			Control limit recovery 30–130% for each target analyte	Matrix spike and matrix spike duplicates	A
			Control limit recovery 60-120% for each target analyte	Laboratory control samples	A
			Surrogate control recovery 30-130% for TMX and DCB[4]	All samples and associated quality controls	A
			80-120% of expected value for ICV; 85-115% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	2.0 μg/kg wet	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]DDT and metabolites, hexachlorobenzene
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.[4]TMX – tetrachloro-m-xylene; DCB - decachlorobiphenyl

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
OCDWEP fish and macroinvertebrate data	Onondaga Lake Ambient Monitoring Plan Annual Reports, Onondaga County Department of Water and Environment Protection, 2000-2006	OCDWEP, data includes count, length, weight and unit effort for fish, count and area sampled for benthic macroinvertebrates and zebra mussels	The data will be used for comparison to new data to determine trends in abundance and community composition.	No limitations.
NYSDEC fish data	NYSDEC database	Data include mercury concentration, lipid content, and percent moisture from fillet samples in largemouth and smallmouth bass.	The data will be used for comparison of current mercury levels to historical data.	No limitations.

Sampling Tasks:

1. Adult sport fish and prey fish sampling via electroshocking, netting, or angling. Fillets and tissue plugs will be taken from sport fish consistent with SOP SB-3 (see Worksheet #21) while single-species whole body composites will be collected for prey fish. Total length and weight measurements of individuals will be taken and sex will be determined if possible. Scales will be sampled from adult sport fish to estimate age. Gut contents will be assessed on adult sport fish prior to processing fish using gastric lavage per SOP SB-4 (see Worksheet #21).
2. For adult individuals, eight locations will be sampled to collect 50 individuals of four species (smallmouth bass, walleye, brown bullhead, pumpkinseed sunfish). If possible, adult sport fish will be evenly distributed among the sampling locations.
3. A maximum of five composite samples will be collected from each of eight locations for prey fish during summer. Composites will consist of 10 to 15 individuals of one species. Reasonable attempts will be made to include at least two alewife composites (less than 180 mm total length) in the prey fish samples from each location.
4. Benthic invertebrates and zebra mussels will be collected at 18 littoral locations (1.0 to 1.5 m water depth) in 2008 using a petite ponar sampler. Samples will be collected for tissue analysis as well as community composition from each location. Two additional community composition samples will be collected from the profundal zone in approximately 13 m water depth, one in the north basin and one in the south basin.
5. Phytophilous invertebrates will be collected for assessment of community composition at 18 littoral locations within the macrophyte beds as close to the benthic invertebrate locations as possible in 2008 using a petite ponar sampler.
6. Co-located sediment will be collected at each invertebrate littoral location with a sediment core and segmented at 0-2 cm and 2-15 cm.
7. Littoral water will be collected as surface grabs at six locations once during the summer and twice following fall turnover, corresponding to invertebrate and/or fish sampling locations.

Analysis Tasks:

1. Brooks Rand will perform methylmercury analysis on invertebrate tissue, sediment, and water samples. TestAmerica will perform all other analyses.
2. Fish catch results will be analyzed for community composition per SOP SB-6 (see Worksheet #21) and select species will have population estimates calculated per SOP SB-5 (see Worksheet #21).
3. Separate macroinvertebrate samples will be analyzed for community composition

Quality Control Tasks:

1. The QEA field team leader will evaluate all samples and applicable field quality control samples for acceptability for transport/submission to the laboratory.
2. Implement SOPs for sample collection, packaging, transport, and storage prior to analysis. QC sample handling protocols are described on

Worksheet #26.

Secondary Data:

1. See Worksheet #13.

Data Management Tasks:

Records generated during sample collection and analyses document the validity and authenticity of the project data. The project team will maintain a field database as a temporary repository for all sampling records generated in the field. Field and analytical data from the laboratory will later be transferred to the LocusFocus data management system maintained by Parsons for Honeywell, Inc.

Documentation and Records:

1. This QAPP will be distributed to each contractor responsible for the collection, generation, and interpretation of field and analytical data. The QA Program Manager will be responsible for ensuring that necessary changes occur so that the QAPP is up to date with actual practices.
2. Appropriate records will be maintained to provide adequate documentation of the entire data generation process, including field sampling and laboratory analysis.
3. Field sampling records will include
   a. Electronic field logs and field notebooks to records daily activities and conditions;
   b. an electronic field data management system (database) and
   c. sample Chain-of-Custody documentation.
4. Lab documentation will include
   a. operational calibration records,
   b. maintenance records,
   c. nonconformance memos,
   d. corrective action memos, and
   e. analytical data reports.

Assessment/Audit Tasks:

1. Project oversight (field and laboratory) will consist of periodic inspection and audits of sampling and analytical techniques, as required by NELAC/ELAP (annual internal laboratory and field audit; external audit by NELAC/ELAP certified inspectors every two years). No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken, and any client whose work is affected will be notified immediately in writing.

2. The following reports may be completed if a deviation from the field sample matrix or QAPP is encountered, or to document an audit:
    a. Corrective action reports documenting any problems encountered during field activities and corrective actions taken;
    b. System and performance audit reports completed during the investigation and a summary of any changes made to documented procedures, and the rationale for the changes.
3. See Worksheets #31 and #32 for explanation of project assessments, assessment findings, and corrective action responses.

Data Review Tasks:

1. The laboratories will perform data reduction as described in each test method for this project and will submit sample results and QA/QC results.
2. The laboratory quality assurance officer and/or laboratory director are responsible for reviewing the laboratory data and QA/QC reports, and checking data reduction prior to submittal to Honeywell. The laboratory will correct any transcription or computational errors identified during this review.
3. Test results are certified to meet all requirements of the NELAC standards, or reasons are provided if they do not.

Matrix: Fish and Invertebrate Tissue
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	NA		0.007 µg/g wet	0.034 µg/g wet	0.007 µg/g[3] wet	0.034 µg/g[3] wet
Methyl mercury	22967-92-6	NA		3.0 ng/g wet	9.0 ng/g wet	3.0 ng/g[4] wet	9.0 ng/g[4] wet

[1]Analytical MDLs and QLs are those documented in validated methods. Test America is analyzing total mercury; Brooks Rand is analyzing methylmercury.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
[3]The MDL and QL concentrations are dependent on the amount of tissue collected. For an analysis of 0.3 g, the MDL is 0.007 µg/g.
[4]The MDL and QL concentrations are dependent on amount of tissue collected or the volume of digest used during analysis. For an analysis of 100mg, the MDL is 1.0 ng/g, and the QL is 3.0 ng/g.

Matrix: Fish Tissue
Analytical Group: Lipids
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	DLs (%)	QLs (%)
Percent Lipids	LP001	NA	%			0.1	0.1

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Sediment
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	NA		0.007 µg/g	0.034 µg/g	0.007 µg/g[3]	0.034 µg/g[3]
Methyl mercury	22967-92-6	NA		0.008 ng/g wet	0.025 ng/g wet	0.008 ng/g wet	0.025 ng/g wet

[1]Analytical MDLs and QLs are those documented in validated methods. TestAmerica is analyzing total mercury; Brooks Rand is analyzing methylmercury.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
[3]The MDL and QL concentrations are dependent on the sample mass. For an analysis of 0.3 g, the MDL is 0.007 µg/g.

