APPENDIX N: MONITORED NATURAL RECOVERY ONONDAGA LAKE FEASIBILITY STUDY

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EXECUTIVE SUMMARY

The purpose of this appendix is to determine whether monitored natural recovery (MNR) is a feasible technology for remediating contaminated sediments in Onondaga Lake. MNR could be applied either as the primary remedial technology or as an adjunct to other remedial technologies (e.g., thin-layer capping). This appendix evaluates conditions and locations within the lake where MNR may be effective, and considers the uncertainties associated with this evaluation. This appendix is not intended to provide a full evaluation of MNR under every possible remedial scenario or set of remedial alternatives. Follow-on feasibility study (FS) evaluations will provide a more focused evaluation of MNR integrated with other remedial technologies.

This appendix evaluates MNR for those areas that currently exceed one or more relevant sediment toxicity benchmarks. For example, some areas of the littoral zone do not currently exceed the probable effects concentration (PEC, one potential benchmark). It is assumed for the purposes of this appendix that areas currently below relevant remedial benchmarks would not require a remedy such as MNR.

MNR can occur through a variety of physical, chemical, and biological processes that act singly or in combination to reduce chemical concentrations, exposure, or mobility. This process can occur in all matrices at a site (e.g., water, sediments and fish tissue). Because sediments are usually an important sink for chemicals and a potential exposure pathway to organisms, the focus of MNR is often on contaminated sediments and the mechanisms that affect them. The primary focus of this appendix is natural recovery in sediments, which explicitly includes a monitoring and contingent response component implemented over the recovery period. Thus, MNR is not to be equated with "no action."

The U.S. Environmental Protection Agency (USEPA) is currently formulating a framework for the evaluation of MNR at sediment remediation sites (USEPA, 2002). USEPA is working with groups such as the Remediation Technologies Development Forum (RTDF) to develop a weight-of-evidence approach for evaluating MNR at contaminated sediment sites (Evison, 2003). The process being developed includes steps such as data assessment, modeling, and site monitoring to facilitate a thorough evaluation of MNR for contaminated sediment sites. USEPA's MNR framework is intended to promote appropriate technical evaluation, increase certainty, and provide decision-makers greater confidence in the selection and implementation of this remedial option as a permanent, effective means of risk reduction.

Recent discussions within USEPA and the RTDF of these approaches have focused on five primary lines of evidence. These include:

- Source characterization;
- Fate and transport processes;
- Historical chemistry trends;

- Historical biological trends; and
- Predictive modeling.

The primary conclusions of this natural recovery appendix based on these five lines of evidence are the following:

- Ongoing source controls by others and Honeywell can be expected to lead to a small reduction in total suspended solids (TSS) loading and a more substantial reduction in mercury loading to the lake.
- Fate and transport processes indicate profundal sediments (at depths of more than 30 ft [9 m]) are more stable. Thus, they are more amenable to natural recovery, while recovery of sediments in upper littoral areas (water depths of less than 20 ft [6 m]) is expected to be less effective.
- Water column, sediment, and biological tissue chemistry trends all appear to have been relatively stable (neither increasing nor decreasing) over the last 10 years, although statistical uncertainty/variability associated with the historical database preclude a rigorous trend analysis.
- These stable historical trends do not account for source control efforts expected to significantly reduce mercury loads to the lake. Thus, predictive modeling is needed to reliably forecast future conditions in the lake associated with MNR.
- Predictive modeling indicates that decreases in mercury surface sediment concentrations can be expected for all profundal and deeper littoral sediments. Sediments in these areas that contain up to 6.7 milligrams per kilogram (mg/kg) total mercury, as measured in 1992, are expected to achieve the PEC of 2.2 mg/kg within a period of 10 years following upland and lake remediation. The profundal and deeper littoral areas would also be expected to meet the apparent effects threshold (AET) of 13 mg/kg, particularly because the vast majority of these areas already meet this benchmark concentration.
- Modeling indicates that the current surface weighted average mercury concentration in profundal sediments of approximately 2.6 mg/kg would be reduced to between 0.7 mg/kg (assuming ongoing anaerobic conditions) and 1.2 mg/kg (assuming an aerobic hypolimnion and benthic recolonization) within 10 years following remediation of upland and internal sources of mercury.
- Modeling indicates that surface sediment mercury concentrations will approach the settling sediment mercury concentrations over time.
- Evaluation of methylmercury fluxes from the profundal sediments using the predictive model indicates overall, with considerable uncertainty, that profundal sediments are a sink rather than a source of methylmercury to the hypolimnion. There may be seasonal variations that cause this balance to reverse, which are not reflected in the predictive model.

- The predictive model suggests that MNR by itself is not likely to substantially reduce the upward flux rate of methylmercury from the profundal sediments. However, this conclusion is based on the assumption that source controls will have little impact on the concentrations of methylmercury in settling sediments, which may not be the case.
- The predictive model suggests that MNR combined with aeration (oxygenation) may cause a substantial reduction in methylmercury fluxes from the profundal sediments over time.

A computer model that mimics the natural processes in sediments is presented in this appendix, and the results of that model are used to make some of the conclusions noted above. The purpose of the model is to better understand natural processes that may be very complex. The output or results from the model are presented in terms of expected future chemical (usually mercury) concentrations in surface sediments in the deep areas of the lake. The model looks at present-day conditions and predicts how those conditions are expected to change several years in the future. Thus, the model estimates how high a chemical concentration observed today (or in 1992 when the last comprehensive data were collected) will be able to attain a desired chemical concentration sometime in the near future.

Overall, MNR is a feasible remedial technology for the profundal sediments of Onondaga Lake. This technology appears to have value both by itself and potentially in combination with thin-layer capping in any areas of relatively high baseline mercury concentrations (e.g., >6.7 mg/kg; 1992 data), where they may exist in the profundal sediments.

The concentrations noted above are based on the most recent available data set, which is from 1992. Additional data will be collected as a part of the remedial design process, and these data will be used in any future predictions of natural recovery projected forward for the appropriate natural recovery period as determined by NYSDEC. Thus, the concentrations noted above will not be used to make remedial design decisions regarding the exact areas suitable for MNR versus thin-layer capping.

SECTION N.1

INTRODUCTION

N.1.1 PURPOSE OF THIS APPENDIX

The purpose of this appendix is to determine whether monitored natural recovery (MNR) is a feasible remedial technology for Onondaga Lake remediation. This includes an evaluation of conditions and locations within the lake where MNR may be effective, as well as consideration of the uncertainties associated with this evaluation.

This appendix is not intended to provide a full evaluation of MNR under every possible remedial scenario or set of remedial alternatives. However, this appendix supports scenariobased evaluations and comparisons in the main text of the feasibility study (FS) in a consistent and scientifically appropriate manner. It is anticipated that evaluations from this appendix and/or the main text of the FS may need to be further augmented in the pre-design process for selected alternatives that may involve MNR, including updating baseline data on sediment chemistry, detailed long-term monitoring methods, compliance criteria, and contingency measures.

N.1.2 IMPORTANT SITE CHARACTERISTICS

The general characteristics of Onondaga Lake are described in the 2002 remedial investigation (RI) (TAMS, 2002) and summarized in Section 1 of the FS. However, it is worthwhile to briefly review some of these characteristics that are important for a discussion of MNR.

The lake has a surface area of approximately 4.6 square miles (12 million square meters) with a maximum depth of about 60 ft (19 m). It is generally classified as eutrophic due to a variety of historical and ongoing urban inputs.

The lake is commonly divided into vertical strata, the definition of which can vary depending on the purpose of the discussion. From a water column perspective, the lake in summer is separated into the warm epilimnion (upper layer) and cold hypolimnion (lower layer). They are divided by the thermocline, which commonly occurs at approximately 30 ft (9 m) below the water surface during the summer months. Throughout the summer, the hypolimnion is generally anoxic. There is a weak inverse stratification (cold water above warmer water) under the ice in the winter, with turnover in the spring and fall.

Sediments in the lake are differentiated into the littoral shoreline and profundal basin sediment beds. This division reflects differences in biological characteristics and sediment stability. The littoral areas are subject to substantially greater light penetration, wave action, resuspension, and drift along the shoreline, compared to the more light-limited and depositional environment characteristic of the deeper profundal zone sediment bed. Although there is a continuum of biological and physical characteristics of sediments, the division between littoral and profundal sediments has been defined by the New York State Department of Environmental Conservation (NYSDEC) for the purposes of the FS as 30 ft (9 m) water depth (TAMS, 2002).

Sediment coring records show that sediments permanently settle in the profundal basins and that these are net depositional areas. However, there may be some mechanisms, such as ebullition of methane gas bubbles (discussed more below), that contribute to some disturbance of these sediments.

N.1.3 CHEMICALS INVESTIGATED

The sediment bed in both the littoral and profundal areas contains elevated concentrations of chemicals from a variety of industrial and urban sources around the lake. Mercury has been of particular concern because of the relatively high concentrations of this metal in some areas of the lake, its spatial ubiquity, and its propensity to bioaccumulate as methylmercury in biological food chains. The distribution of total mercury in the top 6 inches (15 centimeters [cm]) of bed sediments in the lake is shown in Figure N.1. Chemical parameters of interest (CPOIs) based on toxicity are:

- Mercury
- Ethylbenzene and xylenes
- Chlorobenzene
- Dichlorobenzenes
- Polycyclic aromatic hydrocarbons (PAHs)
- Polychlorinated biphenyls (PCBs)
- PCDD/PCDFs (dioxin/furans)

Most of these chemicals occur at concentrations of potential concern in portions of the sediment bed in the lake. These chemicals can also occur in conjunction with physical wastes, with the most notable being the in-lake waste deposit (ILWD) in the Harbor Brook area at the southern end of the lake. The distributions of these chemicals and wastes are described in more detail in Section 1 of the FS.

The organic CPOIs are subject to breakdown (or biodegradation) into other organic constituents over time. This process is often mediated by microorganisms in waters and sediments. The rates of biodegradation of these chemicals can vary widely depending on the concentrations and prevailing site-specific conditions.

Total mercury cannot degrade. Therefore, it does not benefit from this process in natural recovery scenarios. This fact, combined with the relatively high concentrations of mercury in most areas and matrices of the site, indicates that a focus on mercury in this appendix is warranted. Mercury can be viewed as the most important chemical "driver" of the natural recovery process and can act as a conservative surrogate for most chemicals.

The RI (TAMS, 2002) was reviewed regarding organic chemical concentrations in surface sediments. Outside of the well-identified areas of concern, including Sediment Management Units (SMUs) 1, 2, 3, 4, 6, and 7, the concentrations of benzene, toluene, ethylbenzene, and

xylene (BTEX), chlorobenzenes, and low molecular weight PAHs (LPAHs) are generally near or below toxicity benchmarks of potential significance identified in the RI. High molecular weight PAHs (HPAHs) and PCBs show elevated levels relative to toxicity benchmarks in the RI in some profundal areas. However, these chemicals rarely result in overall toxicity as measured by the mean probable effects concentration quotient (PECQ). (The mean PECQ and its use are discussed more in Appendix J, sediment effect concentrations [SECs]). As shown in Figure N.2, there are no exceedances of the mean PECQ2 in the profundal area and very few exceedances of the mean PECQ1. Consequently, it is appropriate to focus on mercury as the primary CPOI with regard to effectiveness of MNR.

SECTION N.2

DESCRIPTION OF MONITORED NATURAL RECOVERY AS A REMEDIAL TECHNOLOGY

N.2.1 CONCEPT

MNR involves allowing natural processes to decrease the concentration, mobility, bioavailability, toxicity, and/or exposure of chemicals following implementation of effective source controls. Generally, MNR occurs in a specified time frame over which attainment of site-specific cleanup levels is expected to occur. MNR includes a monitoring component to confirm that decreases in chemical concentrations or exposures occur as expected. It also includes contingency planning procedures in the event that the effectiveness of natural recovery processes is not confirmed. Such contingency planning might involve a range of activities from additional monitoring to implementing more active remedial technologies.

As summarized in *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (USEPA, 2002), MNR has been selected as a remedial technology for numerous Superfund contaminated sediment sites containing a variety of chemical contaminants. It has usually, although not always, been used in combination with other remedial technologies such as dredging and/or capping of higher-concentration sediment deposits. For example:

- MNR was selected as part of the final remedy for portions of the Eagle Harbor Superfund Site in Washington to address "moderate effect" sediment areas containing mercury and PAHs (USEPA, 1994).
- In Lake Hartwell, South Carolina, MNR was used to remediate residual sediment PCB contamination following upstream source control efforts (Magar *et al.*, 2003).
- MNR has been an integral part of the overall remedy for Bellingham Bay, Washington where mercury in sediments from a chlor/alkali plant is the primary chemical of concern (Washington State, 2002).

USEPA has noted that although partial natural recovery has been observed in many areas, there is not yet an extensive body of literature documenting complete recovery at contaminated sediment sites in general. Also, in some systems such as Lake Hartwell, trends in fish tissue chemical concentrations may not be identical to those trends seen in sediments. However, as noted by USEPA (e.g., Swindoll *et al.* 2000; USEPA, 2001a; USEPA, 2001b; Washington State, 2002), monitoring results from some areas are promising.

When MNR has been selected as part of the final cleanup remedy for a site, it has generally been applied over a defined recovery period, typically beginning with the completion of effective source controls or in-water remedial actions, whichever occurs later. For example, at the Commencement Bay Superfund Site in Tacoma, Washington, the CERCLA record of decision (ROD) specifies that marginally contaminated areas are expected to recover naturally to meet the project sediment quality objectives within 10 years after source control and remediation (USEPA, 1989). Areas that will not meet sediment quality objectives in 10 years are considered unsuitable for natural recovery as a remedial technology. Chemicals of concern in Commencement Bay include mercury, a number of other metals, chlorobenzenes, PAHs, pesticides, and PCBs. At the Fox River Superfund site in Wisconsin, the ROD remedial action objective for PCBs in fish establishes the expectation of fish tissue recovery within 10 to 30 years after source control and remediation, depending on beneficial use being protected (WDNR and USEPA, 2003).

Another important concept is that MNR would apply to those areas of the site that currently exceed relevant chemical toxicity benchmarks such as the ER-L, probable effects concentration (PEC), or site-specific bioaccumulation based values. For example, surface sediment concentrations of mercury presented in the RI (TAMS, 2002) indicate that many of the littoral areas, particularly in SMUs 3 and 5, are below concentrations of potential concern, relative to at least some of these benchmarks. Consequently, evaluations of MNR for this chemical would not focus on these types of areas.

N.2.2 MECHANISMS OF NATURAL RECOVERY

MNR can occur through a variety of physical, chemical, and biological processes that act singly or in combination to reduce chemical concentrations, exposure, or mobility. MNR can occur in all matrices at a site, such as water, sediments, and fish tissue. Because sediments are usually an important sink for chemicals and a potential exposure pathway to organisms, the focus of MNR is often on contaminated sediments and the mechanisms that affect them.

Accordingly, the primary focus of this appendix is natural recovery in sediments. However, recovery in other matrices is included more generally in this evaluation. Recovery of biological systems is one of the key measures of MNR that relates to all matrices of potential concern and is a primary component of MNR evaluation as an effective remedial technology.

N.2.2.1 General Mechanisms

MNR can include several mechanisms that affect the surface and near surface of the sediment bed. General mechanisms for MNR in sediments are illustrated in Figure N.3. These mechanisms include:

- Mixing of incoming (settling) clean sediments from the water column with bed sediment chemicals. This dilutes the chemical concentrations and often is the first step before burial.
- Burial of bed sediments containing chemicals by incoming clean, sediments from the water column.
- Degradation (aerobic and/or anaerobic) of organic compounds within sediments.
- Reduction of chemical mobility or toxicity by conversion to less toxic forms (e.g., metals bound to sulfides) and/or forms that are more highly adsorbed to bed sediments.

- Diffusion/advection of chemicals to the water column (i.e., depletion to the water column).
- Transport of sediments containing chemicals and dispersion over wider areas at lower concentrations.

These processes are interrelated, but they do not always work in concert. For example, if sediments from the water column containing high chemical concentrations are settling onto bed sediments, these chemical inputs may overwhelm any decreases in sediment chemical concentrations caused by burial, diffusion/advection, and/or degradation. For this reason, effective source control is a necessary first step in any MNR scenario.

The last two of these MNR mechanisms may not always be desirable. Clearly, if dispersion of chemicals over wider adjacent areas or to other matrices increases toxicity in those areas, such processes are not considered effective in natural recovery. Thus, it is important that natural recovery evaluations consider these processes in the overall recovery evaluation.

Burial, which isolates contaminated sediments under a layer of new, cleaner sediments, is often a key process for natural recovery. The most simplistic form of burial is when sediments settling out of the water column cover the existing sediment bed and remain in place permanently. While this is generally the case in very quiescent areas, the process of burial is often dynamic. In many cases, the overall trend may be one of net sedimentation and burial of sediments over time, but this may include episodes of resuspension of some portion of the sediment bed due to physical disturbances such as wind/wave-generated currents. This process causes both vertical and lateral mixing and can smooth chemical gradients that might otherwise exist in the sediment bed. Thus, it is important to distinguish between gross and net deposition rates when evaluating burial as a natural recovery mechanism and recognize that the bed sediments themselves (either from the same or other areas) may be a component of the material settling on and interacting with the sediment bed at any one time or location.

Even in quiescent areas, burial rarely results in discrete layers of sediment deposition. Biological activity in surface sediments can cause mixing and turnover of material within the upper sediment layer in a process referred to as bioturbation. Physical forces, as discussed above, can cause movement and mixing even when complete resuspension of sediment particles is not achieved. These processes also contribute to the dynamic nature of burial.

N.2.2.2 Mechanisms in Onondaga Lake

This subsection provides a brief review of some critical issues related to MNR mechanisms as they apply to Onondaga Lake. Section N.4 incorporates these factors in a detailed review of fate and transport processes in Onondaga Lake.

Degradation, conversion of toxic forms of chemicals, and diffusion/advection from the sediment bed are chemical processes that are known to occur in a variety of aquatic systems, including freshwater lakes such as Onondaga Lake. The rates of these processes and the conversions that take place can vary widely and depend on the chemicals involved, the geochemistry of the sediments, and the chemistry of overlying waters.