Matrix: Sediment
Analytical Group: Total organic carbon
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total organic carbon		NA				90 mg/kg	500 mg/kg

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Fish Tissue
Analytical Group: PCBs (Aroclors)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (µg/kg)	QLs (µg/kg wet)
Aroclor 1016		NA					13
Aroclor 1221		NA					13
Aroclor 1232		NA					13
Aroclor 1242		NA					13
Aroclor 1248		NA					13
Aroclor 1254		NA					13
Aroclor 1260		NA					13
Aroclor 1262		NA					13
Aroclor 1268		NA					13

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Fish Tissue
Analytical Group: PCDD/PCDFs
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs (*pg/g wet*)	MDLs[3] (*pg/g wet*)	QLs (*pg/g wet*)
2,3,7,8-TCDD	1746-01-6	NA	NA	NA	1.0	0.38	1.0
1,2,3,7,8-PeCDD	40321-76-4	NA	NA	NA	5.0	0.43	5.0
1,2,3,4,7,8-HxCDD	39227-28-6	NA	NA	NA	5.0	0.49	5.0
1,2,3,6,7,8-HxCDD	57653-85-7	NA	NA	NA	5.0	0.45	5.0
1,2,3,7,8,9-HxCDD	19408-74-3	NA	NA	NA	5.0	0.30	5.0
1,2,3,4,6,7,8-HPCDD	35822-46-9	NA	NA	NA	5.0	0.57	5.0
OCDD	3268-87-9	NA	NA	NA	10	0.52	10
2,3,7,8-TCDF	51207-31-9	NA	NA	NA	1.0	0.39	1.0
1,2,3,7,8-PECDF	57117-41-6	NA	NA	NA	5.0	1.2	5.0
2,3,4,7,8-PECDF	57117-31-4	NA	NA	NA	5.0	0.59	5.0
1,2,3,4,7,8-HXCDF	70648-26-9	NA	NA	NA	5.0	0.74	5.0
1,2,3,6,7,8-HXCDF	57117-44-9	NA	NA	NA	5.0	0.39	5.0
2,3,4,6,7,8-HXCDF	60851-34-5	NA	NA	NA	5.0	0.59	5.0
1,2,3,7,8,9-HXCDF	72918-21-9	NA	NA	NA	5.0	0.54	5.0
1,2,3,4,6,7,8-HPCDF	67562-39-4	NA	NA	NA	5.0	0.79	5.0
1,2,3,4,7,8,9-HPCDF	55673-89-7	NA	NA	NA	5.0	0.46	5.0
OCDF	39001-02-0	NA	NA	NA	10	5.2	10

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
[3]Laboratory will report sample specific estimated detection limits (EDLs), based on achieved signal-to-noise during sample analysis.

Matrix: Water
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	0.7 ng/L	0.5 ng/L	0.2 ng/L	0.5 ng/L	0.12 ng/L	0.5 ng/L
Methyl mercury	22967-92-6	0.1 ng/L	0.05 ng/L	0.02 ng/L	0.05 ng/L	0.020 ng/L	0.05 ng/L

[1]Analytical MDLs and QLs are those documented in validated methods. TestAmerica is analyzing total mercury; Brooks Rand is analyzing methylmercury.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
TestAmerica is analyzing total mercury; Brooks Rand is analyzing methylmercury.

Matrix: Fish tissue
Analytical Group: Pesticides
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
DDT and metabolites		NA			2.0 µg/kg wet		2.0 µg/kg wet
Hexachlorobenzene		NA			2.0 µg/kg wet		2.0 µg/kg wet

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Activities	Organization	Dates (2008)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Mobilization	ESF/OCDWEP/QEA	July	August	NA	NA
Fish tissue sampling	ESF/OCDWEP/QEA	July	August	Data	March 2009
Fish community assessment	ESF/OCDWEP	May	October	Data	March 2009
Macroinvertebrate sampling (tissue and community composition)	OCDWEP/QEA	August	August (tissue and community composition); November (tissue only)	Data	March 2009
Fish gut analysis	ESF	June	October	Data	March 2009
Sediment	OCDWEP/QEA	July	November	Data	March 2009
Water	QEA	July	November	Data	March 2009
Phytophilous invertebrate community analysis	ESF	July	August	Data	March 2009
Field database	QEA	May	Late November	Field database exports	September/October 2008 and December/January 2009
Scientific oversight	QEA/Exponent	May	Late November	NA	NA
Sample analysis	TestAmerica	August	December	Unvalidated data	Quarterly
Sample analysis	Brooks Rand	August	December	Unvalidated data	Quarterly
Data Usability and Summary Report (DUSR)	QEA/Exponent	January 2009	March 2009	2008 DUSR	March 2009

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):
Locations for fish sampling will be dispersed around the lake coinciding with historic sampling locations from the Remedial Investigation and Onondaga County's Ambient Monitoring Program. Fish sampling locations will be dispersed among eight locations around the lake, coinciding with historical tissue sampling locations occupied during the RI, as well as sampling locations occupied by OCDWEP.

Benthic macroinvertebrates will be collected at 18 locations in the littoral zone, in approximately 1.5 meter water depth, from around the lake to represent conditions in the near-shore zone within each SMU. In addition, two locations will be in approximately 13 meter water depth to assess benthic macroinvertebrate community composition in the profundal zone. Co-located sediment will be collected at each littoral zone location to characterize the chemical conditions of the substrate. Littoral water samples will be collected at six stations co-located with invertebrate and/or fish sampling locations.

Zebra mussels will be collected at the same locations as benthic macroinvertebrates to characterize tissue concentrations within the different SMUs.

Phytophilous macroinvertebrates will be collected at 18 locations in the littoral zone, in close proximity to the benthic macroinvertebrate locations to assess community composition within the macrophyte beds.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

See Figures 1 and 2 in Book 2 work plan for sampling locations. See Worksheet #18 for matrices, analytical groups, concentration levels, and number of samples. The number of locations, samples per location, sampling duration within each month is presented in the table below.

Activity	Number of Locations[1]	Number of samples per location	Number of species	Sample Preparation	Duration
Adult sport fish tissue	8	6-7	4	Fillets and tissue plugs	Approximately 15 days in late July/August
Prey fish tissue	8	5	Variable (samples are composites of a prey species)	Whole body composite	Approximately 5 days in August
Benthic Invertebrate tissue	18	1	3	Whole body composite	Approximately 10 days in August and following fall turnover (late October/early November)
Benthic Invertebrate Community Analysis	18	5	N/A	N/A	Approximately 10 days in August
Phytophilous Invertebrate Community Analysis	18	5	N/A	N/A	Approximately 10 days in August
Water	6	1	N/A	N/A	Three events from August to November
Sediment	18	2	N/A	N/A	Approximately 10 days in August and following fall turnover (October/November)

[1] Adult samples will be targeted from eight locations around the lake; if sampling is difficult in some locations, a maximum of 25 adults per species will be collected from each basin.

[2] Water samples will be surface grabs.

[3] Sediment samples will consist of two segments 0-2 cm and 2-15 cm.

Sampling Location/ID Number	Matrix	Depth (units)	Analytical Group	Concentration Level	Number of Samples (field duplicates)[1]	Sampling SOP Reference[2]	Rationale for Sampling Location
Lakewide	Adult sport fish (4 species)	Littoral zone	Total mercury	Low	400	SB-1	See Worksheet #17
			PCBs	Low	48		
			DDT and metabolites	Low	48		
			Hexachlorobenzene	Low	48		
			Dioxins/Furans	Low	20		
			%Lipids	Low	48		
Lakewide	Prey fish (composite samples)	Littoral zone	Total mercury	Low	40	SB-1	
			PCBs	Low	10		
			DDT and metabolites	Low	10		
			Hexachlorobenzene	Low	10		
Lakewide	Benthic macroinvertebrate tissue (Zebra mussels, chironomids, amphipods)	1.0 to 1.5 m	Total mercury[3]	Low	108	SB-2	
			Methyl mercury[3]	Low	108		
Lakewide	Macroinvertebrate Community	1.0 to 1.5 m	None	None	180[4]	SB-2; SB-8	
Lakewide	Water	Littoral zone	Total mercury	Low	18 (3)	SB-9	
			Methyl mercury	Low	18 (3)		
Lakewide	Sediment	1.0 to 1.5 m	Total mercury	Low	72 (4)	SB-7	
			Methyl mercury	Low	72 (4)		
			Total organic carbon	Medium	72 (4)		

[1] Field duplicates not collected for tissue.
[2] See Worksheet #21.
[3] If sample mass is limited, sample will be analyzed for methylmercury only.
[4] Five replicate samples collected per location for benthic macroinvertebrates and phytophilous macroinvertebrates**.**