For degradation and conversion reactions, the presence of oxygen is often one of the most critical factors in determining the rates of degradation. Biodegradation rates of many organic compounds vary widely in anaerobic versus aerobic environments, often being slower in anaerobic environments (Aronson and Howard, 1997) such as those occurring in the profundal sediments of Onondaga Lake. For example, Aronson and Howard (1997) reported that benzene often does not degrade at all under anaerobic conditions but has aerobic half-lives (the time it takes for half the chemical present to degrade) from 0.02 to 1.46 years.

The forms of some metals, such as mercury, are highly dependent on the reduction-oxidation (redox) potential of the system, as well as other factors such as pH. The production of methylmercury (the bioaccumulative form of mercury) occurs more readily in reducing, anoxic environments. As a result, the conversion reactions could vary in the surface layers of profundal versus the littoral sediments of Onondaga Lake.

Diffusion rates are determined by the properties of a chemical and the concentration gradients that exist in the aquatic system. Diffusion is likely to occur almost anywhere in the lake, but the rates depend on the differences in concentrations present in, for example, sediment porewater versus the water column. Advection rates are determined primarily by the movement of groundwater, which has the potential to be greater in nearshore areas versus profundal areas (Appendix D, groundwater issues; Effler, 1996).

Mixing, burial, and dispersion of sediments typically vary between profundal and littoral sediments. Shallow littoral areas are more dynamic, with greater resuspension due to wind/wave action, slower net burial (except near river/creek mouths, where substantial material may be deposited) or greater erosional loss over time, and active mixing of sediments by bioturbation and physical forces. Due to the quiescence and periodic anoxia in the profundal basins, these sediments have little or no resuspension, little if any bioturbation, and mixing is likely extremely limited (Effler, 1996). In between, in the deeper littoral areas from 20 to 30 ft (6 to 9 m) below the water surface, there is likely a continuum from the more dynamic shallow littoral processes toward the profundal sedimentation processes.

N.2.3 MONITORING – A CRITICAL COMPONENT OF THE TECHNOLOGY

MNR includes monitoring and contingency response components. The primary difference between MNR and "no action" is the monitoring and contingency plans that are prepared and then implemented during the natural recovery period.

Selection of MNR as a remedial technology involves a prediction of future conditions. Regardless of the amount of existing data and/or detail of predictive modeling, some amount of uncertainty will exist regarding future conditions at a site. The monitoring component of MNR is needed to track the progress of changes in the matrices of interest and determine whether the expected and/or acceptable changes are actually occurring.

The monitoring plan should focus on those measures that will be used to determine the acceptability of future conditions and answer questions of scientific, regulatory, or public concern about the future environment. Thus, the monitoring plan should have measures and specific performance criteria that are tailored to each site and situation. However, some general

recommendations have been made by the Remedial Technologies Development Forum (RTDF) (e.g., Patmont, 2003) for all MNR monitoring programs, including:

- Statistically based sediment chemistry monitoring, including both surface and subsurface sediment samples collected at regular intervals and
- Statistically based biological monitoring focused on key exposure and risk endpoints such as tissue chemistry.

If MNR becomes part of the lake-wide remedial alternative selected for the ROD, a detailed monitoring plan following these general guidelines will need to be developed. The monitoring plan should include baseline monitoring of surface sediments and other agreed-upon measurement endpoints (such as fish tissue) at the start of the remedial action period. These data will support the determination of the actual amount of natural recovery that has occurred since detailed sampling of profundal sediments in 1992. This would also provide additional information regarding the accuracy of modeling presented in this appendix and could be used to calibrate future modeling of natural recovery after the ROD.

In addition to monitoring with clear performance criteria for determination of success, it is necessary to have contingency planning procedures in the event that the expected natural recovery does not occur. Contingency plans should contain a detailed set of procedures for triggering additional activities and a description of those activities in the event that performance criteria are not met. Contingency measures often include:

- Additional analysis of existing data to clarify monitoring results and underlying processes;
- Additional or different types of monitoring, observations, or measurements to clarify results;
- Additional institutional or other controls to limited human exposures during the MNR period;
- Pilot scale testing of alternate remedial actions (e.g., thin-layer capping) to determine their performance relative to MNR in light of data provided by the monitoring program; and
- Guidelines for implementing full-scale remedial technologies. Some that could be considered for Onondaga Lake include aeration (oxygenation), thin-layer capping, isolation capping, dredging, and treatment.

The contingency plan should allow for decisions that lead to contingency activities without necessarily proceeding through the activities in any particular order. This flexibility might be particularly important where, for example, MNR performance criteria are missed by a wide margin. In cases where MNR performance criteria are nearly or mostly met, the above order of activities might represent a logical sequence from low-level to high-level intervention.

N.2.4 STATE OF SCIENCE – EVALUATION OF MONITORED NATURAL RECOVERY

The USEPA is currently formulating a framework for the evaluation of MNR at sediment remediation sites (USEPA, 2002). USEPA is working with groups such as the RTDF to develop a weight-of-evidence approach for evaluating MNR at contaminated sediment sites (Evison, 2003). The process being developed includes steps such as data assessment, modeling, and site monitoring to facilitate a thorough evaluation of MNR for contaminated sediment sites. USEPA's MNR framework is intended to promote appropriate technical evaluation, increase certainty, and provide decision-makers with greater confidence in the selection and implementation of this remedial option as a permanent, effective means of risk reduction.

The USEPA and RTDF are focusing on five primary lines of evidence, as follows:

Characterize contamination sources and controls – This line of evidence includes characterizing historic and current contaminant loading to the sediments. Sediment trap data often provide a cost-effective method for characterizing ongoing sources. It can be important to distinguish between and evaluate external upland/watershed sources versus internal sources associated with legacy sediments. For external sources, this may include assessing both point and non-point sources, including the potential for future control of those sources. For internal sources, this may include evaluation of resuspension from other areas that may or may not be undergoing more active remediation.

Characterize fate and transport processes – An understanding of environmental processes affecting sediment and contaminants is needed for most MNR investigations. Key processes that may affect sediments include erosion, settling and deposition, burial, bed consolidation, mixing in surface sediments, diagenesis of sediment particles, and sediment sorting and grading processes due to water currents. Key processes that may affect contaminants include advection/dispersion, diffusion (mechanical, molecular), partitioning, sorption/desorption, and abiotic and biotic transformation reactions.

Establish historical record for contaminants in sediment – The purpose of this line of evidence is to evaluate the reduction in chemical exposure based on temporal trends in sediment chemical data. This usually entails compiling data from past sampling of surface sediments, waters, and/or sources to establish a record for contaminated sediments. Where sources have been controlled or partially controlled, this information can provide an indication of the potential for future natural recovery. It is important when evaluating historical data to consider its quality relative to the data evaluations being conducted (that is, the adequacy of the quality assurance and quality control [QA/QC] measures that were applied to all phases of data collection). In addition to time-series data, sediment chemistry and/or radioisotope dating of subsurface cores can be particularly useful. Such core data can provide a history of system reactions to past reductions in source loads and provide evidence regarding the timeframe of expected future responses of the system to similar additional reductions in sources.

Corroborate MNR based on biological endpoints – The primary purpose of this line of evidence is to determine whether any reduction found in chemical record results in similar improvements in the biological data. The biological endpoints that may be of interest are site

dependent, but often include fish or invertebrate tissue chemistry, histopathology/biomarkers, sediment bioassays, and fish or benthic community analysis. As with chemistry data, the quality (as demonstrated by QA/QC documentation) of historical biological data and variations in field and laboratory techniques between sampling events should be considered.

Develop acceptable and defensible predictive tools – This final line of evidence is to determine whether evidence of past reductions (where sources have been controlled) can be expected to continue or be augmented in the future with further source controls. In a few cases, extrapolation of historical trends may be sufficient, but in most cases well-constructed computer models of varying complexity (i.e., one-, two-, or three-dimensional) can be useful tools to predicting future behavior of the system. Accurate forecasting of future trends requires sufficient measurement of key process rates, calibration to long-term trends, and reasonable confidence that future conditions will be similar to conditions during model calibration or methods to account for changed conditions in a quantitative manner.

MNR is normally considered to be a highly effective remedial technology where substantial evidence supporting its success exists in each of these five areas. However, a site with less clear evidence in one or a few of these areas may still be a potential candidate for MNR, depending on the particular circumstances. For example, a site may show no historical record of natural recovery because source controls have never been implemented. If source controls are implemented as a part of an overall remedy, future natural recovery may, in fact, be indicated by the other lines of evidence.

Sections N.3 through N.7 describe the potential for natural recovery in Onondaga Lake based on each of these five lines of evidence. Conclusions based on the analysis of the five lines of evidence are provided in Section N.8.

SECTION N.3

CHARACTERIZATION OF ONONDAGA LAKE HISTORICAL CONTAMINANT SOURCES AND CONTROLS

This section reviews historical contaminant sources in Onondaga Lake and the existing and future controls of those sources. This represents the first line of evidence that typically supports MNR evaluations, as described in Subsection N.2.4.

N.3.1 EXTERNAL SOURCES OF CHEMICALS OF INTEREST

N.3.1.1 Historical Sources

There is a relatively well-understood history regarding sources of chemicals to Onondaga Lake. However, the historical inputs to the lake can only be reconstructed in general terms; quantitative, time-series measurements of historical loading to the lake are generally not available. In addition, the earlier data are more qualitative than recent data.

Much of this history is described in detail in the RI (TAMS, 2002). Figure N.4, which is reproduced from the RI, provides a timeline of major events related to sources to the lake. Some of the major sources from Honeywell's past operations are described briefly below.

Honeywell's industrial operations along Onondaga Lake began in 1884. The last production ended in 1986. These operations were based on four major product lines:

- Production of soda ash (sodium carbonate) and related products such as baking soda (sodium bicarbonate), sodium nitrite, ammonium bicarbonate, ammonium chloride, calcium chloride, and caustic soda (sodium hydroxide) by a non-electrolytic cell process known as the Solvay process.
- Benzene, toluene, xylene, naphthalene, and tar products from the recovery of coke byproducts.
- Chlorobenzenes and byproduct hydrochloric acid from the chlorination of benzene.
- Chlor-alkali products, including liquid chlorine, caustic potash (potassium hydroxide), caustic soda (sodium hydroxide), and byproducts, including potassium carbonate, hydrogen gas, and hydrogen peroxide.

These products were generated at a number of facilities and plants around the southwestern shoreline of the lake. Their exact locations and times of operation are detailed in the RI. Through this time, a number of landfills and impoundments were constructed to contain various waste materials and dredge spoils. The most extensive of these impoundments are known as the Solvay wastebeds, which contain soda ash production wastes and other waste products. These wastebeds and their locations are described in detail in the RI and the FS. In addition, some wastes accumulated directly in the south end of the lake in the ILWD.

Other industrial activities that likely contributed chemicals to the lake (including some of the CPOIs identified for the Onondaga Lake FS), as described in the RI, include:

- Landfills, dredging sites, and General Motors sites in the Ley Creek area;
- Historical industrial operations in the Oil City area;
- Former Niagara Mohawk Power Corporation, American Bag and Metal, and Roth Steel sites on Onondaga Creek;
- Crucible Material Corporation site; and
- Electronics Park facility on Bloody Brook.

Municipal discharges occurred in a relatively disorganized fashion in the late 19th century and early 20th century from combined sanitary/stormwater sewer systems. A series of sewage transport and treatment upgrades occurred to these systems since 1925. Since the area was settled in the 1780s, there has been a long history of urban stormwater, untreated and treated sewage, and waste discharges from developed areas around the lake.

Important source control events that could have a direct relationship to the history of sediment and water chemical concentrations in the lake and its natural recovery include:

- 1960 Metropolitan Syracuse Wastewater Treatment Plant (Metro Plant) is established.
- 1970 BETX and naphthalene production at Honeywell's Syracuse Works is ended.
- 1970 Syracuse Works effluent mercury loading reduced from 21 pounds to 1 pound per day
- 1977 Production of chlorinated benzene and chlor-alkali products (including mercury electrolytic cell process) is ended at Honeywell's Willis Avenue Plant. This reduces mercury loading from Bridge Street Plant to 0.028 pounds per day
- 1981 Solvay settling basin overflows are re-directed to Metro Plant.
- 1985 Phase 1 Onondaga County combined sewer overflow abatement program is completed.
- 1986 Soda ash and related production at Syracuse Works is ended.
- 1986 Major manufacturing processes by Honeywell related companies are ended.
- 1988 Alkali production using mercury cell process by the Linden Chemicals and Plastics (LCP) Bridge Street Plant is ended.

Mechanisms of chemical transport to the lake include inputs from tributary streams, direct discharges from industrial and municipal plants, and groundwater flow from industrial upland sites. Contributions from each of these sources have varied over time.

Chemicals from tributary streams may have originated from some of the industrial sites discussed above. In other cases, chemicals may have originated from more diffuse, difficult-to-identify urban sources within the surrounding watersheds. Major direct discharges occurred both from Honeywell's wastewater outfalls and discharges, other industrial sources noted above, and the county sewage treatment facility. Inputs of chemicals from groundwater occurred mainly from Honeywell's upland facilities and sites.

Table N.1 provides a summary of inputs in terms of water flow, total suspended solids (TSS), and total mercury loads to the lake. Most of the data used in Table N.1 were collected from 1990 through 2002. There are few details of discharge loadings prior to this time. However, information on Honeywell's permit loadings for total mercury in the 1970s provides a point of comparison about the relative magnitude of mercury source control that has been implemented since that time. Mercury information is provided as a general indicator chemical that is also of prime importance in terms of risks to the lake.

TSS are included in the table because of their importance as a sedimentation source in the lake, which can drive natural recovery. TSS are also important in terms of general fate and transport characteristics, as many chemicals tend to adsorb to particulates in surface water.

It should be noted that porewater diffusion from profundal sediments is sometimes also discussed as an "input" to the lake. However, for Table N.1, chemicals present in sediments are defined as having already entered the lake and are sometimes referred to as "internal" sources (see below).

N.3.1.2 Current Conditions

Table N.1 provides a good summary of most current source loading estimates for TSS and mercury to the lake, with 2002 and 1990s data providing the bulk of the information for these "current" conditions. Most of the available data focus on particular years or windows of time in this period.

There has been considerable concern expressed that sources of TSS and chemicals to the lake may have changed substantially in the last few years. Therefore, these loading estimates may not adequately represent current conditions. Recent trends in chemistry in the lake are discussed in more detail, in Section N.5. This information suggests that there have not been large-scale recent changes in inputs to the lake, although there is considerable uncertainty associated with such a conclusion. Consequently, for the overall purpose of considering the general magnitude of current source loadings and extrapolating to future conditions, it is reasonable to use the information presented in Table N.1.

N.3.1.3 Proposed Future Source Controls

The most notable proposed source control is the remediation of the various upland and other industrial sites by Honeywell. Most of these efforts are in the planning stages. Status and schedule information for these sites are summarized in the FS.

The county is currently conducting a phased, 15-year program of upgrades and improvements to the Metro Plant's wastewater collection and treatment system. This program includes:

- Changes to the wastewater and stormwater collection systems to reduce combined sewer overflows (CSOs).
- Improvements to the Metro Plant to provide a higher level of treatment to wastewater prior to discharge (Onondaga Lake Partnership, 2003).

For both the Honeywell and Metro Plant projects, the general objectives are known, but few if any, specific estimates of expected chemical mass loading reductions have been made. For upland remediation activities, the potential general impact on sources is summarized in the FS. For Metro Plant improvements, the Onondaga Lake management plan indicates that these improvements will result in substantial reductions in the frequency and duration of CSOs as well as improvements in treated water discharges from the sewage treatment plant.

The Tully mud boil remediation substantially reduced TSS loads in Onondaga Creek (Onondaga Lake Partnership, 2003). Additional remediation efforts are planned that may create further TSS load reductions in the future (Onondaga Lake Partnership, 2003). Past remediation efforts starting in 1992 reduced the net annual TSS load from the mud boils to approximately 250,000 kilograms (kg) to Onondaga Creek. Onondaga Lake Partnership (2003) reports an annual TSS load of approximately 7.5 million kg from the mud boils in 1992, which represented nearly 45 percent of the total TSS load to Onondaga Lake (14.7 million kg) according to 1991 TSS loading estimates by Onondaga County (2003). As discussed in detail in Subsection N.4.1.2, there appears to be no commensurate decrease in TSS loading to Onondaga Lake during the period from 1992 to 2002. Consequently, the original estimates of mud boil TSS contributions in 1992 may be in error. Additional remediation efforts of the mud boils are expected to further reduce the estimated annual TSS load of approximately 250,000 kg from Onondaga Lake Partnership, 2003).

Table N.2 summarizes approximate estimates of TSS and total mercury reductions that are expected from the above remediation efforts. Available information indicates that upland remediation efforts will result in nearly complete control of groundwater mercury loads to the lake. For surface water discharges, upland remediation will likely only eliminate mercury loads from Harbor Brook, East Flume, and Tributary 5A, where Honeywell sources likely represent most of the mercury load to these tributaries.

Honeywell sources are also substantial contributors to mercury loads to Ninemile Creek. Because such an estimate might tend to over-predict the likelihood of natural recovery, it is assumed in Table N.2 that upland remediation reduces mercury loads from Ninemile Creek by 80 percent. This reduction estimate is arbitrary, but helps to account for the fact that there may be substantial uncontrolled sources of mercury in the wider urbanized watershed upstream of Honeywell sources. A 50 percent reduction in Metro Plant mercury loads due to the planned upgrades is included in Table N.2. This number is also arbitrary, but in the absence of specific estimates by Onondaga County, it accounts for some level of reduction that would be expected from the planned upgrades.

For TSS reductions, the Onondaga Creek TSS loads are reduced by 250,000 kg to account for the Tully mud boil remediation (as discussed above). The Honeywell upland remedial efforts are estimated to have no impact on TSS loads to the lake because none of these efforts are specifically targeting TSS reductions and the stability of surface soils, stream morphology, and amount of impervious surfaces may not substantially change due to these efforts. As with mercury loads, the TSS reductions from Metro Plant discharges are set at an arbitrary 50 percent to account in some way for the expected upgrades to this system.

Based on these general estimates, there would be an approximate 5 percent reduction in TSS load and an approximate 71 percent reduction in total mercury load to the lake (Table N.2). However, there are considerable uncertainties associated with these estimates, as discussed above.

N.3.2 INTERNAL SOURCES OF CHEMICALS OF INTEREST

The term internal sources usually refers to the movement of chemicals from one matrix or compartment in the lake to another. For example, most of the mass balance estimates conducted for mercury have had the following compartments (Effler, 1996; TAMS, 2002; Sharpe, 2003):

- Epilimnion;
- Hypolimnion;
- Profundal sediment; and
- Littoral sediment.

In the case of sediments, the division into compartments is somewhat arbitrary and relies on professional judgment of where resuspension of sediments might be likely to occur. Rather than a hard boundary at some water depth, there likely exists a continuum of conditions from almost daily resuspension and movement of sediments in the shallow, shoreline areas to virtually no resuspension in the very deep, profundal areas. In the case of the water column, the division between epilimnion and hypolimnion for inter-compartmental chemical movement is potentially a very useful concept, because of the observed increases in mercury in the hypolimnion during summer stratification, where conversion to methylmercury likely takes place.

Analysis of inter-compartmental chemical movement has been conducted for a variety of reasons. The primary issues of interest are:

- How might inter-compartmental movement help or hinder sediment and lake remediation efforts?
- How might these movements cause or increase ongoing or potential future risks?

The inter-compartmental movements that have been of the greatest concern, and therefore most studied, are:

- Resuspension of contaminated sediments in the littoral areas, which has the potential to:
 - o Transport chemicals to less contaminated sediments or remediated areas;
 - Increase availability of chemicals in the water column;
 - Contribute to total mercury available for conversion to methylmercury in the hypolimnion and profundal sediments; and
 - Decrease the rate of any natural recovery in profundal sediments.
- Diffusion/advection of chemicals from profundal sediments to the hypolimnion, which has the potential to:
 - Increase availability of chemicals in the water column and
 - Contribute to methylmercury in the hypolimnion.
- Ebullition-mediated transport of chemicals from profundal sediments via advected particles and increased diffusion rates to the hypolimnion, which has the potential to:
 - Increase availability of chemicals in the water column and
 - Contribute to methylmercury in hypolimnion.
- Settling sediment movement from the epilimnion to the hypolimnion and then to profundal sediments, which has the potential to:
 - o Increase profundal sediment chemical concentrations and
 - Affect the rate of any natural recovery in sediments.
- Movement of chemicals from the hypolimnion to the epilimnion or the destratified condition, which has the potential to:
 - o Increase availability of chemicals in biologically productive areas and
 - Mediate movement of methylmercury to fish tissue.

Obviously, these chemical movements and issues are inter-related.

N.3.2.1 Current Conditions

A number of researchers have attempted to construct mass balance inventories of mercury and methylmercury in the lake including movements between these internal compartments (Effler, 1996; TAMS, 2002; Sharpe, 2003). Figure N.5 presents the mass balance for mercury and methylmercury from the 2002 RI (TAMS, 2002). It should be noted that the Figure N.5 mass balance is for only the stratified period (120 days) studied during the RI and differs from mass loads presented on an annualized basis in Tables N.1, N.2, and N.3.

This mass balance estimate indicates a net loss of mercury in the lake water. The vast majority of this loss is via sedimentation and subsequent burial of mercury in the profundal sediments. This substantial loss of mercury to profundal sediments results in a considerable

deficit in the mass balance estimate. TAMS (2002) pointed out that this deficit indicates that there is an unidentified source of mercury to the system. Two general source mechanisms have been advanced to explain this apparent deficit: external sources and internal sources. TAMS (2002) indicate that this deficit is greater than, but a similar order of magnitude to, all identified external inputs. Regarding internal sources, TAMS (2002) indicate that two internal sources are possible:

- Release from sediments caused by increased diffusion and advection due to ebullition of methane gas and, in the case of methylmercury, production of this compound in the upper sediment layers. (Thus, some of the mercury "lost" to sedimentation to the profundal is actually recycled back to the hypolimnion.)
- Resuspension of sediments in contaminated littoral areas, most notably the ILWD.

These internal sources are poorly accounted for in the mass balance models of the lake system developed to date. However, TAMS points out that the increased profundal sediment release mechanism would not account for the overall lake deficit under almost any reasonable scenario, but could account for the deficit related specifically to the profundal portion of the mass balance (2002). Conversely, resuspension may cause a substantial potential range of releases to the overall lake system. Estimating such release rates is clearly a complex task, and TAMS indicates that there is considerable uncertainty inherent in the approximations of resuspension flux rates presented in the RI (2002). These approximations are presented in Figure N.5, and range from 2 to 20 kg total mercury during the stratified period.

It also appears possible that unaccounted upland sources may exist. For example, TAMS nearly doubled the total mercury input above the estimate made by Effler (1996) after examining the potential upland sources, groundwater in particular, in greater detail (2002). Sharpe indicates that his estimates of resuspension do not account for the balance deficit and that additional external sources may exist that have not been documented (2003).

Examples of poorly understood external sources of mercury inputs are stormwater discharges from drainages such as Sawmill Creek and Bloody Brook, and other direct discharges. Although these examples by themselves are likely a trivial contribution, taken together, a large number of these types of unidentified sources could be relevant to the mass-loading estimates. While it is unlikely that these unexamined sources would make up the entire deficit, they may be of the same magnitude as other internal release mechanisms such as ebullition of methane gas.

N.3.2.2 Effect of Potential In-Lake Remedies on Internal Sources to Profundal Sediments

There are two potential ways that in-lake remedies could change the cycling of internal chemical sources within the lake:

- Reduction of chemical flux due to resuspension by remediation of littoral areas and
- Reduction in chemical flux from profundal sediments due to remediation in profundal areas.

The preferred remedy for the lake has not yet been selected by NYSDEC. However, it is likely that at least some littoral areas will be subject to capping and/or dredging. These remedies would directly remove or reduce the availability of chemicals in surface sediments for resuspension and redistribution.

For profundal areas, remedies might include dredging, but more likely would include technologies like isolated areas of thin-layer capping and/or aeration (oxygenation). Thin-layer capping would likely reduce the flux of chemicals from the profundal sediments, since it would provide an immediate dilution of the chemical concentrations present in the surface sediments. Assuming that sedimentation continues at a reasonable rate (and incoming sediments are not highly contaminated), this would continue to bury the sediments and isolate contaminated sediments deeper in the sediment profile.

It is unclear whether aeration (oxygenation) or *in situ* treatment of profundal sediments (e.g., with alum, gypsum, or calcium nitrate) would greatly reduce mercury or methylmercury release from the profundal sediments. Oxygenation of hypolimnion would likely result in the oxidation of the top centimeter or few millimeters of profundal sediments, and thus, reduce methylmercury production in this layer. Oxygenation might also reduce the amount of methane gas ebullition in the top layers of profundal sediments, and thereby reduce any advective transport of particulate mercury via methane bubble release. Chemical treatments may have no direct effect on mercury release, but could assist in reducing methane gas production and its associated releases. However, for determining changes in natural recovery of profundal sediment chemical concentrations, all these processes would result in losses of chemicals to the water column and may contribute to reductions in sediment chemical concentrations. Thus, for predicting recovery of sediment concentrations, it is conservative to assume that no reduction in these fluxes will occur due to aeration (oxygenation) or treatments of the profundal sediments. The issue of flux itself and its importance for recovery in other lake components (e.g., the water column) are discussed in more detail in Section N.7.

The greatest internal source is likely to be resuspension of littoral sediments. TAMS estimated the resuspension flux from the ILWD sediments alone ranging from approximately 2 to 20 kg during the 120-day stratified period (Figure N.5) or approximately 5.2 and 52 kg annually, assuming that no resuspension takes place during the 54 days that the lake is covered by ice (2002; ice coverage data from Onondaga County, 2003). As noted by TAMS, the high-range estimate more than accounts for the mass balance deficit to the hypolimnion by several times, and probably is an overestimate (2002).

Remediation of littoral sediments would be expected to have little effect on the TSS flux to the profundal sediments. Dredging and capping alternatives would both result in similar, new, clean, sediment beds that would be a similar source of sediment resuspension and movement around the lake.

N.3.3 POTENTIAL EFFECT OF ALL SOURCE CONTROLS ON CONTAMINANT INPUTS

Using the above estimates of external and internal source reductions, estimates of the total mercury and TSS loads to profundal sediment are shown in Table N.3 for both existing and potential future source-control conditions.

Internal TSS loads to the profundal were estimated using 1992 data from the two hypolimnetic sediment traps, which indicate an average total sediment load from all sources of 26.4 million kilograms per year (kg/yr)to the profundal sediment bed. The external source TSS load observed in 2002 (from Table N.2 or 20.3 million kg/yr) was subtracted from the total load (26.4 million kg/yr) to obtain the internal TSS load due to resuspension (6 million kg/yr) in the "high estimate" column of Table N.3.

In the "low estimate" column of Table N.3, the external TSS load was obtained using the lower 20th percentile of external TSS loads observed between 1989 and 2002 (approximately 10 million kg/yr; Onondaga County, 2003). For this same column, the internal TSS load was obtained by subtracting the 1992 estimates of external loads (15 million kg/yr; from Onondaga County, 2003) from the total 1992 sediment trap load (26.4 million kg/yr).

The reductions in external TSS loads in Table N.3 are the same as those presented in N.2. Combining all sources and source controls results in an estimated TSS load reduction of between 3.5 percent and 4.3 percent (Table N.3).

For the total mercury reduction estimate, the load reductions from Table N.2 are combined with an assumed 100 percent reduction in internal mercury load due to resuspension. High and low estimates are based on the ranges presented in Figure N.5, which were annualized as noted above. The resulting mercury load reductions range between 80 percent and 95 percent.

SECTION N.4

CHARACTERIZATION OF FATE AND TRANSPORT PROCESSES IN ONONDAGA LAKE

This section presents a general review of the current state of knowledge regarding fate and transport of chemicals in Onondaga Lake. This represents the second line of evidence that typically supports MNR evaluations, as described in Subsection N.2.4.

N.4.1 PHYSICAL PROCESSES

N.4.1.1 Wind/Wave and Current Forces

Wind generates waves and circulation of water, resulting in currents in the lake. The breaking of waves at the shoreline creates direct forces on littoral areas and sediments. Inputs and outputs of water at the various tributary mouths also cause currents within the lake.

On a large scale, water currents in the lake are driven mostly by wind. Currents at the surface of the lake are generally with the wind direction, while currents at the bottom of the lake are generally against the wind direction (Effler, 1996). Current velocities deep within the lake are generally slow enough that disturbance of the profundal sediment bed would be unusual.

On a smaller scale, the momentum of inflows is generally dissipated within relatively small distances from tributary entrances or other discharges (Effler, 1996) and generally affects only upper littoral and epilimnion areas. Historically, when the waters of Ninemile Creek were more saline, discharges from Ninemile Creek could at times "plunge" into the hypolimnion. Presently, during turnover when the lake is uniform in density, the Ninemile Creek discharge can plunge to the bottom of the lake before eventually being mixed into the rest of the water column by wind-driven turnover.

Wave action creates much higher forces in the littoral areas than any wind-generated circulation or tributary inflow currents. The forces created by waves on the littoral sediments was studied for Appendix H, capping issues; it was found that the 100-year-return-frequency storm would disturb and resuspend surface sediments in the sand size range that were shallower than 20 ft (6 m) of water depth. These are unusual conditions, but they indicate that smaller windstorm events could routinely resuspend sediments in shallow littoral zones. In addition, internal waves are known to occur at the thermocline in most stratified lakes. These waves will break at the littoral/profundal interface and can cause resuspension in sediment there. No information quantifying the potential amount of resuspension from internal waves was found for Onondaga Lake.

N.4.1.2 Profundal Sedimentation Processes

Wind-generated waves and currents appear to have little effect on the profundal sediments. The profundal sediments have been defined in the RI by NYSDEC as those areas greater than 30 ft (9 m) of water depth. This definition was based on the typical location of the lake thermocline.

This area constitutes about two-thirds of the bottom area of the lake or 3 square miles (8 million square meters) (TAMS, 2002).

The silty consistency of the sediments within the profundal areas is consistent with the concept that these basins are quiescent areas where water column suspended sediments deposit consistently over the long term. Effler reports that surface sediments in the profundal basins have a mean particle diameter in the coarse to medium silt range (indicating that a large proportion of the sediment grains are finer than this) and mean water content in the 70 to 72 percent range (1996). Subsurface cores in the profundal sediments show very fine striations of depositional layers with little if any evidence of disturbance of these layers once they are deposited (Effler, 1996).

These observations are corroborated by a number of subsurface cores that were subjected to radioisotope analyses for ²¹⁰Pb (lead) or ¹³⁷Cs (cesium), which are typically used to assess sediment stability and quantify historical deposition rates in sediments. For example, patterns of ¹³⁷Cs concentrations in sediment layers can be compared to nuclear bomb testing fallout, which started to rise in 1954 and peaked in 1963, to determine sediment stability.

Figure N.6 presents four radioisotope cores that were collected in the north and south basins of the profundal areas (TAMS, 2002). An additional two cores were taken in the profundal area. Five of the six cores sampled show a clear trend of ¹³⁷Cs deposition consistent with historical sources of this isotope (see examples in Figure N.6), and subsequent sediment stability that preserved that historical record. The demarcations of interest, such as the appearance of ¹³⁷Cs associated with nuclear testing starting in 1954 and the peak of that testing in 1963, have good resolution. This indicates little disturbance to the sediments since that time.

One core taken near Ninemile Creek does not show these distinct trends, although it shows a clear increase of ¹³⁷Cs activity with depth. This profile is probably related to deposition of ¹³⁷Cs from the creek itself, which could have occurred in more sporadic events associated with periodic watershed runoff and erosion that blurred the concentration profile. Dredging conducted in the 1960s may have also affected this profile.

Effler (1996) and Hairston *et al.* (1999) present radioisotope core results for three additional cores. The two Effler cores were collected in 1988 and were subjected to both ¹³⁷Cs and ²¹⁰Pb analysis. The Hairston *et al.* core was collected in 1997 and was subjected to ²¹⁰Pb analysis. (Sharpe subsequently obtained archive samples of this core and subjected them to mercury analysis as well [2003]). All three of these cores show clear evidence of long-term undisturbed deposition (i.e., stability), consistent with the findings of the RI cores.

In addition to demonstrating sediment stability over the past 50 years, radioisotope core data provide a method to estimate deposition of sediment to the profundal areas. Because core data indicate the profundal sediments are clearly a depositional environment, sediment trap data are a useful measure of net deposition rates in these areas. Typically, sediment traps capture all sediment regardless of whether it might normally resuspend at some later time and provide a "gross" sedimentation rate. However, in quiescent areas like the profundal basins, sediment

traps provide an indication of "net" deposition rates, because very little of the sediments are expected to resuspend.

Table N.4 presents the sedimentation rates that have been obtained by various researchers. These include estimates presented in the text of the 2002 RI and estimates directly from the core profile figures also presented in the 2002 RI. In addition, data from 1996 coring and sediment traps were reviewed. The sources of all data provided at least some information or methods that allow assessment of variability in core or sediment trap data, and these were summarized into mid-range (usually means or medians), minimum, and maximum reported or derived values. Figure N.7 presents these same data graphically, one for sediment traps in units of grams per square centimeter per year (g/cm²/yr) and one for cores in units of centimeters per year (cm/yr). Data points from cores are shown at the mid-point of the period evaluated in the core profile.

Sedimentation rates shown in Table N.4 obtained from sediment traps collected mostly in summer months vary in a range of approximately 0.1 to 1.4 g/cm²/yr (average 0.5 g/cm²/yr) after 1986. The high value in this range represents the maximum result from sediment trap samples from Effler (1996) collected in 1988. The low-end value is based on the minimum value obtained from sediment traps deployed in 1996 for one month in the summer. Thus, it is unlikely that this low value is representative of overall annual deposition rates within the lake. Further, because all of the sediment trap data are collected during mostly summer months, they represent only a limited range of the seasonal conditions in the lake. It is possible due to factors such as decreased biological production and reduced runoff that sedimentation rates in winter months could be less, resulting in overall annual sedimentation rates that are lower than the summer time sediment trap values shown in Figure N.7.

Sedimentation rates measured by cores shown in Table N.4 vary in a range of approximately 0.3 cm/yr to 0.6 cm/yr (average 0.4 cm/yr) after 1986. Rates after 1986 are all based on data from Hairston *et al.* 1997, which is the only recent coring study to present information on a post-1986 period. TAMS (2004) estimated sedimentation rates in cm/yr from RI high-resolution cores using a mercury peak potentially associated with approximately halfway through 1986. This analysis yielded a range of results from 0.5 to 0.6 cm/yr.

For the reasons noted above, as well as potential differential compaction artifacts in core samples, it is difficult to consistently compare sediment trap data directly to coring data. However, sediment trap data can be converted to units of cm/yr by using an assumed density of material in the upper sediment layers. Thus, if an in-situ density of 0.675 grams per cubic meter (g/cm^3) is assumed (based on a porosity of 0.75 and dry particle density of 2.7 g/cm³), then the sediment trap data after 1986 range from 0.2 to 2 cm/yr, with an average of 0.8 cm/yr. This average result is somewhat higher than the core-based sedimentation values discussed above and may reflect the fact that sediment trap data do not measure potential decreased sedimentation rates that occur during the winter period.