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Mass or Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Fish Tissue	Total mercury	Low	LB-1	2-10 g; 1 g for tissue plug analysis	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C, or freeze dry	6 months (preserved)
	Total PCBs (Aroclor)	Low	LB-4	40 g	appropriate-sized wide mouth glass jar w/Teflon® lined cap[2]	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C	1 year to extraction, 40 days to analysis
	Pesticides: DDT and metabolites, hexachlorobenzene	Low	LB-9	10 g	Appropriate-sized wide mouth glass jar w/Teflon® lined cap[2]	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C	1 year to extraction, 40 days to analysis
	PCDD/PCDF	Low	LB-2	50 g	Appropriate-sized wide mouth glass jar w/Teflon® lined cap[2]	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C	1 year to extraction, 40 days to analysis
	Percent lipids	Low	LB-6	20 g	Appropriate-sized wide mouth glass jar w/Teflon® lined cap[2]	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C	1 year to extraction, 40 days to analysis
Invertebrates (BMI and ZM)	Total mercury	Low	LB-1	2-10 g	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C, or freeze dry	6 months (preserved)

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Mass or Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
	Methylmercury	Low	LB-3	2-10 g	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C, or freeze dry	6 months (preserved)
Water	Total mercury	Low	LB-8	500 mL	Plastic[2], glass or Teflon bottle (500 mL or 1 L)	HCl, cool, 4°C	28 days (unpreserved), 90 days (preserved)
	Methylmercury	Low	LB-3	500 mL	Plastic[2] or Teflon bottle (500 mL or 1 L)	HCl, cool, 4°C	6 months (preserved)
Sediment	Total mercury	Low	LB-1	2-10 g	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2C, Refrigerate 4°±2C	6 months (preserved)
	Methylmercury	Low	LB-3	2-10 g	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2C, freeze to <-18°C, or freeze dry	6 months (preserved)
	Total organic carbon	Medium	LB-5	5 g	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2C, Refrigerate 4°±2C	14 days

[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).
[2] After homogenization of sample.

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS[3]	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Fish Tissue	Total mercury	Low	LB-1	440[4]	NA	NA	NA	NA		440
	Total PCBs (Aroclor)	Low	LB-4, LB-7	58[5]						58
	Pesticides: DDT and metabolites andhexachlorobenzene	Low	LB-9							58
	PCDD/ PCDFs	Low	LB-2	20[5]						20
	Percent lipids	Low	LB-6	58[5]						58
Invertebrates	Total mercury	Low	LB-1	18 locations, 3 invert types, twice (108 samples)	NA	12	NA	NA		120[6]
	Methyl mercury	Low	LB-3		NA	12	NA	NA		120[6]
Water	Total mercury	Low	LB-8	6 locations, 3 events (18 samples)	3	6	3[7]	3		33
	Methyl mercury	Low	LB-3		3	6	3[7]	3		33
Sediment	Total mercury	Low	LB-1	18 locations, 2 depths, twice (72 samples)	4	8		4[8]		88
	Methyl mercury	Low	LB-3		4	8		4[8]		88
	Total organic carbon	Medium	LB-5		4	8		4[8]		88

[1]See Analytical SOP References table (Worksheet #23).

[2]If samples will be collected at different depths at the same location, count each discrete sampling depth as a separate sampling location or station.
[3]Matrix spike and matrix spike duplicate samples will be prepared by the laboratory at a frequency of at least one pair per 20 samples, unless otherwise noted.
[4]For adults: 8 locations, 4 species, 50 fish per species for a total of 200 fillet samples. In addition, 200 tissue plug samples (4 species, 50fish per species) will be analyzed. For prey fish, 8 locations, 5 composites per location, for a total of 40 samples.
[5]PCB, DDT and metabolites, hexachlorobenzene, and lipids analysis on 48 adult sport fish samples and 10 prey fish samples. PCDD/PCDF analysis on 20 adult sport fish samples.
[6] If sample mass is limited, sample will be analyzed for methylmercury only.
[7] A field blank for total mercury and methylmercury will consist of mercury-free water (i.e., water containing mercury at concentrations below the minimum detection limit) placed in a clean sample bottle in the laboratory, transported to the field, and then poured into a second clean sample bottle for transport back to the laboratory.
[8] Field (equipment/rinsate) blanks for sediment sampling will be collected at a rate of one per 20 samples consistent with the PDI QAPP (Parsons, 2005).

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
SB-1	Fish Collection	QEA	Seine, gill net, trap net, electroshocking boat, pop net, balance for weighing fish, measuring board, aluminum foil, resealable plastic bags	N	Includes information on decon procedures and sample handling
SB-2	Benthic Macroinvertebrate Collection	QEA	Ponar dredge, sieves, peristaltic pump, sample containers, boat	N	Includes information on decon procedures and sample handling
SB-3	Biota Tissue Processing	QEA	Knife, scale, dermal punch	N	Includes information on decon procedures and sample handling
SB-4	Fish Stomach Sampling	QEA	Hand-pumped compression sprayer, polyethylene tubing, funnel with 500 um mesh	N	
SB-5	Adult Sport Fish Population Estimate	QEA	Dip nets, fish holding tanks or live wells, knife or scissors for fin clips, tagging gun, T-anchor tags, measuring board, marking gun	N	
SB-6	Fish Community Assessment	QEA	Fish holding tanks or live wells, measuring board, balance for weights, water quality meter	N	
SB-7	Sediment Sample Collection	QEA	Core sampler, sieves, peristaltic pump, sample containers, boat	N	Includes information on decon procedures and sample handling
SB-8	Phytophilous Macroinvertebrate Sampling	QEA	Ponar dredge, sieves, sample containers, boat	N	
SB-9	Littoral Zone Surface Water Sampling	QEA	Sample containers, boat, gloves, water quality meter	N	Includes information on decon procedures and sample handling, including clean hands technique

Sampling SOPs are provided in Appendix A of this work plan.

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Water quality meter	Calibration prior to each day's activity according to manufactures recommendations	Rinse all sensors with DI water, gently wipe all sensors dry using optical lens paper	DI water checks	Charging batteries, check for damage, surface dirt or debris	Daily		Repair as soon as possible (in field or at lab)	Field Crew Manager	SB-1, SB-2, SB-8, SB-9
Balance	Calibration check prior to each day's use with known weights	In accordance with manufacturers recommendations	Checking with known weights	Charging batteries, check for damage	Daily		Repair as soon as possible (in field or at lab)	Field Crew Manager	SB-1, SB-2

[1]Specify the appropriate reference letter or number from the Project Sampling SOP References table (Worksheet #21).

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
LB-1	Mercury (Cold Vapor Technique) [SW-846 Method 7471A], BR-ME-004, Revision11	Definitive	Total mercury (tissue and sediment)	Mercury Auto-Analyzer; Leeman Labs PS 200 and Leeman Labs Hydra AA with Autosampler or equivalent	Test America	N
LB-2	Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Method 8290, 1613B, 23, 0023A, and TO-9A, KNOX-ID-0004, Revision 7	Definitive	Dioxins/furans	HR GC/MS	TestAmerica	N
LB-3	Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630, SOP #BR-0011, Revision 12	Definitive	Methylmercury (tissue and sediment)	Brooks Rand Model III CVAFS	Brooks Rand	N
LB-4	Polychlorinated biphenyls (PCBs) by Gas Chromatography [SW-846 Methods 8082], BR-GC-005, Revision 8.	Definitive	Total PCBs	GC/ECD	TestAmerica	N
LB-5	Total Organic Carbon in Soils and Sediments, BR-WC-008, Revision 11	Definitive	TOC	Elemental Analyzer	TestAmerica	N

LB-6	Percent Lipid Determination, BR-EX-016, Revision 6	Definitive	Lipids	Balance	TestAmerica	N
LB-7	Extract Cleanup Procedure [SW-846], BR-EX-002, Revision 7	Definitive	Cleanup for organic extracts	NA	TestAmerica	N
LB-8	Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7, NC-MT-0001, Revision 5.1	Definitive	Total mercury (water)	Atomic Fluorescence Spectrophotometer	TestAmerica	N
LB-9	Organochlorine Pesticides by Gas Chromatography [SW-846 Method 8081A], BR-GC-006, Revision 8	Definitive	DDT and metabolites; and hexachlorobenzene	GC/ECD	TestAmerica	N
LB-10	Homogenization of Biota/Tissue, BR-EX-009, Revision 5	Definitive	All analytes	NA	TestAmerica	N
LB-11	Determination of Limits of Detection, Limits of Quantification, and Reporting Limits SOP No. BR-QA-005, Revision 7	Definitive	All analytes	NA	TestAmerica	N

Analytical SOPs are provided in Appendix A of this work plan.