It has been hypothesized that activities such as the Tully mud boil remediation commencing in 1992, closure of the soda ash plant in 1986, and Metro Plant upgrades completed in 1986 have resulted in decreased sediment loads to the lake, and therefore, recent decreases in profundal sedimentation rates. Figure N.7 indicates little if any trend of decreasing sedimentation rates after 1986 measured either by sediment traps or cores., while rates measured on or around 1986 are relatively high and likely still reflect soda ash plant and Metro pre-upgrade inputs. This information is consistent with Onondaga County's (2003) monitoring report, which presents estimated TSS data since 1985 (Figure N.8). While these data appear to suggest some decrease in TSS concentrations between 1987 and 1993, the post-1993 concentrations are generally within the same range as this earlier period, and do not appear to reflect any clear trend of decreasing TSS in the lake. In addition, that same report calculates overall TSS loads from all monitored sources; these data are shown in Figure N.9. After 1986, there has been no downward trend in TSS concentrations or TSS loads. Consequently, it appears valid to use sedimentation data from approximately 1987 onward as representative of current conditions in the lake.

N.4.1.3 Littoral Sedimentation Processes

Unlike the profundal sediments, the littoral areas of the lake are subjected to regular wave and current action that can disturb and redistribute sediments. Both the wind/wave analysis conducted for Appendix H (capping issues) and information from Effler (1996) on currents in the lake indicate that disturbance and redistribution of sediments decreases with increasing depth. Specifically, the capping analysis indicated that disturbance of sands greater than 20 ft (6 m) deep during the 100-year storm would not be expected. Thus, the lower littoral areas from about 20 to 30 ft (6 to 9 m) water depth are likely to receive only very sporadic disturbance due to very large-scale storm events. Sediment categories from Effler (1996) of relatively silty sediments cover much of this area between the depths of 20 and 30 ft (6 and 9 m). All this information indicates that the 20 to 30 ft deep (6 to 9 m deep) water depth portion of the littoral may have sedimenta are generally sandy throughout the lake, with the exception of SMU 6 and 7 on the south end of the lake (Effler, 1996).

A pattern of resuspension and redistribution of materials in the upper littoral areas (less than 20 ft [6 m] water depth) is consistent with the overall pattern of mercury contamination. As shown in Figure N.1, outside of SMUs 1, 2, 4, and 7 where physical wastes are present, mercury concentrations in the upper littoral areas are lower than in profundal areas. Thus, it is apparent that mercury particles have either not settled here or have been subsequently resuspended and deposited elsewhere. This conceptual model is corroborated by the TAMS sampling of TSS and chemical concentrations near the ILWD during wind events, which provide direct evidence of this resuspension mechanism (2002). Based on this information, it is likely that any net sedimentation in upper littoral areas (less than 20 ft [6 m] water depth) would be slow and would occur in a dynamic process, which could include periods of substantial loss in bed sediments to other adjacent or deeper areas.

The one exception appears to be portions of SMU 6. As noted above, this littoral SMU does not have the same physical characteristics of most of the other littoral SMUs, and appears to be subject to some deposition. Sediment traps deployed in the profundal area very near the edge of this SMU in 1992 indicated substantial gross sedimentation rates in the range of 0.1 to 1.7 cm/yr (TAMS, 2002). The concentrations of mercury in these settling sediments were much higher than those found in traps from other profundal areas, indicating that a substantial component of

this sedimentation is likely from resuspended material from this and adjacent SMUs that contain relatively high concentrations of mercury.

A ¹³⁷Cs core (S12) taken near the mouth of Onondaga Creek in SMU 6 (Figure N.10) shows substantial ¹³⁷Cs activity, but the concentration profile is not well resolved, showing a slight increase in concentrations with depth. Such a profile would be consistent with a pattern of overall deposition that is periodically or continually interrupted by episodes of resuspension so that the concentration profile is smeared out over sediment depths. It is noteworthy that this profile is distinctly different than Core S73 taken in the littoral areas near Bloody Brook, which shows virtually no ¹³⁷Cs activity (Figure N.10). The S73 core profile is consistent with an erosional environment. That is, any ¹³⁷Cs that was deposited has likely been scoured and transported to other areas. This is also consistent with the sandy characteristic and low mercury concentrations of the littoral sediments near Bloody Brook.

N.4.1.4 Groundwater Advection

Groundwater discharge to littoral shoreline areas is known to occur and is discussed in the FS and in detail in Appendix D, groundwater issues. In general, groundwater advection rates decrease with distance from the shore in littoral areas. Groundwater discharge to the profundal sediments is likely small relative to these shoreline discharges. The upper-bound estimated groundwater flux to the profundal zone is less than 1.5 cm/yr. Three lines of evidence support this value as an upper-bound estimate of groundwater flux to the profundal zone:

- Chloride profiles in sediment porewater from the south basin;
- Chloride balance for the lake; and
- Groundwater flow model.

Chloride concentrations in sediment porewater in the profundal zone typically increase linearly with depth in the upper few meters of sediment. In a core from the southern basin (Station S51), chloride concentrations increased from background levels linearly to 42,000 milligrams per liter (mg/L) at a depth of 16 ft (5 m) (TAMS, 2002). Similar linear profiles were observed in 36 of 42 cores collected in the profundal zone (TAMS, 2002). The linear chloride profiles indicate that the distribution of chloride in sediments is controlled by upward diffusion from natural brines beneath the lake. If upward groundwater velocity was significant, the profile would not be linear. Based on analyses of the linear chloride profiles described in TAMS (2002), it was concluded that the upward groundwater velocity is on the order of 0.04 cm/yr or less. Larger groundwater velocities are inconsistent with the observed profiles. The chloride profiles in the six cores that did not exhibit linear profiles did not exhibit the shape that would occur if upward groundwater velocity was significant; rather, the profiles suggest inhomogeneities within the sediment profile.

Groundwater beneath the profundal zone of Onondaga Lake is natural brine with chloride concentrations in excess of 60,000 mg/L. An upper bound estimate of groundwater discharge to the profundal zone was developed by calculating the chloride loading to the lake from groundwater discharge to the profundal zone. A chloride model of the lake described in Effler (1996) demonstrated that chloride concentrations in the lake can be simulated very well by

considering only chloride loading from surface water inflow; in the chloride model, groundwater inflow from the profundal zone is assumed to be zero. The estimated error in the chloride model is approximately 5 percent, which is equivalent to approximately 20 mg/L of chloride. The discharge of 100 gallons per minute (gpm) of groundwater to the profundal zone would raise the chloride concentration in the lake by at least 20 mg/L. Therefore, this was considered to be an upper-bound estimate of the groundwater discharge to the profundal zone. A groundwater discharge of 100 gpm over the entire profundal zone is equal to an average groundwater flux of 1.4 cm/yr to the profundal zone. This is considered to be an upper bound estimate of groundwater flux to the profundal zone.

A three-dimensional model of the groundwater system beneath and to the southwest of the southern portion of Onondaga Lake has been developed to analyze remedial alternatives for the Semet Residue Ponds and the Willis Avenue Sites (BBL, 2000; O'Brien & Gere, 2002). This groundwater model incorporates available information on the geologic conditions beneath the lake and in surrounding areas. Beneath the profundal zone, there typically is considerably more than 100 ft of fine-grained materials. Groundwater flux to the profundal zone as calculated with the groundwater model is less than 1 cm/yr.

Based on these lines of evidence, it is concluded that the best estimate of groundwater flux to the profundal sediments is approximately 0.04 cm/yr. The upper-bound estimate of groundwater flux is approximately 1.5 cm/yr.

N.4.1.5 Methane Gas Ebullition

Ebullition of methane gas is a physical mechanism in Onondaga Lake sediments that may be of importance to natural recovery evaluations. Ebullition of methane gas from profundal sediments has been measured by Addess (1990) and others (Addess and Effler, 1996). This process is driven by the anoxic decomposition of organic carbon supplied by deposition to the sediment bed (see Table 4.24 and accompanying discussion, from Effler, 1996).

It has been hypothesized that ebullition of methane gas could cause increased movement of sediment chemicals to the water column via increased diffusion of dissolved chemicals within sediment porewaters and advection of particles that adhere to the surface tension of the bubbles (TAMS, 2002; NYSDEC, 2003). Rates of particle advection have been measured in a study conducted in Duluth, Minnesota (SEE, 2002). The Onondaga Lake RI (TAMS, 2002) reviewed this study and reported a particle advection rate of 0.092 g/m²/day. NYSDEC (2003) also stated that diffusion of chemicals could be increased by more than a factor of three due to ebullition-induced changes in sediment structure.

Review of the original Duluth Minnesota study indicated that there was large variability in results from location to location in methane gas ebullition rates and correlated particulate resuspension rates (SEE, 2002). Because of the considerable variability observed even within this one site, there is no reliable method to extrapolate particle advection associated with ebullition rates observed at the Duluth site to particle advection rates that might be applicable to Onondaga Lake. Consequently, it is difficult to determine whether the particle advection rate of

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 $0.092 \text{ g/m}^2/\text{day}$ from Duluth is applicable to the sediment types and ebullition conditions at Onondaga Lake.

There do not appear to be any site-specific data to provide a refinement of the estimates of increased diffusion and particle advection caused by ebullition provided by NYSDEC (2003). Consequently, these estimates are used later in this document to understand their potential impact on upward flux of mercury to the water column (see Section N.7). Further evaluations of ebullition may be needed for the pre-design phase of the project.

N.4.1.6 Bioturbation

In addition to mixing and disturbance of sediments due to physical forces, benthic organisms may move and mix sediments. This is referred to as bioturbation. Bioturbation is likely to take place in the oxic littoral sediments, and probably is one contributor to the overall dynamic sedimentation profiles observed in these areas, as discussed in Subsection N.4.1.3.

In contrast, there are very few organisms present in the profundal anoxic sediments other than microorganisms. Consequently, substantial bioturbation of profundal sediments would not be expected. Effler describes the sediment profiles observed in cores from the profundal sediments as well as the presence of numerous micro- and macro-laminations within those sediments (1996). Such fine laminations are normally not encountered in sediments that are substantially bioturbated. This tends to confirm that bioturbation in profundal sediments is minimal.

Although little, if any, bioturbation of profundal sediments currently occurs, the impacts of remedial efforts on bioturbation should be considered for future predictions of natural recovery. Aeration (oxygenation) in particular could have the potential to promote recolonization of profundal sediments that could result in increased bioturbation in the profundal zone.

N.4.2 CHEMICAL PROCESSES

N.4.2.1 Partitioning of Chemicals

Partitioning of chemicals refers to the ability for many chemicals to exist in various forms associated with particles (e.g., sediment particles) as well as in dissolved aqueous forms. The differentiation between particulate and dissolved forms is an important one, because it often affects the bioavailability of chemicals as well as the methods by which they can be transported. Most of the detailed information on partitioning in Onondaga Lake is available for mercury, both total mercury and methylmercury.

Mercury exists mostly in two oxidation states in normal environmental conditions: Hg^0 (metallic) and Hg^{2+} (mercuric-Hg(II)). The mercuric form can make numerous inorganic and organic chemical compounds. Consequently, most mercury encountered in water, soil, sediments, and biota (all environmental media except the atmosphere) is in the form of inorganic mercuric salts and organomercurics (USEPA, 1997). The two major chemical forms of mercury in freshwaters are in organic Hg(II) and monomethylmercury. Compounds found under environmental conditions are:

- Mercuric salts HgCl₂, Hg(OH)₂, and HgS;
- Methylmercuric chloride (CH₃HgCl) and methylmercuric hydroxide (CH₃HgOH); and
- In small fractions, other organomercurics (i.e., dimethylmercury and phenylmercury).

The physical state, chemical form, and aqueous speciation of mercury varies between and within lakes, depending on such factors as oxidation-reduction potential (Eh), pH, ionic strength, and concentrations of TSS, organic ligands, and sulfides. The solubility and partitioning of each mercury species varies, and is impacted by these environmental conditions.

In general, as the oxidation state of mercury increases, the solubility of mercury generally increases; elemental Hg(0) and Hg(I) are sparingly soluble, whereas Hg(II) is highly soluble (Kaplan *et al.* 2002). Anoxic conditions (such as in the hypolimnion and profundal sediments) have generally lower Eh, thereby promoting the reduction of Hg(II) to Hg(I) or Hg(0). In some instances, the accumulation of reduced sulfur in these conditions, primarily as dissolved sulfide, will precipitate inorganic Hg as a highly insoluble HgS mineral. Also, organic material in waters or sediments may either act as a sorbent or may provide high concentrations of dissolved ligands that form very strong complexes to Hg(II).

Chemical analyses of total and dissolved phases have shown that mercury in the water column in Onondaga Lake is associated with particulates (TAMS, 2002). For example, during the 1999 water sampling event, the partition coefficient (Kd; ratio of solids phase to dissolved phase) for total mercury ranged from approximately 8,000 to 7.4 million, with an average of 1.5 million liters per kilogram (L/kg). Given the ability of various forms of mercury to adsorb onto particulates, this finding would be expected (USEPA, 1997). Methylmercury appears to have lower Kds in the water column. For the 1999 water sampling event, the Kds for methylmercury ranged between 0.1 million to 1.1 million, with an average of 0.4 million.

Mercury in sediments also heavily partitions to the particulate phase, but to a lesser degree. USEPA reports that sediment Kds of 50,000 to 500,000 are not unusual for freshwater aquatic sediments (1997). In Onondaga Lake, porewater was analyzed for mercury in profundal subsurface cores (TAMS, 2002). As shown in Table N.5, the total mercury Kds ranged from 81,000 to 1 million, with an average of 0.5 million L/kg. Methylmercury in sediments shows a lesser tendency for partitioning to the solid phase as compared to total mercury. In the same samples, methylmercury Kds ranged from 600 to 62,000, with an average of 11,700 L/kg (TAMS, 2002).

N.4.2.2 Settling Sediment Chemical Concentrations

The concentrations of chemicals in the sediment settling to the profundal bed are an important factor affecting the recovery of surface sediments. The most direct way to measure these concentrations is through sediment trap data. These data can also be indirectly estimated through examination of chemical and TSS concentrations observed in water samples. However,
this latter type of measurement does not necessarily differentiate between materials that may permanently settle and those that may not.

Table N.6 summarizes the data available from sediment trap and water chemistry for total mercury. The methods for extrapolating solids concentrations from water data are discussed in more detail in Subsection N.5.1. Generally, there is a fairly wide range of total mercury concentrations in settling sediments, but overall, data from littoral areas are notably higher than those from the epilimnion and hypolimnion in the basins. This is consistent with the resuspension mechanisms likely to occur in the littoral areas as discussed in Subsection N.4.1.3.

N.4.2.3 Methylmercury Production and Cycling

The conversion of Hg(II) to monomethylmercury is catalyzed by sulfate-reducing bacteria in anoxic lake waters and sediment. The transformation pathways between the major species of mercury discussed in Subsection N.4.2.1 can be summarized as follows:



The methylated form of mercury is the primary one entering the food chain. The biotransformation of inorganic mercury species to methylated organic species in water bodies is known to occur in sediment and water (USEPA, 1997). Sulfate-reducing bacteria are the primary methylators of mercury in the environment. Abiotically, humic and fulvic acids in solution also appear to methylate mercuric ions. Not all mercury compounds entering an aquatic ecosystem are methylated, and demethylation reactions can mediate the overall rate of methylation (USEPA, 1997).

There is a large degree of scientific uncertainty and variability among water bodies concerning the rates of mercury methylation. Bacterial methylation rates appear to increase under anaerobic conditions, high temperatures, and low pH (USEPA, 1997).

Methylmercury is bioavailable and accumulates in fish through the aquatic food web; nearly 100 percent of the mercury found in fish muscle tissue is methylated (USEPA, 1997). Methylmercury appears to be primarily passed to planktivorous and piscivorous fish via their diets. Larger, longer-lived fish species at the upper end of the food web typically have the highest concentrations of methylmercury.

Because methylmercury production tends to be higher in anaerobic environments, the anoxic hypolimnion and profundal sediments are likely locations for substantial mercury methylation to occur. There has been a great deal of study of the rates and circumstances of mercury methylation within Onondaga Lake. Important points relative to natural recovery include the following:

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- Examination of methylmercury in profundal sediment porewater cores suggests that methylmercury concentrations are highest in the top 4 cm of the profundal sediments (TAMS, 2002).
- This methylmercury will diffuse (even in the absence of advective forces) into the hypolimnion and likely increase the methylmercury concentrations there to some degree (TAMS, 2002).
- Methylation/demethylation reactions occur in the water column, with the assumption that net demethylation occurs in the epilimnion, and net methylation occurs in the hypolimnion (TAMS, 2002). Sharpe presents a mass balance of methylmercury that includes an overall net demethylation in the water column as a whole (2003). Regardless of the various estimates, substantial extrapolations from site data are used to arrive at these net methylation/demethylation rates.
- Methylmercury accumulates in the hypolimnion over the course of the warmer months, and then decreases following turnover (TAMS, 2002).

N.4.2.4 Non-Aqueous Phase Liquid Chemicals

Non-aqueous phase liquid (NAPL) exists at several locations within the southern end of the site that are summarized in the RI (TAMS, 2002; see Figure 5-28). Most of these identified locations are within areas of relatively high chemical concentrations and/or physical wastes. Consequently, it is unlikely that natural recovery will be a proposed remedial technology in any of these areas. If it appears that natural recovery might be proposed in one of these areas, additional analysis of the impact of NAPL on the natural recovery process may be warranted.

N.4.3 BIOLOGICAL PROCESSES

The primary fate and transport mechanism of concern from a natural recovery perspective is the bioaccumulation of chemicals in biological tissues. Bioaccumulation of mercury has been observed in Onondaga Lake at levels that are expected to be associated with potential risk to wildlife and human health. As noted in Subsection N.4.2.3, the primary mechanism of this accumulation is via methylmercury uptake.

As noted in the RI, methylmercury production occurs in the anoxic environments of the hypolimnion and profundal sediments (TAMS, 2002). It is unclear to what extent methylmercury available for uptake is driven more by water or sediment production. However, it is likely that production in the hypolimnion is a major source of methylmercury as noted by Sharpe (2003) and TAMS (2002), which indicates as much as 50 percent of the methylation occurs in the water of the hypolimnion.

However, this conclusion does not preclude the idea that some amount of the mercury present in the water column may be due to flux of mercury from the sediments. The primary question appears to be whether this flux is important relative to ongoing sources and other internal fluxes within the system, such as resuspension.

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SECTION N.5

HISTORICAL RECORD FOR CONTAMINANTS IN ONONDAGA LAKE

This section reviews the available information regarding trends in chemistry in Onondaga Lake. This represents the third line of evidence that typically supports MNR evaluations as described in Subsection N.2.4.

N.5.1 SURFACE WATER AND SETTLING SEDIMENTS

Surface water data can be highly variable over time, and consequently, it can be very difficult to identify trends in water chemistry without very large, consistently collected data sets. A review of the water chemistry data available from the RI (TAMS, 2002), Effler (1996), Onondaga County (2003), and Sharpe (2003) indicates that, with the possible exception of mercury, there is insufficient information to examine trends for all CPOIs listed in Subsection N.1.3. In the case of mercury, there are multiple water sampling events, but they were generally conducted for purposes other than defining long-term trends. The Onondaga County (2003) ambient monitoring program is designed to examine and report on temporal trends for a number of water quality variables, but it does not include mercury or any other potentially toxic chemicals on a regular basis.

Water chemistry data for mercury are available for 1992 (RI, 2002), 1999 (RI), 2000 (Sharpe, 2003), 2001 (RI resuspension study), and 2002 (Onondaga County). The resuspension study targeted areas suspected to have substantial concentrations of mercury from resuspension of sediments in littoral areas, and may not be comparable to the other data sets.

Figure N.11 presents water chemistry data from these studies for total mercury in the summer stratified period, without differentiation by sample location or time within the stratified period. These factors may be important in the differentiation of long-term trends. These factors were initially investigated, and few if any, clear trends by sampling time or area of the lake were visually observed. Figure N.11 provides an overall summary of the ranges of total mercury results found in the past 12 years. Throughout this period, almost all measurements for total mercury in both the epilimnion and hypolimnion have been between 1 nanogram per liter (ng/L) and 100 ng/L. Differences among individual measurements probably reflect differences in study purposes, locations, and timing as well as actual variability of mercury concentrations in the water column.

A considerable amount of sediment trap information was collected in this same period of time. Sediment trap studies were conducted in 1992 (RI), 1996 (RI), and 2000 (Sharpe, 2003). Sediment trap data provide direct information about the concentrations of mercury in particulates settling out of the water column. Trends in these data were also examined. In addition, to augment this data set, water chemistry data were examined for TSS data.

Where water samples were analyzed for both total mercury and TSS, the concentration of mercury on sediment particles in the water was calculated. For this calculation, it was assumed that the entire concentration represented by total mercury in water was present in particulate form. As noted in Subsection N.4.2.1, the 1999 RI water chemistry indicates that usually most of the total mercury is present in the particulate phase rather than in the dissolved phase, although in some cases, the amounts of dissolved and particulate mercury can be nearly equal, particularly in the hypolimnion. Consequently, the assumption that all mercury is in the particulate phase tends to over predict the concentrations of mercury in settling sediments, which is conservative for the purposes of predicting natural recovery trends in the profundal sediment bed.

The concentration of mercury in TSS was obtained by multiplying the water concentration in mg/L divided by the TSS concentration in kg/L to obtain a mercury particulate concentration in mg/kg. Settling and suspended sediment mercury concentrations are shown in Figure N.12. Sediment trap data indicate a slight downward trend in mercury concentrations in settling material over time, while water chemistry data indicate a slight upward trend in suspended sediment mercury concentrations. However, neither of these trends is strong, and overall this information appears to indicate there has been little measurable change in mercury concentrations associated with particulate material in the water column since 1992.

N.5.2 SURFACE SEDIMENTS

Often one of the primary measures of success in natural recovery programs is a reduction in the concentrations of the target contaminants in surface sediment chemistry over time. At Onondaga Lake, the period since about 1987 is of particular interest because the lake was not subject to direct inputs from Honeywell operations in this time.

Despite the large amounts of sediment data collected for the RI, most sampling events after 1992 were designed to fill data gaps for specific purposes and do not provide repetitive sample results from the same sites at different times. For example, considerable additional sediment sampling was conducted in the year 2000. However, all but four of the year 2000 sampling locations were in littoral areas and do not provide a basis for examination of profundal sediment chemistry trends. In other cases, samples were taken from nearby previously sampled areas but at different sediment depths. Because it is known that profundal sediments have a strong vertical mercury concentration gradient with depth (TAMS, 2002), differences in sampling depths can be particularly confounding. Consequently, there appears to be insufficient surface sediment data to make any conclusions regarding trends in surface sediment concentrations since 1987.

N.5.3 SEDIMENT CORE DATING AND PROFILES

In depositional environments such as the profundal basins, sediment core chemical data provide an indirect means of establishing the history of surface sediment chemical concentrations. The advantage of core data is that they allow a representation of a particular location, with no confounding horizontal sampling accuracy issues. The disadvantage of core data is that there may be vertical inaccuracies related to sampling artifacts or the degree of resolution in the sampling of the core. A large number of cores with chemistry profiles were reported in the RI (TAMS, 2002). Effler (1996) and Sharpe (2003) also provided sediment core data for Onondaga Lake.

Total mercury concentrations in several example cores are shown in Figure N.13 (taken in 1988), Figure N.14 (taken in 1992), and Figure N.15 (taken in 1997). All of the cores show a decreasing trend in mercury concentrations since major loadings to the lake from Honeywell operations were reduced in 1970. Thus, the highest concentrations of mercury in sediment are now at least 18 to 20 cm below the surface of profundal sediments. As discussed above, there has been considerable interest in the period since the last Honeywell operations closed in 1986.

Cores taken in 1988 (Figure N.13) show an increase in mercury concentrations in the last few years (or cm) before the core was taken. These results imply an increased mercury loading to the lake around this time. However, cores from four years later (Figure N.14) show that this trend did not continue and, at both sites, mercury concentrations are lower in the most recent sediments. The mercury concentration changes in this period may have been a result of a change in the solids loading in 1986 (as suggested by Rowell, 1992), and the subsequent drop may have been due to a decline in the mercury loading in 1988.

The core collected in 1997 (Figure N.15) also shows that after the peak in 1986 to 1988, it appears that mercury concentrations are relatively stable (showing neither upward nor downward trends). See Sharpe (2003; Figure N.15) for a dated core profile.

The overall long-term pattern in mercury concentrations since 1970 is also reflected in concentration profiles of other metals presented in the RI (TAMS, 2002). Consequently, it appears that long-term trends in mercury recovery have been generally reflected in the recovery of other contaminants. This supports the approach taken in this appendix of focusing on mercury, which is by far the best documented and studied chemical in the lake.

It is noteworthy that the long-term trends since 1970 indicating declining concentrations of mercury in recent layers of sediment cores are based on evidence solely from the profundal areas of the lake. Although there appear to be similar changes in chemical concentrations in cores from some littoral locations throughout the lake (see aerial extent and depth maps in the RI, TAMS, 2002), littoral-zone cores, have generally not shown the clear trends that are evident in cores from the profundal zone. Further, most cores in the littoral areas were not sampled with the relatively fine resolutions of the profundal examples provided above (e.g., samples every few cm). In addition, the more dynamic nature of the littoral areas, as described in Section N.4, indicates that clear concentration gradients with depth would be less expected in these areas.

SECTION N.6

TEMPORAL TRENDS IN BIOLOGY IN ONONDAGA LAKE

This section reviews the available information regarding trends in biology in Onondaga Lake. This represents the fourth line of evidence that typically supports MNR evaluations as described in Subsection N.2.4.

N.6.1 BIOLOGICAL COMMUNITY TRENDS

The trends in biological communities have been studied for the RI baseline environmental risk assessment (BERA) and by Onondaga County (2003) for their ambient monitoring program. The Onondaga County ambient monitoring program appears to focus mainly on plankton communities, zebra mussels, and fish communities. Changes in plankton communities appear to be mostly related to nutrient inputs rather than toxic chemicals such as mercury and, thus, probably do not reflect any past trends related to chemical recovery in the lake.

Onondaga County (2003) addresses trends in fish communities and reports recently collected fish are generally in good condition with weights within expected ranges. Game fish catch rates from electro-fishing were typically on the low end of New York State averages for walleye and pike but close to average for bass. The 2002 analysis also indicated that Onondaga Lake contains a rich assemblage of species, with pelagic planktivorous (fish that feed primarily on phytoplanktons and zooplanktons) warm water species most abundant. Finally, non-native fish species were commonly found in the lake and include carp, alewife (*Alosa pseudoharengus*), and white perch. These species are some of the most abundant in the lake. Other invasive fish species, such as blueback herring (*Alosa aestirolis*), ruffe (*Gymnocephalus cernuus*), round goby (*Neogobius melanostomus*) and tubenose goby (*Proterorhinus marmoratus*) are already present in the Great Lakes and could make their way into Onondaga Lake in the near future.

The report also indicates the Onondaga Lake fish community has experienced dramatic changes since the 1800's due to the combined influences of water quality and habitat degradation, regional changes to the indigenous fish community, and invasion of non-indigenous species through the canal system. The historical fish community, likely composed of a diverse assemblage of cold and warm water species was replaced by the early 20th century with a community dominated by warm water species. Gradual improvements to water quality by the end of the 20th century led to the current condition of a diverse community of warm water fish.

None of these changes appears to be closely correlated to concentrations of potentially toxic chemicals in the lake or recent changes in chemical loading to the lake. However, this hypothesis is not specifically evaluated in the Onondaga County (2002) report.

N.6.2 FISH TISSUE CHEMISTRY

The RI indicates mercury concentrations in the tissue of several fish species showed a 2 to 3-fold decline within approximately one decade between 1970 and 1980 (TAMS, 2002). This dramatic drop in fish tissue mercury concentrations corresponds with reductions of mercury releases to Onondaga Lake. Figure N.16 is consistent with how methylmercury concentrations in fish appear to show dramatic reductions after 1970. After about 1980, there appears to be very little change in the fish tissue concentration of mercury. However, it is noteworthy from Figure N.16 that the average concentration of mercury in the tissues of larger piscivorous fish (walleye and bass) is higher than that of other benthic fish (catfish and carp).

The lack of change in fish tissue chemistry after 1980 is consistent with the lack of downward or upward trends in surface water and sediment chemistry since the mid-1980s discussed in Section N.5. As source loading stabilized in the mid-1980s, so did the changes in all these media. The lake appears to be currently at equilibrium among water, sediments, and fish tissue related to a relatively stable input of mercury sources. It is unclear whether fish tissue concentrations are more related to water or sediment mercury concentrations. However, it is noteworthy that the review of water chemistry data presented in Section N.5 indicates no clear trend in decreasing water concentrations since 1990. In the same period from about 1990 to 1996, sediment concentrations have been lower than a peak around 1988 to 1990 (Section 5). Thus, the lack of recovery in fish tissue appears to be more closely related to changes in water rather than sediments over time. However, there are considerable uncertainties associated with such a hypothesis.

SECTION N.7

PREDICTIVE MODELING FOR MNR EFFECTIVENESS IN ONONDAGA LAKE

This section presents a predictive model of natural recovery in Onondaga Lake. This represents the fifth line of evidence that typically supports MNR evaluations as described in Subsection N.2.4.

N.7.1 PURPOSE OF MODEL USE

The primary purpose of the natural recovery model is to understand how natural recovery might occur (or fail to occur) in the future based on what is known about the system as described in the previous sections. Other purposes of the model include the following:

- Provide information on how sediment surfaces might react during and after remedial actions. Because this model focuses on changes in the sediment surface, it can provide information on reactions to inputs such as isolation or thin-layer caps.
- Thin-layer capping is a remediation technique that is evaluated in FS for profundal sediments. Consequently, modeling was conducted to estimate the effects of this remediation technology on surface sediment mercury concentrations.
- The flux of methylmercury from the surface sediments to the overlying water column was estimated using the model to understand whether MNR might provide reductions in these fluxes to the water column.

As described in Section N.2, models of varying complexity can be used to evaluate natural recovery. For this appendix, a relatively simple, one-dimensional model that focused on changes in sediment concentrations in the surface sediments was used.

N.7.2 DESCRIPTION OF MODEL AND IMPLEMENTATION

A numerical model was used to understand potential natural recovery for Onondaga Lake. The model is based on the extensive work done by Boudreau on diagenetic modeling for sediments (1997).

The model was used to assess the long-term solid and dissolved contaminant fate and transport associated with natural recovery by simulating the diffusion, bioturbation, groundwater mediated advection, settling, burial, and degradation mechanisms likely to be present at this site. By assessing these mechanisms over time, a prediction of chemical concentrations and fluxes in the future can be obtained.

The model is a one-dimensional simulator, meaning that it assesses fate and transport along the vertical axis of the sediment bed. This assumption is applicable to the vast majority of sediment systems normally encountered (Boudreau, 1997). Review of the extensive information for Onondaga Lake (TAMS, 2002) indicates the overall water-sediment system appears to meet this assumption on a scale applicable to examining lake-wide potential future trends.

The governing equations for the model have been extensively peer-reviewed in the literature and through the publications of Boudreau (1997). In addition, the model has been used and accepted by regulators at sediment Superfund sites, including the Middle Waterway in Tacoma, Washington (Anchor and Foster Wheeler, 2001) and Duwamish/Diagonal CSO in Seattle (Anchor, 2002), among others.

The natural recovery model is based on Boudreau's Equations 3.80 and 3.83 (1997), which determine the integral conservation balances of a species (e.g., a chemical of interest) for dissolved and solid phases in a thoroughly mixed layer of sediments. In this case, the "mixed layer" is the surface sediments of Onondaga Lake. The governing equation for the natural recovery model, referred to here as the "standard model," is:

$$\frac{\partial M}{\partial t} = D_o \left[\frac{\varphi}{\theta^2} \frac{\partial C}{\partial x} \right]_L + \left[\varphi D_B \frac{\partial C}{\partial x} \right]_L + \left[\varphi u C \right]_L + \left[\varphi_s w B \right]_0 - D_o \left[\frac{\varphi}{\theta^2} \frac{\partial C}{\partial x} \right]_0 - \left[\varphi D_B \frac{\partial C}{\partial x} \right]_0 - \left[\varphi u C \right]_0 - \left[\varphi_s w B \right]_L - \sum_{0}^{L} R dx$$

where:

М	= mass of chemical of interest (mg)
t	= time (years)
D_0	= molecular diffusion coefficient (cm^2/yr)
φ	= porosity of sediments (unitless)
θ	= tortuosity of sediments (unitless)
С	= concentration of chemical in dissolved phase (mg/L)
x	= spatial variable (along the depth of sediments) (cm)
L	= where $x = L$; the bottom of the mixed layer (cm)
D_B	= biodiffusion or mixing coefficient for sediments (cm^2/yr)
и	= velocity of porewater (cm/yr)
φ_s	= solid fraction volume (unitless)
W	= burial velocity of solids (or settling rate) (cm/yr)
В	= concentration of chemical in solid phase (mg/kg)
0	= where $x = 0$; top of the mixed layer (sediment water interface) (cm)

R = reaction of chemical through depth interval (i.e., biodegradation loss) (mg)

This equation provides the change in chemical mass over the specified time interval. By assuming a unit volume of mixed layer sediment, this equation can be used directly to calculate concentrations of the chemical of interest in the mixed layer over the same time. The net change in mixed layer mass is determined by the sum of changes produced by diffusion, biodiffusion (diffusion driven by bioturbation of sediments), groundwater advection, sediment settling, burial, and biodegradation (for organic chemicals).

The model is applicable to any chemical species, and a review of Boudreau (1997) indicates that there are very few limitations in terms of chemicals that might be modeled. The most

important factor is that mass conservation is observed by ensuring that all production and destruction reactions that are thought to be important are accounted for in the R term. This model has been applied a variety of sites, as noted above. It has proved applicable to numerous types of chemical species, including mercury, other metals, PAHs, and PCBs.

Following numerous examples in Boudreau (1997), the partial differential equation noted above was converted to a series of ordinary differential equations by substituting spatial finite differences for spatial derivatives. The resulting ordinary differential equations are solved numerically using Euler's method. The model was executed with STELLA Research® software.

The variable R represents the total mass change due to all chemical production/destruction reactions that occur in the mixed layer. The only such reaction typically considered is anaerobic biodegradation for organic chemicals, which is normally assumed to follow a first-order decay relationship of:

$$C_{tl} = C_{t0}(1 - e^{-kt})$$

where:

 C_{tl} = concentration of chemical at time one (mg/kg)

 C_{t0} = concentration of chemical at time zero (mg/kg)

k = first order decay constant (/year)

Because only mercury was modeled, biodegradation was not specifically employed for this modeling effort.

The model assumes that mixing of sediments within the surface layer is essentially instantaneous within each time step. Generally, mixing of surface sediments due to physical and biological (bioturbation) activity takes place on a sufficiently short time scale that this assumption is reasonable for the purpose of predicting natural recovery over a period of years (Boudreau 1997, Berner 1980). The depth of the mixed layer itself can be varied within the model and is dependent on observations of mixed layer depths in the sediments and/or predictions of future changes in those mixed layer depths.

The equation includes both dissolved-phase and solid-phase chemicals. Consequently, equilibrium-partitioning assumptions are used to obtain the mass of chemical present in each phase at any given time in the model. Distribution coefficients discussed in Subsection N.4.2.1 and presented in Table N.5 were obtained from site-specific sediment/porewater chemical concentration data in subsurface cores (TAMS, 2002). These coefficients were used to describe the equilibrium partitioning of the chemicals across solid/aqueous phases in the mixed layer and buried layer.

The model was run for mercury for a period of 22 years, starting in 1992 and ending in 2014. This period was chosen for two reasons. First, virtually all data on mercury surface sediment concentrations in the profundal zone are from 1992. Predictions of natural recovery from these baseline conditions must consider that these 1992 data no longer represent current conditions and should cover the period from 1992 to the time that remedial design is likely to

commence. For the purposes of this modeling, remedial design was conservatively assumed to occur in 2004, which is approximately 12 years from 1992. This is conservative because it ignores any natural recovery that might take place between 2004 and the time when upland and lake remedies are actually implemented, which is likely to be sometime after 2004.