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
TestAmerica Gravimetric determination (% lipids)	Refer to SOP	Daily balance calibration	1g (0.995-1.005) 10g (9.980-10.020) 20g (19.980-20.020)	1. Inspect system 2. Correct problem 3. Rerun calibration	Laboratory Staff	LB-6
Brooks Rand Model III CVAFS	Refer to SOP	Initial calibration after instrument set up	5 standards with the RSD $\leq$15%, or R2 $\geq$ 0.995; Low Std. Recovery 65-135%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	LB-3
		ICV immediately after initial calibration	80-120% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
		CCV after every ten samples and at the end of the run	67-133% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3.All samples analyzed after the last passing CCV must be reanalyzed		
TestAmerica GC/ECD	Refer to SOP	Initial calibration after instrument set up, after major instrument changes, and when continuing calibration criteria are not met.	Initial Calibration % RSD $\leq$20%. CCV $\leq$15% drift.	1. Inspect system 2. Correct problem 3. Rerun calibration and affected samples	Laboratory Staff	LB-4

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
TestAmerica HR GC/MS	Refer to SOP	Initial calibration after instrument set up, after major instrument changes, and when continuing calibration criteria are not met.	Five standards with the % RSD for native analytes ≤ +/- 20% with the exception of OCDF and 1,2,3,7,8,9-HxCDD which are +/-35%, internal standards +/-35%	1. Inspect system 2.Correct problem 3.Rerun calibration and affected samples	Laboratory Staff	LB-2
TestAmerica CVAFS	Refer to SOP	Initial Calibration - Daily prior to sample analysis	6 standards with the RSD ≤15%, or R2 ≥ 0.995 Low Std. Recovery 75–125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	LB-8
		Initial Calibration Verification - Immediately after Initial calibration	85-115% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
		Continuing Calibration Verification - After every ten samples and at the end of the run	77-123 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed		

[1]See the Analytical SOP References table (Worksheet #23).

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Brooks Rand Model III CVAFS	Check ethylation agent and analytical system	Analyze primer and blank	Visually check shape of peak and response	At start of an analysis run	Calibration curve should have a ≤15%, or R2 ≥ 0.995	Re-calibrate, compare against 2nd source, and OPR	Analyst	LB-3
Gravimetric Determination-Balance	Quarterly check and annual calibration	As specified in Worksheet #24	Check that balance is level, clean, and free of draft and vibration	As specified in SOP	As specified in Worksheet #24	As specified in Worksheet #24	Analyst	LB-2
TestAmerica GC/ECD	Perform column maintenance, replace injection port liner, clean/bake-out detector	As specified in Worksheet #24	Check gas supply, check solvent reservoir, check temperature program and instrument method	As specified in SOP	As specified in Worksheet #24	As specified in Worksheet #24	Analyst	LB-4
TestAmerica HR GC/MS	Perform column maintenance, replace septum, replace injection port liner, clean ion source, clean ion volume, replace filaments	As specified in Worksheet #24	Check gas supply, check solvent reservoir, check temperature program and instrument method	As specified in SOP	As specified in Worksheet #24	As specified in Worksheet #24	Analyst	LB-2

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Leeman Labs Hydra AF gold plus, CVAFS	Routine inspections, check intensity of Hg lamp, inspect liquid/gas separator and Nafion Dryer	Change liquid/gas separator and Nafion Dryer	Check argon flow, pump tubing, drain, and soda lime drying tube	Daily except check intensity of Hg lamp semiannually and inspect/change liquid/gas separator and Nafion Dryer as needed		Change Hg lamp and/or liquid/gas separator and Nafion Dryer	Analyst	LB-8

[1]See the Analytical SOP References table (Worksheet #23).

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization):Margaret H. Murphy, QEA
Sample Packaging (Personnel/Organization): Margaret H. Murphy, QEA
Coordination of Shipment (Personnel/Organization): Margaret H. Murphy, QEA
Type of Shipment/Carrier: Samples for chemical analysis shipped on ice by overnight shipment to Brooks Rand and TestAmerica
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization):Brooks Rand and TestAmerica
Sample Custody and Storage (Personnel/Organization Laboratory Staff/Brooks Rand and Laboratory Staff /TestAmerica
Sample Preparation (Personnel/Organization): Laboratory Staff/Brooks Rand and Laboratory Staff/TestAmerica
Sample Determinative Analysis (Personnel/Organization): Laboratory Staff/Brooks Rand and Laboratory Staff/TestAmerica
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): See Worksheet #19
Sample Extract/Digestate Storage (No. of days from extraction/digestion): See Worksheet #19
Biological Sample Storage (No. of days from sample collection): See Worksheet #19
SAMPLE DISPOSAL
Personnel/Organization: Laboratory Staff/Brooks Rand and TestAmerica
Number of Days from Analysis: 60 days (Brooks Rand); 6 months (TestAmerica)

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

Standard procedures for sample collection and shipping will be followed such that samples are preserved and stored as required (Worksheet #19). All field measurements and sample collection activities will follow approved standard operating procedures. The general procedure is as follows:

- Tissue and sediment samples will be collected according to the sampling SOPs.
- Appropriate field notes will be taken throughout the sampling process or entered directly into a field database, and sample locations, depths, and types will be checked/verified against the field sampling matrix (FSM) in the project work plan.
- Samples will be kept on ice while in the field.
- Any sample-handling difficulties that are encountered in the field will be described in the field database.
- The samples will be delivered to the appropriate laboratory with a fully documented chain-of-custody form.
- Field personnel are responsible for making sure all documentation has been completed and turned over to the laboratory and/or other support personnel.
- The field log will be reviewed and sample integrity verified as part of the data validation procedures.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

On receipt, laboratory personnel will check samples, and the cooler temperature will be determined. The temperature and condition of the samples will be recorded at the laboratory, and any problems will be described in the narrative for the data report. The field log and narrative will be reviewed during the quality assurance review, and data will be flagged if the sample integrity was compromised. Data may be rejected as unusable if severe handling problems are encountered.

Sample Identification Procedures:

The laboratory will log in the samples, verify the sample containers/labels against the chain of custody, and assign a unique sample identification number to each sample, which will be attached to that sample throughout the life of the sample. Laboratory personnel are responsible for verifying that all required documentation has been completed by field personnel. Laboratory records related to sample handling and analysis are maintained through all stages of the analytical process. All laboratory processes, activities, and SOPs comply with NELAC standards and are fully documented in the Brooks Rand Comprehensive Quality Assurance Plan and TestAmerica's Quality Assurance Manual.

Chain-of-custody Procedures:

A continuous record of the possession and proper handling of samples must be documented, so that sample custody and handling are traceable from the time of sample collection until the analytical data have been validated and accepted for use.