Second, predictions of natural recovery should allow for some time period after remedial design for natural recovery to occur as a remedial technology. Although no specific guidance is available on this project for selecting an appropriate period of natural recovery, periods from 10 to 30 years have been used at other Superfund sites. A 10-year recovery period was used at the Commencement Bay (USEPA, 1989) and Eagle Harbor (USEPA, 1994) sites in Washington, while a 10- to 30-year period for recovery of fish tissue concentrations was used at the Fox River Superfund site (WDNR and USEPA, 2003). To be conservative, a 10-year natural recovery period was chosen, resulting in an overall modeling time of 22 years from baseline 1992 conditions.

N.7.2.1 Time-Dependent Parameters

Most of the parameters in the model are held steady over the course of the time span modeled. However, because the model covers a pre-remediation period from 1992 to 2004 and a post-remediation period from 2004 to 2014, some parameters would be reasonably expected to change after remediation. Specifically, for model runs assuming reductions in mercury inputs due to upland source controls, the reductions are applied to the post-remediation period only.

Source reductions were estimated by applying the source reduction estimates from Section N.3 (in terms of the percent reduction in mass loading of total mercury) to the settling sediment mercury concentrations from the pre-remediation period. This estimation is simplistic because it assumes reduction of the mass loading of mercury into the lake will result in a proportional decrease in the mercury concentrations in settling sediment. However, in the absence of a lake-wide mercury source fate and transport model, this method provides a reasonable first approximation of the effects of source controls. Model runs were made assuming both the full benefit of source controls as well as a "no source control" scenario to understand the uncertainty associated with this assumption.

The other parameter that was varied over the pre- and post-remediation periods was the mixed layer depth, which for some model runs was set at 4 cm from 1992 to 2004 and 10 cm for the remainder of the model time period. This approach was intended to approximate the potential recolonization of profundal sediments by benthic organisms after implementation of remedial measures such as aeration (oxygenation) that would create aerobic conditions in the hypolimnion. Both of these mixed layer depths appear to be consistent with NYSDEC (2003) comments on bioturbation on the draft FS natural recovery modeling. In addition, a model run was conducted assuming that measures such as aeration do not take place. In this case, the mixed layer depth was kept at 4 cm throughout the modeling period.

Both the changes in settling sediment mercury concentrations and mixed-layer depths are assumed to occur over a period of less than a year at the time of remediation (i.e., model year 2004). For source control estimates, this assumption likely underestimates the improvements

caused by source controls. This is because source controls may actually take several years to complete and would be conducted prior to the completion of site-wide remediation during the pre-remediation period. Thus, a very short overall period of time is allowed for natural recovery to proceed with source controls in place under this assumption.

For the mixed-layer depth, it is difficult to predict with any accuracy how fast recolonization impacting the mixed-layer depth is likely to proceed. The assumption of a change in less than one year would be consistent with a sudden change in the lake environment, such as the introduction of oxygen into the hypolimnion, and recolonization estimates presented in the FS of one year.

Changing the mixed-layer depth has important repercussions for the model itself, since essentially a boundary condition is changed in the middle of the modeling period. (Boundary conditions are discussed in more detail below.) To maintain the mass balance of the model, both the chemical and sediment mass introduced into the new, larger mixed-layer depth from the previously buried sediments must be tracked at the conversion from a 4-cm to a 10-cm mixed-layer depth. In addition, because the recently buried layers below 4 cm and the previously mixed layer (top 4 cm) have different porosities, the overall porosity of the new 10-cm mixed layer after deep bioturbation mixing occurs is also changed in the model to a depth-weighted average of the previously separate layers.

The model mercury mass balance was maintained by tracking the amount of mercury buried over the pre-remediation period and then reintroducing a portion of that buried mercury mass back into the mixed layer at the time of the mixed-layer depth change. This reintroduced mercury mass from the buried layer was assumed to be proportional to the total depth buried over the pre-remediation period. Thus, if 20 cm of sediments were buried over the pre-remediation period, 30 percent of the mercury in these buried layer depth changed. The value of 30 percent in this example is obtained by dividing the increase in mixed depth (6 cm) by the total number of cm of sediments buried over the period in question (20 cm). This estimate method is conservative because it assumes that mercury would be equally distributed within the buried sediments, when, in fact, it is more likely that the most contaminated sediments would reside in the deepest layers that would be permanently sequestered from bioturbation.

N.7.2.2 Boundary Conditions

The one-dimensional mixed layer mass or concentration, which is the primary focus of the model, is bounded by surface water at the top (x=0) and buried layer at the bottom (x=L).

The concentration of the chemical in the surface water is assumed to be zero. Generally, surface water concentrations are well below porewater chemical concentrations (particularly for contaminated sediments), so the use of a zero value for surface water does not greatly affect predictions of natural recovery. That is, the standard model is very insensitive to small changes in surface water concentration. The primary input from the surface water is suspended sediment (and associated chemicals) settling on the mixed-layer bed.

The buried layer is assumed to be infinitely thick and to have an infinite source of chemicals at the specified concentration. Because chemical contamination is found relatively deep in most site sediments, this assumption appears valid over the time periods of interest (i.e., several years). Further, this assumption is conservative (i.e., would tend to under predict the likelihood of natural recovery) because it assumes no reduction in chemical flux from the buried layer over time. Where the buried layer has higher concentrations than the mixed layer, the primary inputs from the buried layer are groundwater advective flux and diffusive flux of dissolved chemicals. The dissolved chemical concentrations for the buried layer are obtained from equilibrium partitioning assumptions and data as noted above for the mixed layer. Because the buried layer is defined at the point at which mixing ceases, physical movement of solids from the buried layer to the mixed layer is assumed to be zero (except at the time the boundary condition is changed from a 4- to 10-cm mixed-layer depth, as discussed above).

The ebullition of methane gas bubbles and their potential effect on movement of mercury to the hypolimnion is discussed in Subsection N.4.1.5. The standard model discussed above does not include this mechanism of transport. It is conceivable that this mechanism might affect natural recovery results. As discussed in Subsection N.4.1.5, this process is driven by organic matter deposition from the hypolimnion and decomposition in anoxic conditions. As this organic matter is removed through decomposition the methane production decreases. Deeper sediments would be expected to produce less methane than surface sediments because the source of organic carbon at depth is not infinite. Thus, the overall impact of ebullition would be to increase the flux of chemicals out of the mixed layer. For the standard model, which focuses on changes in surface sediment chemistry over time, the incorporation of ebullition effects would result in faster natural recovery rates. Therefore, exclusion of ebullition effects from the standard model may be conservative (i.e., underestimates the rates of natural recovery of the surface sediments).

N.7.2.3 Thin-Layer Cap Modeling

The standard model described above was also used to assess the effects of thin-layer capping on the profundal sediments. In this case, the one additional model input was the placement of either 10 or 15 cm of clean sand material over the top of the existing profundal sediment bed.

As with the standard model, the thin-layer cap modeling includes a pre-remediation period up to 2004 and then a 10-year post-remediation period. Thin-layer capping is assumed to occur in model year 2004.

At that time, two time-dependent inputs change in the following sequence: (1) the mixed layer depth changes from 4 cm to 10 cm and (2) 10 or 15 cm of new, clean sand with porosity of 0.4 is input to, and completely mixed with, the top 15 cm of the existing sediment bed. This mixing assumption is reasonable because some mixing of the cap sands and underlying sediments would be expected during placement. By assuming complete mixing of the two layers, the mercury concentrations in the thin-layer cap should be conservatively (i.e., higher concentrations) estimated.

This second step causes an immediate reduction of the mercury concentrations in the new mixed layer relative to the previously uncapped sediments. The mixing calculation accounts for

the *in situ* densities of the two sediments and results in a new mixed layer with an *in situ* density and mercury concentrations intermediate between the capping sand and the surface of the sediment bed. The remainder of the post-remediation period of the model is identical to that discussed for the standard model.

N.7.2.4 Flux Modeling Applications

The standard model described above focuses on changes in sediment chemistry in the mixed layer. NYSDEC (2003) has requested that evaluations of natural recovery also consider the impact of natural recovery on the flux of methylmercury to the hypolimnion. For this purpose, the model results can be examined to determine the fluxes of chemicals out of the mixed layer. Thus, the upward flux due to diffusion, biodiffusion, and groundwater advection can be tracked and summed to obtain a total flux out of the sediments for any unit of time desired. Because the diffusive flux rate is sensitive to overlying surface water concentrations, the upper boundary condition for this application of the model was changed to include the surface water concentration of methylmercury.

There has been specific concern about the potential effects of ebullition on chemical flux to the water column, as discussed in Subsection N.4.1.5. Ebullition may increase the rate of chemical diffusion and cause advection of particles containing chemicals out of the mixed layer (NYSDEC, 2003). The effect of ebullition was modeled in the flux application by increasing the rate of diffusion above that given by molecular diffusion alone and adding an ebullition advection term to the mass balance equation above. This advection term is the same as the burial advection term but expressed in reverse direction and using the particle advection rates recommended by NYSDEC (see Subsection N.4.1.5). The model was run with and without ebullition flux to determine the relative effect of ebullition on the overall flux rates.

N.7.3 SOURCES OF INPUT DATA, RANGES, AND METHODS OF SELECTION

N.7.3.1 Standard Model

For standard modeling runs (as opposed to flux application discussed in Subsection N.7.3.2) of total mercury, the input parameters shown in Table N.7 were used. Standard model runs were conducted for profundal sediment conditions (i.e., SMU 8).

Based on the same review, a similar process is not expected to occur in the shallower portions (less than 20 ft [6 m] in depth) of any littoral SMU with the possible exception of SMU 6. Some preliminary modeling was conducted for shallow areas of SMU 6, assuming that ¹³⁷Cs core data and physical characteristics of sediments discussed in Subsection N.4.1.3 indicate a net depositional environment here. It was found that settling sediment mercury concentrations were high enough (based on littoral sediment trap data from Table N.6) that natural recovery was not indicated. Consequently, natural recovery modeling for shallow littoral areas was not conducted further. The remainder of this section discusses modeling for profundal sediments 20 to 30 ft (6 to 9 m below the water surface) only.

Initial Mixed Layer Concentration – For total mercury, a range of concentrations exist in profundal sediments. A range of inputs was considered, as shown in Table N.7. Unlike other

parameters, the point of using a spread of values was not to determine sensitivity to the model, but rather to determine which starting concentrations (that are representative of general areas) might reasonably achieve a desired goal. Thus, the model was run for each of these starting concentrations to estimate an ending concentration for that representative concentration or area. This includes the surface weighted average concentration (SWAC) of 2.59 mg/kg.

Initial Buried Layer Concentration: Generally, buried total mercury concentrations (deeper than 10 cm) have higher concentrations in the profundal sediments. A range of potential values is shown in Table N.7. However, to be conservative, for all modeling runs discussed in this appendix the upper value of 20 mg/kg was used for the buried layer.

Settling Sediment Concentration: A range of three values was used for this parameter, based on TAMS/NYSDEC-recommended values from three samples representing the top two slices of the 1996 and 1997 cores. The mid-range value is the mean of the samples, and low and high values represent the range of concentrations. Model runs were also completed based on assumed mercury concentrations on settling particulates following remediation, as discussed in Subsection N.3.3.

Partition Coefficients, Mixed Layer: The range of three values for this parameter was obtained directly from the porewater data from the subsurface cores collected in 2000 (TAMS, 2002) as summarized in Subsection N.4.2.1 and Table N.5. Values from the upper 4 cm were used for the mixed layer with the exception of the high value, which was obtained from data including the 0 to 12 cm layer. The high value was chosen from the slightly deeper sediments because the mixed layer is assumed to be up to 10 cm for this model, which covers most of the sampled layer from 0 to 12 cm.

Partition Coefficients, Buried Layer: The same data source as above was used for this parameter. In this case, coefficients derived from samples deeper than 12 cm were used exclusively for the three values in the range used.

Molecular Diffusion Coefficient: This value was obtained using the equation shown in Table N.7 from DiToro, *et al.* (1981) using the molecular weight of elemental mercury.

Mixed Layer Porosity: The porosity value of 0.91 was used based on an evaluation of density data provided by TAMS/NYSDEC. That evaluation used Hairston *et al.*'s 1997 core percent moisture data (provided by TAMS to Honeywell/Anchor Environmental via email on July 16, 2004) in the top 0 to 4 cm and an assumed specific gravity noted below. For modeling runs assuming increased bioturbation starting in model year 2004, the mixed layer porosity was calculated based on a depth-weighted average of the buried-layer porosity (see below) and mixed-layer porosity of 0.91, which yielded a new mixed layer porosity of 0.88.

Buried Layer Porosity: The porosity value of 0.86 was used based on the density evaluation provided by TAMS/NYSDEC using the same evaluation noted for the mixed-layer porosity and slightly deeper layers in those cores.

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Biodiffusion Coefficient: Boudreau presents a relationship between this parameter and burial velocity based on empirical data (1997). The equations shown in Table N.7 were used to determine the biodiffusion coefficients shown. A settling sediment flux of $g/cm^2/yr$ (w) was converted to a burial velocity (s) in cm/yr based on porosity (j) and particle specific gravity (SG) of the sediment using the following equation:

s = w / ((1-j)*SG)

Velocity of Porewater: The effective velocity of porewater through the profundal sediments was estimated as discussed in Subsection N.4.1.4. A mid-point value of 0.72 cm/yr was extrapolated between the high and low values of 0.04 and 1.4 cm/yr.

Settling Sediment Flux: The range of three values used for settling sediment flux were obtained from TAMS/NYSDEC estimates based on a re-evaluation of high-resolution cores using a 1986.5 marker and density information as discussed above for porosity.

Depth of Mixed Layer: A value of 4 cm was used for the pre-remediation period and a value of 10 cm was used for the post-remediation period. Both values are consistent with NYSDEC (2003) comments on the draft FS. The 4 cm value appears reasonable for existing sediments that are anoxic and are expected to be subject to little, if any, bioturbation. The 10 cm value appears reasonable for potential future conditions assuming that remediation using aeration (oxygenation) technology might encourage bioturbation in the profundal areas through the creation of aerobic conditions.

Specific Gravity: This value is also known as particle density, and typical values for many types of sediment grains are in the range of 2.6 to 2.7 g/cm³, with the latter value being used for this model. Specific gravity is used to determine the *in situ* density of the mixed layer using the porosity (derived from water content as noted above) and relationship noted for biodiffusion (e.g., (1-j)*SG).

Thin-Layer Cap Characteristics: Where thin-layer capping was modeled, the thin-layer capping depth was set at either 10 cm or 15 cm under separate model scenarios. The thin-layer cap material was assumed to have a porosity of 0.4, typical of clean sand placed through a water column. After mixing with the sediment bed (at porosity 0.91) due to construction, this results in a new mixed layer porosity of 0.66 (with 15 cm placement) and 0.71 (with 10 cm placement). This would result in an effective reduction in mixed layer mercury concentrations of about 50 percent and 40 percent for the 15 and 10 cm placements, respectively.

N.7.3.2 Flux Application Modeling

As discussed above, the model was also used to examine the flux rates of methylmercury from the mixed layer to the water column. This model includes the additional parameter of ebullition-driven diffusion and advection of particles. The input parameters for methylmercury are summarized in Table N.8. For physical parameters, the modeling inputs are similar to the standard model, although slightly different porosities and settling sediment flux rates were used. Chemical-specific values are discussed below.

Methylmercury Initial Mixed Layer Concentration: For methylmercury, a range of concentrations exists in profundal sediments. The range of inputs used was based on information from the 2000 profundal cores, 0 to 4 cm interval (TAMS, 2002).

Methylmercury Initial Buried Layer Concentration: Generally, buried methylmercury concentrations (deeper than 4 cm) have lower concentrations in the profundal sediments. A range of potential values is shown in Table N.8. However, for all modeling runs discussed in this appendix a conservative upper value of 0.02 mg/kg (corresponding to the "high" value in Table N.8) was used for the buried layer.

Methylmercury Settling Sediment Concentration: A range of three values was used for this parameter from the average of the low, mid-value, and maximum results from the various sediment trap studies. Only non-littoral sediment trap data were used. Sediment concentrations estimated from water chemistry data were not used due to the inherent uncertainties associated with this estimation method.

Methylmercury Partition Coefficients, Mixed Layer: The range of three values for this parameter was obtained directly from the porewater data from the subsurface cores collected in 2000 (TAMS, 2002) as summarized in Subsection N.4.2.1 and Table N.5. Values from the upper 4 cm were used for the mixed layer because this appears to be where methylmercury concentrations are highest.

Partition Coefficients, Buried Layer: The same data source as above was used for this parameter. In this case, coefficients derived from samples deeper than 12 cm were used exclusively for the three values in the range used.

Several researchers have discussed the rate of methylmercury production in the surface sediments of Onondaga Lake and presented rate constants for this reaction (TAMS, 2002; Sharpe, 2003). A methylmercury production rate was assumed for some preliminary runs of the flux application model using values from the sources cited above as well as general estimates from literature (USEPA, 1997).

Using these production rates, it was found that methylmercury production overwhelms diffusive loss, and methylmercury concentrations in the profundal sediments quickly (within a few years) exceeded any values ever measured in Onondaga Lake. Thus, it appeared that inclusion of this parameter in the model does not calibrate to current observed conditions. Consequently, this production parameter was not used further in the flux modeling. However, it appears that partitioning assumptions of the model generally provide for complete replenishment of the mixed layer methylmercury porewater concentrations. That is, as long as the mixed layer methylmercury sediment concentrations remain relatively constant during the period of modeling, the concentration of methylmercury in the porewater remains relatively similar to present-day measured conditions. Thus, assuming additional production beyond this equilibrium conversion from sediment to porewater, which does not appear to reflect empirical data.

N.7.4 MODEL RESULTS

As discussed above, the model was run in two major scenarios: (1) the standard model that addresses changes in surface sediment chemical concentrations and (2) the flux application that addresses dissolved flux of chemicals from the sediments to the hypolimnion. Results from each scenario are discussed in this section.

N.7.4.1 Standard Model – Mixed Layer Sediment Chemical Concentrations

The results of modeling runs over the 22-year model period (starting in 1992) are presented in Table N.9. Model runs using both the mid-point values and "worst-case" values from Table N.7 are shown in Table N.9. The "worst-case" is obtained by setting input parameters to that combination of values that produces the slowest decrease (or fastest increase) in sediment chemical concentrations over time.

Based on all of the information available, the mid-values were picked as the most likely input parameters. Thus, the mid-value scenario provides the most probable outcome of natural recovery.

Conversely, the "worst-case" scenario chooses outlier values for every parameter. Probabilistic modeling conducted by Anchor for other sites (e.g., Hylebos Area 5106 in Washington and the St. Louis River/Interlake/Duluth Tar Site in Minnesota), with similar dissolved-phase models indicates that such worst-case scenarios are generally exceedingly improbable. The reason for this is straight forward. If each low value in the model represents an outlier for an independent variable input (e.g., a value with a 5 percent or 10 percent probability of occurring), the probability that all these low input parameters would coincidentally occur at the site together is given by multiplying the probabilities of the various parameters. Thus, a simple multiplicative model using three 5th-percentile independent input values would result in an overall result that has a 0.013 percent chance of occurring (i.e., 5 percent³). There are at least eight low-probability values in the "worst-case" scenario discussed above. Thus, the probability of such a scenario actually occurring is exceedingly unlikely. Detailed probabilistic modeling was beyond the scope of this appendix, but could be conducted to quantify the probabilities of these unlikely scenarios.

The results in Table N.9 (based on mid-point input values) indicate that areas with high 1992 surface sediment mercury concentrations would be expected to have substantially decreased by 2014. The percent reduction for these areas of high concentration is similar regardless of whether it is assumed that proposed source controls take place. However, the final predicted mercury surface sediment concentrations are significantly lower for all scenarios when source controls are assumed.

Areas that have low 1992 surface mercury concentrations (e.g., 1.5 mg/kg) would be expected to have relatively small decreases over time, to 0.93 mg/kg, using the mid-point input values, source controls assumption, and a post-remediation mixed layer depth of 10 cm (Table N.9). This result is expected because the settling sediment mercury concentration after source controls of 0.28 mg/kg is relatively similar to the starting mercury concentration in bed sediments of 1.5 mg/kg. Because the model is sensitive to settling sediment mercury

concentrations (see sensitivity analysis below), the surface sediment concentrations will be largely determined by this settling sediment concentration over time. Thus, relatively little change in the surface sediment mercury concentrations would be expected where there is a small difference between these two values.

Table N.9 also shows predicted reductions based on a starting mercury concentration of approximately 2.6 mg/kg, which is the current mercury SWAC in the profundal area. These model runs were used to predict SWACs following MNR. Assuming source controls and deeper bioturbation after aeration, and using mid-point values, the model predicts a post MNR SWAC of 1.2 mg/kg if the hypolimnion becomes aerobic, resulting in benthic recolonization.

Table N.10 shows the maximum 1992 surface sediment mercury concentrations that would be expected to achieve either the PEC or apparent effects threshold (AET) (two SEC values under consideration), assuming a post-remediation mixed layer depth of 10 cm. Any area with an observed total mercury concentration of 6.7 mg/kg or less in 1992 would be expected to achieve the PEC of 2.2 mg/kg by 2014, using the most likely mid-point input values and assuming source controls take place. Areas with greater than 30 mg/kg mercury in 1992 would be expected to meet the AET of 13 mg/kg by 2014 using the same modeling assumptions. Note that no areas would be expected to meet the ER-L of 0.51 mg/kg, so this benchmark is not presented in Table N.10. A bioaccumulation-based sediment value of 0.8 mg/kg mercury was developed in the FS (Appendix I). As shown in Table N.9, model runs assuming increased bioturbation due to aeration do not achieve the bioaccumulation value for any starting concentration. However, where source controls and no aeration are assumed and the mixed layer remains at 4 cm thick, starting concentrations as high a 4 mg/kg in 1992 would be expected to achieve the bioaccumulation value by 2014. If no source controls is assumed, the bioaccumulation value cannot be achieved even in areas that have relatively low 1992 mercury concentrations (e.g., 1.5 mg/kg). As discussed in the FS, compliance with the criterion of 0.8 mg/kg would be based on consideration of the post remediation SWAC measured over subsets of the lake that combine littoral and profundal areas, to be determined as part of the pre-design investigation and design process

Figure N.17 shows a typical standard model result over time. This particular example assumes source controls, a post-remediation mixed layer depth of 10 cm, and starting concentration of 6.7 mg/kg (the critical 1992 value noted above). The figure illustrates the impact of changing the mixed layer depth from 4 to 10 cm at model year 2004 (year 12). The mercury concentrations increase at year 2004 as previously buried mercury is reintroduced into the mixed layer. However, this increase is temporary, and concentrations decrease again throughout the post-remediation period, finally achieving a lower concentration as that originally present at the end of the pre-remediation period. Also, with the greater 10-cm mixed depth in the post-remediation period, the reaction of the surface sediments to new inputs is slower than in the pre-remediation period when the mixed depth was only 4 cm. This result is expected because of the greater reservoir of sediments present in a 10-cm mixed layer.

It should be noted that these results are based on 1992 starting concentrations because these are the data available at this time. Additional surface sediment samples should be collected as a part of the pre-design process. Once those data are available, model predictions from 1992 to

2004 can be validated and modeling updated, if necessary, to reflect the actual historical trends in lake sediments. In addition, at that time any future modeling predictions of natural recovery would use the pre-design sediment data and project forward for the appropriate natural recovery period (as determined by NYSDEC) to estimate future areas and concentrations that would be expected to achieve the various potential remedial targets discussed above. Thus, any future determinations of areas expected to achieve specific remedial targets will be based on the predesign data year rather than the 1992 data year that is discussed in this MNR Appendix.

Figure N.17 also shows a typical result for thin layer capping assuming no source controls, mid-point input values, and placement of 15 cm of clean sand. Similar to MNR results, an increase in mercury surface sediment concentrations is observed at year 12 when the mixed layer depth changes. When the thin-layer cap is placed the next year, a large decrease in surface mercury concentrations is observed as this new material is mixed into existing sediments. After the thin layer placement, mercury concentrations actually increase due to the inputs of settling sediment mercury concentrations that are higher than the new sediment surface provided by thin-layer cap.

N.7.4.2 Flux Application of Model – Flux to Water Column

The results of the flux modeling are shown in Figure N.18. Results for methylmercury, both with and without ebullition, are shown. For all model runs, minimum Kds and maximum groundwater advection rates were used to be conservative in the estimate of flux rates. All other inputs were based on mid-point values shown in Table N.8.

The model predicts the flux of methylmercury out of the entire profundal sediment area (8 million m^2) in the first model year (1992) in the range of 0.8 to 2 kg/yr without and with ebullition of effects, respectively. Thus, upward flux of methylmercury is about 2.5 times higher with the assumption of ebullition acting both upon upward diffusion and particle advection. The upward flux rate of 0.8 kg/yr without ebullition is substantially higher than the rate presented by TAMS (2002), which as shown in Figure N.5, is 0.022 kg over the stratified period, or about 0.067 kg/yr. However, the modeled flux rate is lower than a similar estimate made by Sharpe (2003) of approximately 1.9 kg/yr methylmercury based on mass balance calculations. The sources of these differences in flux estimates are due to both the porewater/sediment data used in the various calculations as well as the methods of calculation.

The modeled methylmercury upward fluxes of 0.8 to 2 kg/yr are similar to the downward fluxes (Figure N.5) due to sedimentation presented by TAMS (2002), which were about 0.6 kg over the stratified period or about 1.6 kg/yr. The downward methylmercury fluxes using the mid-point value sediment trap data presented in Table N.8 are about 2.6 kg/yr. Comparisons of this latter number to model results of upward flux are more appropriate from a data consistency standpoint. Based on this, the downward flux of methylmercury is somewhere between three times higher to nearly equivalent to the upward flux calculated in the model. Thus, on balance, it appears more likely that the profundal sediments are a net sink of methylmercury to the lake system.

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The primary purpose of the flux application modeling is to understand the effect of MNR on methylmercury flux rates. Thus, despite differences in the absolute rate of flux from these various studies, the relative predicted impacts of MNR on the flux of methymercury to the water column can be understood by examining the change in upward flux rate over the modeling period as shown in Figure N.18. When no ebullition is assumed, the rate of methymercury upward flux remains relatively constant throughout the modeling period. Thus, any losses of methylmercury to the water column are balanced by downward fluxes of methylmercury due to sedimentation, which "replenish" the reservoir of methylmercury in the mixed layer sediments.

It is noteworthy that these estimates assume no reduction in methylmercury downward fluxes due to source controls. This assumption was made because of the uncertainties associated with estimating the impact of total mercury load reductions to the lake on methylmercury production in the hypolimnion. Although difficult to quantify, it is possible that the source controls might cause decreases in methylmercury downward flux that would tip the balance between upward and downward flux to and from profundal sediments and result in decreased methylmercury upward flux to the water column over time.

When ebullition is assumed, the results are somewhat different, as shown in Figure N.18. In this case, ebullition causes a net loss of methylmercury from the surface sediments and methylmercury fluxes move to a lower equilibrium as methylmercury concentrations in the mixed sediment layer decrease over time due to these processes.

Overall, if the effects of remedial source controls on methylmercury in the water column are assumed to be negligible (which appears open to debate), MNR would be expected to have little positive or negative impact on methymercury flux to the water column.

Figure N.18 also shows the potential effects of aeration (oxygenation) on flux rates of methylmercury from the profundal zone. Under this modeling scenario, it is assumed that aeration (oxygenation) causes a 50 percent decrease in the methylmercury concentrations present in settling sediments. This estimate is based on the mass balance estimates by TAMS, which indicate about half the methylmercury entering the lake occurs through production within the anoxic hypolimnion (2002). Thus, if aeration (oxygenation) is assumed to reduce this source of methymercury production, the downward flux of methylmercury can also reasonably be expected to be impacted to the same degree. Although there is great uncertainty associated with this assumption, Figure N.18 shows that reductions in methymercury production in the hypolimnion could cause substantial decreases in the upward flux of methylmercury from the profundal sediments over time. Thus, under this scenario, MNR combined with aeration (oxygenation) could substantially and positively alter the equilibrium of methymercury fluxes that appear to currently exist within the lake system.

N.7.5 IMPACT OF ESTIMATED FUTURE SOURCE CONTROLS

Table N.9 presents the results of the standard model for total mercury with and without source controls assumed. Source controls reductions are based on the values shown in Table N.3. Specifically, it was assumed that there would be:

- A 4 percent reduction in TSS loads (resulting in a similar reduction in sedimentation rates) and
- An 80 percent reduction in mercury loads (resulting in a similar reduction in settling sediment concentrations).

There are a number of substantial extrapolations associated with these assumptions and, thus the uncertainties of the results are large. However, these results provide a general indication how expected source load reductions could effect the course of the MNR.

Table N.9 shows that with the above source-control assumptions, total mercury concentrations in profundal sediments would be measurably lower than under the no-source-control assumption, after the same time period. The difference between ending mercury concentrations with and without source controls is larger when the starting sediment concentrations are relatively low (e.g. 1.5 mg/kg). Where starting sediment mercury concentrations are relatively high (e.g., 20 mg/kg), the resulting mercury concentrations at the end of the MNR period are relatively similar (Table N.9).

N.7.6 SENSITIVITY/UNCERTAINTY ANALYSIS

The standard model was evaluated for sensitivity to various input parameters and the results of this analysis are shown in Table N.11. Generally, the model is very sensitive to variations in settling rates, settling sediment mercury concentrations, mixed-layer depth, and mixed layer porosity inputs. The mixed-layer depth sensitivity is expected, since it defines the size of the "reservoir" that is impacted by transport processes. A larger reservoir will show less responsiveness to variations in flux to and from the mixed layer over time. Porosity is sensitive for the same reason, because it is the primary factor determining the *in situ* density of sediments present in the mixed layer.

The model is relatively insensitive to changes in partition coefficients, buried layer mercury concentrations, and groundwater velocities. Additional runs of the model indicated that the partition coefficients would have to be considerably lower (in the 1,000 to 10,000 L/kg) range before any of these parameters would have a substantial effect on the model. Thus, because mercury appears to be strongly associated with sediment particles, processes involving particulate movement dominate over dissolved-phase transport processes like porewater advection. This means that stable layers of new sediment will effectively isolate older layers of even highly contaminated sediment. This finding is consistent with the distinct variations with depth in the mercury concentration core profiles, indicating that dissolved phase transport has not "smeared" these profiles over time.

This finding also indicates that the greatest potential for uncertainty lies with the particulate phase processes of sedimentation and incoming concentrations of settling sediments. As noted before, there appears to be a considerable quantity of information to support the ranges used in the modeling. Consequently, the uncertainty associated with use of the mid-range value is relatively low.

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Other important uncertainties include the accuracy and calibration of the model to determine if major processes or parameters are being overlooked. This is the subject of the next section.

N.7.7 COMPARISON TO HISTORICAL TRENDS/CALIBRATION

The accuracy of the model was tested by comparing it to a recent core profile taken by Hairston, *et al.* (1999) and analyzed for total mercury by Sharpe (2003). This is the same core that was described in Subsection N.5.3 and Figure N.15. The model was run for a period from 1965 to 1996 and compared to the core data from the same period (with dating determined from ²¹⁰Pb results presented in Hairston, *et al.*, 1999). Relatively high-value input parameters for settling sediment mercury concentrations (1.9 mg/kg) and sediment settling rate (0.95 g/cm²/yr) were used for one of the model runs. These relatively high values were judged to be more representative of the period 1965 to 1996 because major inputs of TSS and mercury were still ongoing throughout much of this period from former Honeywell operations. All other parameters were set at the mid-point values in Table N.7, except porosity, which was set at 0.75.

In addition, the model was run using sedimentation rates from ²¹⁰Pb data and mercury concentrations derived from the 1997 core itself. In this case, the core was assumed to provide a record of the sedimentation rates and mercury concentrations at this particular location throughout the period, and these input parameters were varied as appropriate over the duration of the model run.

The results of these calibration runs are shown in Figure N.19. Both model runs provided results that are very similar to the record provided by the 1996 core data. The model run using high-value input parameters from Table N.7 appears to over-predict the actual rate of natural recovery observed in the core. This result is expected to some extent because it is likely that the mercury concentrations in the period from 1965 to 1986 were considerably higher than those assumed by this model run (which come from data collected in the 1990s). As would be expected, the model run using the core-derived input parameters (i.e., considerably higher mercury concentrations in settling sediments) shows a closer correlation to actual core data.

Importantly, both model runs appear to predict higher ending sediment mercury concentrations than were actually observed in the core. It is likely that this is due to a number of the conservative assumptions in the model construction as detailed above in modeling methods. Consequently, it appears that the model provides an accurate, if somewhat conservative, estimate of natural recovery processes of total mercury in the lake. Because of this, no further calibration or adjustment of the model was judged necessary.

As noted above, additional sediment sampling will take place for the pre-design process. Once obtained, this data set should be used to validate the model by comparing model predictions from 1992 to the date of pre-design sampling to actual pre-design results. Depending on the results of this validation process, the model presented here may need refining, or perhaps other models may be needed that might more accurately predict the actual changes in sediment chemistry observed since 1992.

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SECTION N.8

CONCLUSIONS ON EFFECTIVENESS OF MONITORED NATURAL RECOVERY

The primary conclusions of this natural recovery appendix are the following:

- State-of-the-art evaluation techniques for natural recovery indicate five major lines of evidence should be evaluated for these efforts. They include: characterization of sources, fate and transport processes, historical chemistry trends, historical biological trends, and predictive modeling.
- Ongoing source controls by others and Honeywell can be expected to lead to a small reduction in total suspended solids (TSS) loading and a more substantial reduction in mercury loading to the lake.
- Fate and transport processes indicate profundal sediments (at depths of more than 30 ft [9 m]) are more stable. Thus, they are more amenable to natural recovery, while recovery of sediments in upper littoral areas (water depths of less than 20 ft [6 m]) is expected to be less effective.
- Water column, sediment, and biological tissue chemistry trends all appear to have been relatively stable (neither increasing nor decreasing) over the last 10 years, although statistical uncertainty/variability associated with the historical database preclude a rigorous trend analysis.
- These stable historical trends do not account for source control efforts expected to significantly reduce mercury loads to the lake. Thus, predictive modeling is needed to reliably forecast future conditions in the lake associated with MNR.
- Predictive modeling indicates that decreases in mercury surface sediment concentrations can be expected for all profundal and deeper littoral sediments. Sediments in these areas that contain up to 6.7 milligrams per kilogram (mg/kg) total mercury, as measured in 1992, are expected to achieve the PEC of 2.2 mg/kg within a period of 10 years following upland and lake remediation. The profundal and deeper littoral areas would also be expected to meet the AET of 13 mg/kg, particularly because the vast majority of these areas already meet this benchmark concentration.
- Modeling indicates that the current surface weighted average mercury concentration in profundal sediments of approximately 2.6 mg/kg would be reduced to between 0.7 mg/kg (assuming ongoing anaerobic conditions) and 1.2 mg/kg (assuming an aerobic hypolimnion and benthic recolonization) within 10 years following remediation of upland and internal sources of mercury.
- Modeling indicates that surface sediment mercury concentrations will approach the settling sediment mercury concentrations over time.

- Evaluation of methylmercury fluxes from the profundal sediments using the predictive model indicates overall, with considerable uncertainty, that profundal sediments are a sink rather than a source of methylmercury to the hypolimnion. There may be seasonal variations that cause this balance to reverse, which are not reflected in the predictive model.
- The predictive model suggests that MNR by itself is not likely to substantially reduce the upward flux rate of methylmercury from the profundal sediments. However, this conclusion is based on the assumption that source controls will have little impact on the concentrations of methylmercury in settling sediments, which may not be the case.
- The predictive model suggests that MNR combined with aeration (oxygenation) may cause a substantial reduction in methylmercury fluxes from the profundal sediments over time.

Overall, MNR is a feasible remedial technology for the profundal sediments of Onondaga Lake. This technology appears to have value both by itself, and potentially in combination with thin-layer capping in any areas of relatively high baseline mercury concentrations (e.g., >6.7 mg/kg), that may exist in the profundal sediments.