Matrix	Tissue
Analytical Group	Total Mercury
Concentration Level	Low
Sampling SOP	SB-1, SB-2, SB-3
Analytical Method/ SOP Reference	LB-1, LB-10
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	Test America
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	1 per every batch of sample	<1/2 RL	• Reanalyze for verification • If criteria are still not met, reprepare and reanalyze batch.	Lab	Contamination	<1/2 RL
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	90-110% for ICV; 80-120% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Lab	Accuracy	90-110% for ICV; 80-120% for CCV
Laboratory control samples (LCS)	1 with every batch of samples	85-115%	• Reanalyze • If criteria are still not met, reprep LCS and all associated samples. • If recovery is high and the analyte is not detected, document excursion only	Lab	Accuracy	85-115%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 20 samples	85-115%	• If recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data.	Lab	Accuracy	85-115%

Matrix	Tissue
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SB-1, SB-2, SB-3
Analytical Method/ SOP Reference	LB-3, LB-10
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	Brooks Rand
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory duplicate	1 every 10 samples	RPD ≤35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision - Lab	RPD ≤35%
Ongoing Precision and Recover (OPR)	1 at the beginning and end of every batch	67-133%	• If initial is out, reanalyze. • If closing is out, reanalyze, if still out, review last CCV that was ran and follow CCV criteria.	Frank McFarland	Precision - Lab	67-133%
Method blank	3 per every batch of sample	Average less than 2x MDL; StDev less than 2/3rds MDL	• Reanalyze for verification • If criteria are still not met, calculate batch specific MDL using standard deviation of the method blanks	Frank McFarland	Contamination	Average less than 2x MDL; StDev less than 2/3rds MDL

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial calibration	Calibrate prior to sample analysis/as per method	5 standards with the RSD ≤15%, Low Std. Recovery 65-135%	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Frank McFarland	Accuracy	5 standards with the RSD ≤15%, Low Std. Recovery 69-135%
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	80-120% for for ICV; 67-133% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Frank McFarland	Accuracy	80-120% for ICV; 67-133% for CCV
Quality control sample (QCS)	Immediately after initial calibration	65-135%	• Reanalyze • Remake and reanalyze ICV • If criteria are still not met, repeat initial calibration	Frank McFarland	Accuracy	65-135%
Laboratory control samples (LCS)	1 with every batch of samples	65-135%	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Frank McFarland	Accuracy	65-135%
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	65-135%	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recover y is within QC limit, and RPD criterion is not met, reanalyze.	Frank McFarland	Accuracy	65-135%

Matrix	Tissue
Analytical Group	Percent Lipids
Concentration Level	Low
Sampling SOP	SB-1, SB-3
Analytical Method/ SOP Reference	LB-6, LB-10
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory duplicate	1 every 20 samples	RPD 20%	• If difference between results should be >2x the RL when at least one result is ≤5x the RL, MS/MSD will be used for precision • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Laboratory Staff	Precision - Lab	RPD 20%
Laboratory blank	1 with every batch of samples	<RL	• Reanalyze • If criteria are still not met, reprep blank and all associated sample.	Laboratory Staff	Accuracy	<RL

Matrix	Tissue
Analytical Group	PCBs (Aroclors)
Concentration Level	Low
Sampling SOP	SB-1, SB-3
Analytical Method/ SOP Reference	LB-4, LB-7, LB-10
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	1 per every batch of sample	< 1/2RL	• Reanalyze for verification • If >RL, reprepare and reanalyze batch If sample results >20x blank or ND, report results	Lab	Contamination	< 1/2RL
Initial calibration	Calibrate prior to sample analysis/as per method	%RSD≤20%	• Reanalyze standards • Remake and reanalyze standards		Accuracy	%RSD≤20%
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 20 samples or every 12 hours, and at the end of each run	ICV 80-120%R CCV≤15%D	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed		Accuracy	ICV 80-120%R CCV≤15%D

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	Aroclor 1016 and 1260 60-120% Recovery	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Laboratory staff	Accuracy	Aroclor 1016 and 1260 60-120% Recovery
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 MS/MSD with every batch of 20 samples	Aroclor 1016 and 1260 30-130% Recovery	• If Recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data		Accuracy	Aroclor 1016 and 1260 30-130% Recovery
Surrogate	Each method blank, LCS, field sample, andMS/MSD	30-130%	• Reanalyze • If recovery is low, reprep sample (or associated samples). • If recovery is high and the analyte is not detected, document excursion only		Accuracy	30-130%

Matrix	Tissue
Analytical Group	PCDD/PCDFs
Concentration Level	Low
Sampling SOP	SB-1, SB-3
Analytical Method/ SOP Reference	LB-2, LB-10
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	1 per every batch of sample	< Minimum Level	• Reanalyze for verification • If >RL, reprepare and reanalyze batch or flag data in consultation with client. If sample results >20x blank or ND, report results	Lab	Contamination	< Minimum Level
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration and every 12 hours	See SOP	• Reanalyze • If criteria are still not met, repeat initial calibration	Lab	Accuracy	See SOP

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	See SOP	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Lab	Accuracy	See SOP
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	Laboratory Limits	• If Recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data	Lab	Accuracy	Laboratory Limits

Matrix	Sediment
Analytical Group	Total mercury
Concentration Level	Low
Sampling SOP	SB-7
Analytical Method/ SOP Reference	LB-1
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	Test America
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Samples are collected in duplicate	RPD 35%			Precision - Field	RPD 35%
Method blank	1 per every batch of samples	<1/2 RL	• Reanalyze for verification • If criteria are still not met, reprepare and reanalyze batch.	Lab	Contamination	<1/2 RL
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	90-110% for ICV; 80-120% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Lab	Accuracy	90-110% for ICV; 80-120% for CCV

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	85-115%	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Lab	Accuracy	85-115%
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 20 samples	85-115%	• If Recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data.	Lab	Accuracy	85-115%

Matrix	Sediment
Analytical Group	Methylmercury
Concentration Level	Low
Sampling SOP	SB-7
Analytical Method/ SOP Reference	LB-3
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	Brooks Rand
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Samples are collected in duplicate	RPD 35%			Precision - Field	RPD 35%
Laboratory duplicate	1 every 10 samples	RPD% ≤35%	• If <5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision - Lab	RPD% ≤35%
Laboratory blank	1 with every batch of samples	<RL	• Reanalyze for verification • Qualify affected samples	Frank McFarland	Accuracy	<RL

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	65-135%	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Frank McFarland	Accuracy	65-135%
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	65-135%	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recovery is within QC limit, and RPD criterion is not met, reanalyze.	Frank McFarland	Accuracy	65-135%

Matrix	Sediment
Analytical Group	Total organic carbon
Concentration Level	Low
Sampling SOP	SB-7
Analytical Method/ SOP Reference	LB-5
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Samples are collected in duplicate	RPD 20%			Precision - Field	RPD 20%
ICAL	Following each column change	$R \geq 0.995$	• Standards check • Recalibration	Lab	Accuracy	$R \geq 0.995$
Laboratory blank	1 with every batch of 20 samples	<RL	• Reanalyze for verification • Qualify affected samples	Lab	Accuracy	<RL
Laboratory control samples (LCS)	1 with every batch of 20 samples	75-125%	• Reanalyze for verification • If criteria are still not met, reprep LCS and all associated samples. • If criteria are still not met, reprep LCS and all associated samples.	Lab	Accuracy	75-125%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Acetanilide	Every 20 drops and at the end of the analytical run	85-115%	• Reprepare and reanalyze samples not surrounded by passing Acetanilides	Lab	Accuracy	85-115%
Blank (paired with Acetanilide)	Following each Acetanilide	< RL	• Reprepare and reanalyze batch	Lab	Accuracy	<RL
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	75-125%	• If recovery is not within QC limits, and an RPD criterion is met document excursion. • If recover y is within QC limit, and RPD criterion is not met, reanalyze. • If the LCS is acceptable and the MS is outside of QC limits, then a matrix effect is indicated and narrated accordingly.	Lab	Accuracy	75-125%

Matrix	Water
Analytical Group	Total Mercury
Concentration Level	Ultra Low
Sampling SOP	SB-9
Analytical Method/ SOP Reference	LB-8
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RPD 20%	If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision - Field	RPD 20%
Equipment rinsate blank (Sampling equipment)	4 per sampling season		• Reanalyze • If criteria are still not met, repeat initial calibration	Lab	Contamination	< MRL
Laboratory duplicate	At request of client	RPD 24%	• Reanalyze for verification • Notify client	Lab	Precision - Lab	RPD 20%
Initial Calibration Verification (ICV/QCS)	Beginning of every analytical sequence	80-120%	• If initial is out, terminate analysis; correct the problem; recalibrate or reprep with calibration curve.	Lab	Precision - Lab	80-120% of expected value for ICV.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per sample preparation batch of up to 20 samples. Note: additional prep blanks(s) required if additional BrCl needed in some sample(s).	The result must be within +/- RL.	• Redigest and reanalyze samples • Sample results greater than 20x the blank concentration are acceptable.	Lab	Contamination	The result must be within +/- the RL
Initial Calibration Blank (ICB)	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL (0.5 ng/L for aqueous, 1.25 ng/L for solid)	• Terminate analysis; correct the problem; recalibrate or reprep with calibration curve.	Lab	Contamination	The result must be within +/- the RL
Initial calibration	Daily prior to sample analysis/as per method	6 standards with the RSD ≤15%, Low Std One standard must be at the reporting limit.	• Correct the problem and reanalyze standards • Remake and reanalyze standards	Lab	Accuracy/Bias	6 standards with the RSD ≤15%
Continuing calibration verification samples (CCV/OPR)	After every 10 samples and at the end of each run	77-123% of expected value for CCV samples	• Terminate analysis, correct the problem • Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve.	Lab	Accuracy/Bias	77-123% of expected value for CCV samples
Laboratory control samples (LCS)	One per sample preparation batch of up to 20 samples	75-125% of expected value for aqueous samples	• Terminate analysis, correct the problem • If recovery is high and the analyte is not detected, document excursion only • Redigest and reanalyze all samples associated with the LCS.	Lab	Accuracy/Bias	Recovery within appropriate control limits (75–125%)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike and matrix spike duplicate samples (MS/MSD)	2 sets per sample preparation batch of up to 20 samples. If insufficient volume has been provided a Duplicate Laboratory Control Sample may be prepared and analyzed.	Recovery (71–125%) and RPD (<24%)	• If Recovery is not within QC limits, the LCS must be in control. • If the RPD is >24 %, document the excursion.	Lab	Accuracy/Bias	Flag the data, no flag required if the sample level is > 4Xthe spike added.

Matrix	Water
Analytical Group	Methyl Mercury
Concentration Level	Ultra Low
Sampling SOP	SB-9
Analytical Method/ SOP Reference	LB-3
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	Brooks Rand
No. of Sample Locations	See Worksheet #18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RSD 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision – Field	RSD 35%
Equipment rinsate blank (Sampling equipment)	4 per sampling season	< MRL	• Reanalyze for verification • Notify client	Frank McFarland	Contamination	< MRL
Laboratory duplicate	1 every 10 samples	RPD 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision – Lab	RPD 35%
Initial precision and recovery (IPR)	Set of four analyses	IPR within s (31%) and X (69–131%)	• Reanalyze	Frank McFarland	Initial method implementation and Precision – Lab	IPR within s (31%) and X (69–131%)
Ethylation Blank	Immediately after initial calibration,	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • Change air bubble tubing	Frank McFarland		

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	3 with every batch of samples	Average less than 2x MDL; StDev less than 2/3rds MDL	• Reanalyze for verification • If criteria are still not met, calculate batch specific MDL using standard deviation of the method blanks • If samples are non-detects using elevated detection limits, then redistill the affected samples and reanalyze at client's request	Frank McFarland	Contamination	Average less than 2x MDL; StDev less than 2/3rds MDL
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze until passes • If criteria are still not met, repeat initial calibration • All samples analyzed on affected equipment must be reanalyzed	Frank McFarland	Contamination	Less than reporting limit
Initial calibration	Calibrate prior to sample analysis/as per method	5 standards with the RSD ≤15%, Low Std. Recovery 65-135%	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Frank McFarland	Accuracy/Bias	5 standards with the RSD ≤15%, Low Std. Recovery 65–135%
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	80-120% of expected value for ICV; 67-133% of expected value for CCV samples	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Frank McFarland	Accuracy/Bias	80-120% of expected value for ICV; 67-133% of expected value for CCV samples
Laboratory control samples (LCS)	1 with every batch of samples	Recovery within appropriate control limits (70-130%) or as specified in QAPP.	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Frank McFarland	Accuracy/Bias	Recovery within appropriate control limits (70–130%)
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	Recovery (65-130%) and RPD (35%) or as specified in QAPP	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recovery is within QC limit, and RPD criterion is not met, reanalyze.	Frank McFarland	Accuracy/Bias	Recovery 65–135%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Detection Limit (MDL) Minimum reportable Limit (MRL)	Daily prior to sample analysis	0.02 ng/L 0.05 ng/L	• Reanalyze • If criteria are still not met, reprep blank and all associated samples • If concentration is high and the analyte is not detected, document excursion	Frank McFarland	Accuracy/Bias	0.02 ng/L 0.05 ng/L

Matrix	Tissue
Analytical Group	Pesticides[1]
Concentration Level	Low
Sampling SOP	SB-1, SB-3
Analytical Method/ SOP Reference	LB-9, LB-7, LB-10
Sampler's Name	Staff
Field Sampling Organization	QEA
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	1 per every batch of sample	< 1/2RL	• Reanalyze for verification • If >RL, reprepare and reanalyze batch If sample results >20x blank or ND, report results	Lab	Contamination	< 1/2RL
Initial calibration	Calibrate prior to sample analysis/as per method	%RSD≤20%	• Reanalyze standards • Remake and reanalyze standards		Accuracy	%RSD≤20%
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 20 samples or every 12 hours, and at the end of each run	ICV 80-120%R CCV 85-115% R	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed		Accuracy	ICV 80-120%R CCV 85-115%R

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	Control limit recovery 60-120% for each target analyte	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Frank McFarland	Accuracy	Control limit recovery 60-120% for each target analyte
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 MS/MSD with every batch of 20 samples	Control limit recovery 30-130% for each target analyte	• If Recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data		Accuracy	Control limit recovery 30-130% for each target analyte
Surrogate	Each method blank, LCS, field sample, and MS/MSD	30-130% recovery	• Reanalyze • If recovery is low, reprep sample (or associated samples). • If recovery is high and the analyte is not detected, document excursion only		Accuracy	30-130% recovery

[1]DDT and metabolites; hexachlorobenzene

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
Field notes Chain-of-custody records Corrective action forms		Sample receipt, custody, and tracking records Standard traceability logs Equipment calibration logs Sample preparation logs Run logs Equipment maintenance, testing, and inspection logs Corrective action forms Reported field sample results Reported results for standards, QC checks, and QC samples Instrument printouts (raw data) for field samples, standards, QC checks, and QC samples Sample disposal records Telephone logs Raw data (stored on CD or DVD)	Field sampling audit checklists Field analysis audit checklists Fixed laboratory audit checklists Data Usability Summary Report Corrective action forms	

Matrix	Analytical Group	Concentration Level	Sample Locations/ID Numbers	Analytical SOP	Data Package Turnaround Time[1]	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Fish Tissue, Invertebrates, Sediment	Total mercury	Low	See Worksheet #17	LB-1	28 days	TestAmerica Burlington 30 Community Drive Suite 11 South Burlington, VT 05403 Kirk Young 802-923-1017	N/A
Invertebrates, Sediment, Water	Methylmercury	Low	See Worksheet #17	LB-3	28 days		N/A
Fish Tissue	Total PCBs	Low	See Worksheet #17	LB-4	28 days		N/A
	Pesticides: DDT and metabolites, hexachlorobenzene	Low	See Worksheet #17	LB-9	28 days		N/A
	PCDD/PCDFs	Low	See Worksheet #17	LB-2	28 days		N/A
	Lipids	Medium	See Worksheet #17	LB-6	28 days		N/A
Water	Total mercury	Low	See Worksheet #17	LB-8	28 days		N/A
Sediment	Total organic carbon	Medium	See Worksheet #17	LB-5	28 days		N/A

[1]Turnaround times for Brooks Rand analyses (methylmercury analyses in invertebrate tissue, sediment, and water) begin when samples come off hold (i.e., if samples are held until the 5-sample minimum sample delivery group is met).

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Field sampling technical systems audit	Yearly	Internal	QEA	Margaret Murphy, Project Manager, QEA	Field staff, QEA	Field staff, QEA	Field staff, QEA

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Field sampling Technical Systems Audit (TSA)	Verbal communication or written audit report	Maryanne Kosciewicz, QA Officer and/or Ed Glaza, Project Manager, Parsons	48 hrs	Written document (electronic or hardcopy)	Maryanne Kosciewicz, QA Officer and/or Ed Glaza, Project Manager, Parsons	48 hrs

Project oversight (field and laboratory) will consist of periodic inspection and audits of sampling and analytical techniques, as required by NELAC/ELAP (annual internal laboratory and field audit; external audit by NELAC/ELAP certified inspectors every two years). No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken, and any client whose work is affected will be notified immediately in writing.

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Field sampling technical systems audit report	Yearly	Deficiencies reported within 48 hours of audit and Corrective Action Response within 48 hours of audit report receipt	Margaret Murphy, Project Manager, QEA	Ed Glaza, Project Manager, Parsons
Data usability assessment report	Yearly	June following field season	Exponent and/or Parsons	Tim Larson, NYSDEC

Verification Input	Description	Internal/ External	Responsible for Verification (Name, Organization)
Chain-of-custody forms	Chain-of-custody forms will be reviewed internally upon their completion and verified against the packed sample coolers they represent. A copy of the chain-of-custody forms will be attached to the data report.	I	Respective Laboratory Staff, Brooks Rand and TestAmerica
Field notes	Field notes will be reviewed internally and placed in the site file. A copy of the field notes will be attached to the final report. TestAmerica Project Manager will review notes as provided by Parsons with chain-of-custody documentation.	I	Respective Laboratory Staff, Brooks Rand and TestAmerica
Laboratory data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal. All received data packages will be verified externally according to the data validation procedures specified in Worksheet #36	I, E	Respective Laboratory Staff, Brooks Rand and TestAmerica

For Brooks Rand, the laboratory's QA officer will perform a verification of chemical data. For TestAmerica, the laboratory analyst and group supervisor or experienced peer will perform a verification of chemical data. The laboratory will be responsible for the review and verification of all work sheets and data packages, manual entry or transcription of data, and any professional judgments made by an analyst during sample preparation, analysis, and calculation, and reporting of the final concentrations. The laboratory will also be responsible for reviewing quality control results to determine whether data are of usable quality or reanalysis is required. Any nonconformance issues identified during the laboratory's quality assurance checks will be corrected and noted by the laboratory. Close contact will be maintained between the Laboratory Director, the QA Officer, and the Scientific/Technical Manager, so that any quality issues can be resolved in a timely manner. Any data quality deviations will be discussed in the laboratory data narrative, including the direction or magnitude of any bias to the data, if possible.

Responsibilities for verification of data and sampling activities

Project Personnel	Verification Activity
Compliance	
Field Manager/ Parsons QA Officer	Assign appropriate staff to perform the work and ensure that all field personnel are familiar with the field SOPs
	Verify that the proper sampling protocols, including sample preservation, handling, and storage are performed during field work
	Track the samples sent to the laboratories; verify that the chain-of-custody forms are filled out correctly and that samples were received in good condition at the appropriate laboratory
	Verify that the appropriate number of field blanks and sample duplicates/triplicates are collected
	Conduct field data collection audit to ensure that the proper field procedures are followed
Parsons QA Officer/ Brooks Rand QA Officer and TestAmerica Second Level Reviewer	Verify that the laboratory instruments are calibrated, and quality control samples are analyzed (e.g., blanks, duplicates, MS/MSD, LCS)
	Verify that the laboratory conducted proper calibration and quality control sample procedures (i.e., the laboratory followed the contract scope of work)
	Confirm that the analytical data meet specified detection limits in analytical SOPs
Correctness	
	Inspect and ensure that the field and analytical equipment are calibrated and properly functioning in accordance with field instrument user manuals and laboratory QA manuals
Parsons QA Officer Brooks Rand QA OfficerScientific/Technical Manager and TestAmerica Analyst and Second Level Reviewer	Review data reduction process, examine the raw data to verify that the correct calculations of sample results were reported by the laboratory or transferred from field logs, examine the raw data for any anomalies, and verify that there are no transcription or reduction errors
Consistency (Comparability)	
Parsons QA Officer	Ensure that proper data-handling procedures were followed (e.g., the SOPs and contract scope of work are followed consistently throughout the project); recheck any handwritten data in field logs for transcription errors
	Review data transfer procedures and make all efforts to minimize data problems
Completeness	
Field Manager	Verify proper documentation of chain-of-custody and sample handling/transfer procedures, document any problems encountered during sample collection, identify any problems with damaged samples, and confirm with laboratory that all samples have been received

Project Personnel	Verification Activity
Field Manager Parsons QA Officer	Ensure that an accurate record was maintained during sample collection and analysis
Brooks Rand Laboratory Personnel and QA Officers	Document that general quality control measures were conducted (e.g., instrument calibration, routine monitoring of analytical performance, calibration verification)
Test America Analyst, Second Level Reviewer, and Project Manager	Ensure that a unique sample number was assigned to each sample
	Document deviations from scope of work (e.g., analytical procedures), document any corrective actions taken if QC checks identify a problem, ensure that the appropriate analytical method was used.

Note: LCS - laboratory control sample
MS/MSD - matrix spike/matrix spike duplicate
QA/QC - quality assurance and quality control
SOP - standard operating procedure

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	SOPs	Ensure that all sampling and analytical SOPs were followed.	Laboratory Primary and Second level reviewers, TestAmerica; Misty Kennard-Mayer, Brooks Rand
IIa	Documentation of Method QC Results	Establish that all method required QC samples were run and met required limits.	Laboratory Staff at TestAmerica and Brooks Rand
IIb	Documentation of QAPP QC Sample Results	Establish that all QAPP required QC samples were run and met required limits	Laboratory Staff at TestAmerica and Brooks Rand
IIb	Project Quantitation Limits	Establish that all samples results met the project quantitation limits specified in the QAPP	Laboratory Staff at TestAmerica and Brooks Rand
IIa	Raw Data	Review 100% of raw data to confirm manual laboratory calculations and review 10% review of raw data to confirm automated laboratory calculations	Laboratory Staff at TestAmerica and Brooks Rand

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa	All Matrices	All Analyses	Low	QAPP Worksheets #12, #15, and #28	Exponent and/or Parsons

Data verification and assessment will be completed by Exponent and/or Parsons. EPA has not prepared national functional guidelines for the low-level total mercury, methylmercury, total organic carbon, and the conventional parameter analyses. Therefore, chemical data for these analytes will be verified and assessed following the "evaluation procedures" specified in National Functional Guidelines (e.g., assessment of holding times, accuracy, and precision data). For these data, method-specific quality control requirements and laboratory-established control limits (as presented in the QAPP), as they are applicable to the analytical methods being used, will be used to determine whether data require qualification. PCBs data will be verified and assessed according to USEPA's National Functional Guidelines for Organic Data Review (USEPA 1999) and the PCDD/PCDF data will be verified and assessed according to USEPA's National Functional Guidelines for Chlorinated Dioxin/Furan Data Review (USEPA 2005). The method-specific quality control requirements and laboratory-established control limits (as presented in the QAPP) will be relied on for data evaluation and qualification when these limits differ from those presented in the National Functional Guidelines for the PCB and PCDD/PCDF analyses. In addition to the guidance documents cited, a primary source of validation criteria will be applicable USEPA Region 2 data review SOPs. Specifically, SOP HW-2 will be used for total mercury (with slight modification based on differences between the CLP SOW and SW-846); HW-19 for PCDD/PDCFs by 8290; and HW-45 for PCBs by Method 8082A. To the extent applicable, the Region 2 SOPs will take precedence over the more generic National Functional Guidelines.

Consistent with the Pre-Design Investigation QAPP (Parsons 2005), the first phase of the data review process is contract compliance screening (CCS) and involves review of sample data deliverables for completeness. The PDI QAPP describes this process as follows:

> "Completeness is evaluated by ensuring that all required data deliverables are received in a legible format with all required information. The CCS process also includes a review of the chain-of-custody forms, case narratives, and reporting limits. Sample resubmission requests, documentation of nonconformances with respect to data deliverable completeness, and corrective actions often are initiated during the CCS review. The results of the CCS process are incorporated into the data validation process."

The second phase of data review is data validation. As discussed in Worksheet #11, EPA Level III validation protocol will be applied to all analytes except total mercury, methylmercury, and nitrate. These three analytes will be validated according to EPA Level IV validation protocol. The PDI QAPP describes Level III validation as follows:

> The EPA Level III validation protocol….includes a review of summary information to determine adherence to analytical holding times; results from analysis of field duplicates, method blanks, field blanks, surrogate spikes, MS/MSDs, LCSs, and sample temperatures during shipping and storage. Data qualifiers are applied to analytical results during the data validation process based on adherence to method protocols and laboratory-specific QA/QC limits.

For Level III validation, instrument calibrations, calculations, and transcriptions will not be checked because the laboratories will be responsible for 100-percent verification of these results and procedures. For total mercury, methylmercury, total PCBs, DDT and metabolites, hexachlorobenzene, and PCDD/PCDFs (i.e., the Level IV data quality objectives), ten percent of the data will undergo a Level IV validation, which incorporates the Level III validation protocol and adds calculation checks from the raw data of reported and summarized sample data and QC results.

Data qualifiers will be applied to the results according to procedures described in the EPA Contract Laboratory Program national functional guidelines for inorganic data review (U.S. EPA 2004), as applicable, with modifications as appropriate to accommodate method-specific quality control requirements or when specific MQOs and DQIs established for this project (e.g., control limits for bias and precision) are not achieved.

Algorithms to Assess Quality Control Results

Data verification includes checking that quality control procedures were included at the required frequencies and that the quality control results meet control limits defined in the method descriptions. The equations provided below will be used to determine whether measurement targets for project requirements were met for each quality control procedure.

Duplicate and Triplicate Analyses — Precision for duplicate chemical analyses will be calculated as the relative percent difference (RPD), expressed as an absolute value, between the duplicate samples. Replicate precision will only be assessed for sample results greater than 5 times the method detection limit due to increased variability at low concentrations. When replicate results are less than 5 times the method detection limit the absolute difference of the results will be evaluated. The formula that will be used to assess precision for both laboratory and field duplicate samples is as follows:

$$RPD = \left| \frac{D_1 - D_2}{(D_1 + D_2)/2} \right| \times 100$$

where:

D1 = sample value, and

D2 = duplicate sample value.

The percent relative standard deviation of triplicate sample data points will be calculated to evaluate replicate precision. The formula for relative standard deviation is as follows:

$$\%RSD = \frac{100 \times s}{\bar{x}}$$

where:

s = standard deviation, and

$\bar{x}$ = mean sample value.

Matrix Spike Recoveries — Spiked samples provide an indication of the bias of the analytical system. The recovery of MSs will be calculated as the ratio of the recovered spike concentration to the known spiked quantity:

$$\%R = \frac{A - B}{C} \times 100$$

where:

A = the analyte concentration determined experimentally from the spiked sample,

B = the background level determined by a separate analysis of the unspiked sample, and

C = the amount of the spike added.

Completeness — Completeness will be calculated for each sample type by dividing the number of valid measurements (all measurements except rejected data) actually obtained by the number of valid measurements that were planned:

$$\%\text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

To be considered complete, the data sets must also contain all quality control check analyses that verify the precision and accuracy of the results.

Sensitivity — The detection limit of the sample preparation and analysis process is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte is greater than zero" (40 CFR 136B); it is the concentration at which qualitative, not quantitative, identification can be made.

Best professional judgment is used to adjust the limit of detection upward in cases where high instrument precision (i.e., low variability) results in a calculated limit of detection and equivalent instrument response that are less than the absolute sensitivity of the analytical instrument. The actual reporting limit for environmental samples is generally higher than the instrument detection limit, because the sample matrix tends to contribute to fluctuations in the instrument's background signal. Although reporting limits have been established (Worksheet #15 series), achievement of these reporting limits is based on the analysis of samples without matrix interferences. In the event that matrix interferences are encountered (on a sample-specific basis), laboratory personnel will determine whether elevated *reporting limits* are required. Whether to report elevated reporting limits will be determined based on the experience of the laboratory with samples of matrix similar to those collected for this study and on the response of each instrument to samples for this study. The MRLs will be verified during data validation.

Blanks Actions – The data will be assessed in accordance with the general guidance specified by the Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (USEPA, 2004) since the quality control associated with these analyses are similar to the inorganic methods. With the exception of mercury, there are no published data validation procedures for these analytical methods. For this study the data validator will try to limit the negation of results due to blank action levels (U qualified) based on the judgment that imprecise low concentration results are more useful in the analysis for this study then negated results. Sample results will be compared to the associated instrument, method, and field blank results to assess the potential for contamination. Sample results less than 5 times the associated blank concentration will be qualified as estimated and potentially biased high (J+).

Reference:

Parsons. 2005. Onondaga Lake Pre-Design Investigation Quality Assurance Project Plan, Syracuse, New York. Prepared for Honeywell, Morristown, NJ. Parsons, Liverpool, NY.

USEPA. 1999. USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review. EPA-540/R-99-008. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, Washington, DC.

USEPA. 2004. USEPA Contract Laboratory Program national functional guidelines for inorganic data review. EPA/540-R-04-004. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

USEPA. 2005. USEPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Review. EPA-540-R-05-001. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used:
See Worksheet #36 and associated text.

Describe the evaluative procedures used to assess overall measurement error associated with the project:
Algorithms to Assess Quality Control Results
See Worksheet #36 and associated text.

Identify the personnel responsible for performing the usability assessment:

See Worksheet #36 and associated text.

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:
The data quality and usability report will be prepared by Exponent and/or Parsons on behalf of Honeywell. The report will meet the requirements for a NYSDEC data usability and summary report (DUSR) as described in Appendix B of the 2002 Draft Voluntary Cleanup Guide (NYSDEC Division of Environmental Remediation, Albany, NY). The report will summarize the results of the data validation and data quality review and will describe any significant quality assurance problems that were encountered. The report will include the following items:

- Project Objectives and Background
- Description of sample collection methods (including a description of deviations from planned sampling activities that may have occurred and the impact, if any, on the project and quality objectives) and shipping, including chain-of-custody and holding-time documentation
- Description of analytical methods (including a description of deviations in laboratory procedures that may have occurred and the impact, if any, on the project and quality objectives) and detection limits
- Summary of Data Verification performed by the laboratory and a description of any deviations from the work plan and quality assurance project plan
- Summary of Data Validation performed by Exponent and/or Parsons with appendix tables detailing the validation findings
- General overview and test-specific summaries of data usability
- Tables detailing 1) target analyte list, methods, and method detection and reporting limits; 2) listing of study analytes and projected and actual analyses, 3) verification activities and responsible project personnel, 4) analytical components and associated appendix tables, 5) sample analysis summary count by event date, and 6) data usability summary by parameter.
- Appendices containing the data validation summary tables, analytical result summary tables, analytical result graphs, analytical quality control results, chain-of-custody documents, and results of the biological components of the work (i.e, gut analyses, field observations, fish community analysis, invertebrate community analysis)