The concentrations noted above are based on the most recent available data set, which is from 1992. Additional data will be collected as a part of the remedial design process, and these data will be used in any future predictions of natural recovery projected forward for the appropriate natural recovery period as determined by NYSDEC. Thus, the concentrations noted above will not be used to make remedial design decisions regarding the exact areas suitable for MNR versus thin-layer capping.

SECTION N.9

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APPENDIX N

TABLES

		1970-1986	Pre-1970					
	Water Input		TSS Load		Annual	Percent Annual	Annual	Annual
	(millions of	Percent Water	(1000s of	Percent TSS	Mercury Load,	Mercury Load	Mercury	Mercury
Input	$m^{3})^{a}$	Input ^a	kg) ^a	Load ^a	Mean (kg) ^b	$(\mathbf{kg})^{\mathbf{b}}$	Load (kg) ^d	Load (kg) ^d
Tributary Streams								
Sawmill Creek	8.2	1.9%	456.5	2.2%	N/AV	N/AV	N/AV	N/AV
Bloody Brook	8.2	1.9%	456.5	2.2%	N/AV	N/AV	N/AV	N/AV
Ley Creek	37.2	8.4%	1,400	6.9%	0.256	2.5%	N/AV	N/AV
Onondaga Creek	153.0	34.7%	11,075	54.4%	1.052	10.1%	N/AV	N/AV
Harbor Brook	9.1	2.1%	521	2.6%	0.246	2.4%	N/AV	N/AV
East Flume	0.5	0.1%	12	0.1%	0.161	1.5%	N/AV	N/AV
Ninemile Creek	125.0	28.3%	5,009	24.6%	3.857	37.1%	N/AV	N/AV
Tributary 5A	2.8	0.6%	93	0.5%	0.198	1.9%	N/AV	N/AV
Direct Discharges								
Metro Outfall 001	88.8	20.1%	1,132	5.6%	1.858	17.9%	N/AV	N/AV
Metro Outfall 002	3.4	0.8%	178	0.9%	N/AV	N/AV	N/AV	N/AV
Allied's Discharges	Closed	Closed	Closed	Closed	Closed	0.0%	233	3477
Groundwater								
Willis Avenue Site	0.37	0.1%	NA	NA	0.676	6.5%	N/AV	N/AV
Semet Residue Ponds	0.24	0.1%	NA	NA	0.560	5.4%	N/AV	N/AV
I-690 Drains	0.02	0.0%	NA	NA	0.347	3.3%	N/AV	N/AV
Wastebed B/Harbor Brook	0.18	0.0%	NA	NA	0.902	8.7%	N/AV	N/AV
"Background" Groundwater	0.51	0.1%	NA	NA	0.079	0.8%	N/AV	N/AV
Other								
Direct Precipitation	3.4	0.8%	19	0.1%	0.216	2.1%	N/AV	N/AV
Totals ^c	440.9	100.0%	20,352	100.0%	10.409	100.0%	N/AV	N/AV

ESTIMATED ANNUAL WATER, TOTAL SUSPENDED SOLIDS (TSS), AND TOTAL MERCURY INPUTS TO ONONDAGA LAKE

a 2002 data from Onondaga County 2003 (Ambient Monitoring Program Report).

b. Data from RI (TAMS, 2002), generally collected in the 1990s. Where partial year data were available, they were extrapolated to an annual load.

c. For comparative purposes Onondaga County (2003) reports a total TSS load of 14,700,000 kg in 1992 when mercury data were being collected for the RI.

d. These data are extrapolated from general information on historical loadings from Honeywell's operations (TAMS, 2002) and are very approximate.

Note these data are from various informational sources and in some cases extrapolated or calculated using other methods for illustrative purposes. Exact percentages and loads may vary from those presented in various references.

NA Not Applicable

N/AV Not Available

ESTIMATED ANNUAL TOTAL SUSPENDED SOLIDS (TSS) AND TOTAL MERCURY INPUTS TO ONONDAGA LAKE AFTER PROPOSED SOURCE CONTROLS

	Current TSS	Reduced TSS		Current Mercury		
	Load (1000s of	Load (1000s of		Load, Mean	Reduced Mercury	
Input	kg) ^a	kg) ^a	Reduction Reason	(kg) ^b	Load, Mean (kg) ^b	Reduction Reason
Tributary Streams						
Sawmill Creek	456.5	456.5	NA	N/AV	N/AV	NA
Bloody Brook	456.5	456.5	NA	N/AV	N/AV	NA
Ley Creek	1,400	1,400	NA	0.256	0.256	NA
Onondaga Creek	11,075	10,826	Elimination of Tully Mud Boils	1.052	1.052	NA
Harbor Brook	521	521	NA	0.246	0.000	Elimination of Harbor Brook Site inputs
East Flume	12	12	NA	0.161	0.000	Elimination of Willis Ave inputs
Ninemile Creek	5,009	5,009	NA	3.857	0.771	Elimination of LCP and Ninemile inputs
Tributary 5A	93	93	NA	0.198	0.000	Elimination of Semet Ponds inputs
Direct Discharges						
Metro Outfall 001	1,132	566	Metro upgrades	1.858	0.929	Metro upgrades
Metro Outfall 002	178	89	Metro upgrades	N/AV	N/AV	Metro upgrades
Allied's Discharges	Closed	NA	NA	Closed	0	NA
Groundwater						
Willis Avenue Site	NA	NA	NA	0.676	0.000	Elimination of Willis Ave. groundwater
Semet Residue Ponds	NA	NA	NA	0.560	0.000	Elimination of Semet Ponds groundwater
I-690 Drains	NA	NA	NA	0.347	0.000	Elimination Harbor Brook groundwater
Wastebed B/Harbor Brook	NA	NA	NA	0.902	0.000	Elimination of Willis Ave. groundwater
"Background" Groundwater	NA	NA	NA	0.079	0.040	NA
Other						
Direct Precipitation	19	NA	NA	0.216	0	NA
Totals ^c	20,352	19,429		10.41	3.07	
Precent Reduction		4.5%			70.5%	

a 2002 data from Onondaga County, 2003 (Ambient Monitoring Program Report).

b. Data from RI (TAMS, 2002), generally collected in the 1990s. Where partial year data were available, they wereextrapolated to an annual year load.
c. For comparative purposes, Onondaga County (2003) reports a total TSS load of 14,700,000 kg in 1992 when mercury data were being collected for the RI. Note these data are from various informational sources and in some cases extrapolated or calculated using other methods for illustrative purposes. Exact percentages and loads may vary from those presented in various references.
NA Not Applicable

SUMMARY OF ANNUAL LOAD ESTIMATES OF TOTAL MERCURY AND TSS, AND REDUCTIONS POTENTIALLY CAUSED BY SOURCE CONTROLS

	TSS Load To	TSS Load To		
	Profundal	Profundal	Total Mercury	Total Mercury
	Sediments - High	Sediments - Low	Load to Lake	Load to Lake
	Estimate (1000s	Estimate (1000s	Water - High	Water - Low
	kg/yr) ^a	kg/yr) ^b	Estimate (kg/yr) ^c	Estimate (kg/yr) ^d
External Sources				
Existing Inputs	20,352	10,000	10.41	10.41
Inputs with Upland Source Controls	19,429	9,077	3.07	3.07
Percent Reduction	4.5%	9.2%	70.5%	70.5%
Internal Sources (Resuspsension)				
Existing Flux ^e	6,048	11,400	52.00	5.20
Flux with ILWD Remediation	6,048	11,400	0	0
Percent Reduction	0.0%	0.0%	100.0%	100.0%
Total Sources				
Existing Condition	26,400	21,400	62.41	15.61
With Future Source Controls	25,477	20,477	3.069	3.069
Percent Reduction	3.5%	4.3%	95.1%	80.3%

a. TSS loads from year 2002 data from Onondaga County, 2003 (Ambient Monitoring Program Report).

b. TSS load is lower 20th percentile of 1989 to 2002 loads from Onondaga County, 2003 (Ambient Monitoring Program Report).

c. Mercury loads reflect high estimate from resuspension from TAMS, 2002.

d. Mercury loads reflect low estimate from ILWD resuspension from TAMS, 2002.

e. For TSS high estimate, calculated as the difference between all TSS inputs (2002 data; 20.3 million kg/yr) and sedimentation in the profundal (26.4 million kg/yr; as measured by 1992 hypoliminion sediment traps). For TSS low estimate, calculated as the difference between all TSS inputs (1992 data; 15 million kg/yr) and sedimentation in the profundal (1992 hypolimnion sediment traps; 26.4 million kg/yr).

TABLE N.4 SUMMARY OF SEDIMENTATION DATA FOR ONONDAGA LAKE (DEPICTED GRAPHICALLY IN FIGURE N.7)

	Evaluati	on Period		Estimates	
Source	Start Date	Stop Date	Mid-range	Minimum	Maximum
Cores (cm/yr)					
Hairston et al., 1997	1981	1981	0.756	0.667	0.874
Hairston et al., 1997	1984	1984	1.244	1.052	1.481
Hairston et al., 1997	1987	1987	0.563	0.504	0.622
Hairston et al., 1997	1993	1993	0.370	0.341	0.385
Hairston et al., 1997	1997	1997	0.326	0.296	0.341
TAMS, 2002 (discussion of Rowell 1992 cores)	1954	1964	0.280		
TAMS, 2002 (discussion of Rowell 1992 cores)	1964	1988	0.830		
TAMS, 2002 Fig. 6-30 (Rowell 1992)	1954	1963	0.556	0.333	0.778
TAMS, 2002 Fig. 6-30 (Rowell 1992)	1964	1988	0.875	0.833	0.917
TAMS, 2002 (discussion of RI 1992 deep cores)	1954	1964	1.100		
TAMS, 2002 Fig. 6-28 (RI 1992 cores)	1954	1963	1.100	0.900	1.500
TAMS, 2002 Fig. 6-28 (RI 1992 cores)	1963	1992	0.897	0.828	1.034
TAMS, 2002 Fig. 6-29 (RI 1996 Cores)	1954	1963	0.800	0.700	1.000
TAMS, 2002 Fig. 6-29 (RI 1996 Cores)	1964	1996	0.727	0.697	0.788
Direct evaluation of RI 1996 Core Data	1953	1963	0.750	0.625	0.875
Direct evaluation of RI 1996 Core Data	1964	1970	0.714	0.536	0.893
Direct evaluation of RI 1996 Core Data	1971	1996	0.721	0.577	0.769
Effler, 1996 (mercury core p. 634)	1946	1970	0.420		
Effler, 1996 (Cs ¹³⁷ Cores pp. 648, 655)	1954	1963	0.722	0.444	1.000
Effler, 1996 (Cs ¹³⁷ Cores pp. 648, 655)	1964	1988	0.595	0.574	0.616
Effler, 1996 (Pb ²¹⁰ cores p. 649)	1955	1988	1.212	0.909	1.515
Sediment Trong (a/am ² /un)					
TAMS 2002 1002 Sediment Trans (Table 6 10)	1002	1002	0 497	0.270	0.762
TAMS, 2002 1992 Sediment Traps (Table 6-19)	1992	1992	0.467	0.270	0.702
Direct Evolution of 1006 Sediment Tran Date	1992	1992	0.448	0.270	1 152
Effler 1006 Sediment Trans 1086 (np. 606 607)	1990	1990	0.480	0.100	1.135
Effler 1006 Sediment Trans 1986 (pp. 606-607)	1980	1980	2.049	0.800	3.338
Sharpa 2002 Sadiment Trans 2000	1988	1988	0.022	0.102	1.373
Sharpe, 2003 Sediment Traps 2000	2000	2000	0.317	0.138	0.530

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TABLE N.5

SUMMARY OF DISTRIBUTION COEFFICIENTS (Kd) CALCULATED FROM POREWATER DATA IN SUBSURFACE CORES (TAMS, 2002)

	Mercury		Methylmercury				
Depth	Statistic	Kd (L/kg)	Depth	Statistic	Kd (L/kg)		
All Data	Data Low 81,081		All	Low	604		
	Mid	490,669		Mid	11,747		
	High	1,009,146		High	62,083		
0-4 cm	Low	81,081	0-4 cm	Low	604		
	Mid	195,572		Mid	2,681		
	High	379,191		High	4,863		
0-12 cm	Low	81,081	0-12 cm	Low	604		
	Mid	393,304		Mid	10,705		
	High	961,765		High	62,083		
>12 cm	Low	386,332	>12 cm	Low	2,250		
	Mid	709,742		Mid	13,829		
	High	1,009,146		High	21,870		

SUMMARY OF WATER COLUMN SEDIMENT TOTAL MERCURY CONCENTRATIONS (mg/kg) FROM SEDIMENT TRAP AND WATER DATA IN ONONDAGA LAKE

			Epiliminion		Hypolimnion		Littoral		
Data Source	Statistic	Year	North	South	North	South	North	South	Average
1992 Water Data (TAMS, 2002)	Min	1992	0.32	0.35	0.61	0.76			
1992 Trap Data (TAMS, 2002)	Min	1992	1.18	0.29	0.79	0.55	0.95	0.76	
1996 Trap Data (TAMS, 2002)	Min	1996				0.87			
1999 Water Data (TAMS, 2002)	Min	1999	0.90	1.03	0.20	0.17	0.56	0.79	
2000 Trap Data (Sharpe, 2003)	Min	2000		0.21					
2000 Water Data (Sharpe, 2003)	Min	2000		0.24		0.50			
2001 Water Data (TAM,S 2002)	Min	2001		0.68				1.09	
2002 Water Data (Onondaga County, 2003)	Min	2002	0.53	0.70	1.10	1.29			
1992 Water Data (TAMS, 2002)	Avg.	1992	0.51	0.57	0.98	1.22			
1992 Trap Data (TAMS, 2002)	Avg.	1992	1.46	1.23	1.18	1.46	1.73	2.57	
1996 Trap Data (TAMS, 2002)	Avg.	1996				1.70			
1999 Water Data (TAMS, 2002)	Avg.	1999	1.75	2.65	2.05	3.37	1.72	4.15	
2000 Trap Data (Sharpe, 2003)	Avg.	2000		0.56					
2000 Water Data (Sharpe, 2003)	Avg.	2000		0.72		1.50			
2001 Water Data (TAMS, 2002)	Avg.	2001		2.45				2.45	
2002 Water Data (Onondaga County, 2003)	Avg.	2002	1.01	1.56	3.62	3.52			
1992 Water Data (TAMS, 2002)	Max	1992	1.52	1.68	2.89	3.60			
1992 Trap Data (TAMS, 2002)	Max	1992	2.13	1.77	1.43	2.23	1.98	4.41	
1996 Trap Data (TAMS, 2002)	Max	1996				2.99			
1999 Water Data (TAMS, 2002)	Max	1999	2.61	9.45	3.54	9.51	2.95	13.49	
2000 Trap Data (Sharpe, 2003)	Max	2000		0.85					
2000 Water Data (Sharpe, 2003)	Max	2000		1.80		3.26			
2001 Water Data (TAMS, 2002)	Max	2001		6.39				16.47	
2002 Water Data (Onondaga County, 2003)	Max	2002	1.30	2.28	5.21	5.67			
Minimum for Trap Data			1.18	0.21	0.79	0.55	0.95	0.76	0.65
Average for Trap Data			1.46	0.90	1.18	1.58	1.73	2.57	1.26
Maximum for Trap Data			2.13	1.77	1.43	2.99	1.98	4.41	1.90

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			Input Values							
Parameter	Symbol	Units	Low		Mid		High	Information Sources		
Initial Mixed Layer Concentration	B_{LT}	mg/kg	1.5	2.5	4	7.5	20	Range of values found in profundal and deep littoral sediments throughout lake (TAMS, 2002).		
Initial Buried Layer Concentration	B_{BT}	mg/kg	1.5	2.5	4	7.5	20	Range of values found in profundal and deep littoral sediments throughout lake (TAMS, 2002).		
Settling Sediment Concentration	B ₀	mg/kg	0.99		1.39		1.80	NYSDEC recommended value - Based on three samples representing top two slices of the 1996 and 1997 cores. Mid- range is the mean of the samples, and low and high values represent the range of concentrations.		
Partition Coefficient, Mixed Layer	K _d	L/kg	81,081		195,572		961,765	Porewater data from profundal cores (2000) 0-4 cm or 0-12 cm samples, RI Table B1-49. (TAMS, 2002) See Section 4.2.1 for review.		
Partition Coefficient, Buried Layer	K _d	L/kg	386,332		709,742		1,009,146	Porewater data from profundal cores (2000) >12 cm samples, RI Table B1-49. See Section 4.2.1 for review.		
Molecular Diffusion Coefficient	D ₀	cm ² /yr			202			Calculated per DiToro <i>et al</i> ., 1981 ($D_0 = 6935*MW^{-2/3}$)		
Mixed Layer Porosity	j	unitless			0.91			Calculated from NYSDEC provided estimates of Pb		
Buried Layer Porosity	j	unitless			0.86			Calculated from NYSDEC provided estimates of Pb		
Post-2004 Mixed Layer Porosity	j	unitless			0.88			Calucated from depth weighted average of in-situ porosities		
Biodiffusion Coefficient	D _b	cm ² /yr			9.73			Boudreau, 1997, Equation 4.148. $D_b = 15.7 * s^{0.69}$ and $s = w / ((1-j)*SG)$		
Velocity of Porewater	и	cm/yr	0.04		0.72		1.4	Values based on lines of evidence presented in Section 4.1.4.		
Settling Sediment Flux	W	g/cm ² /yr	0.113		0.125		0.158	NYSDEC recommended value - Based on re-evaluation of high resolution cores using 1986.5 marker, and density of 0-4 cm derived by Hairston's 1997 core.		
Depth of Mixed Layer	L	cm			4-10			Assumed rapid increase in bioturbation from 4 cm to 10 cm deep due to hypolimnetic oxygenation and/or recovery of sediments in year 2004 of the model.		
Specific Gravity of Dry Sediment	SG	g/cm ³			2.7			Typical value.		
In-Situ Density Mixed Layer	Pb	g/cm3			0.25			NYSDEC recommended value - Based on Hairston 1997 core, percent moisture and assumed SG value (2.7) for 0 - 4 cm.		
In-Situ Density Buried Layer	Pb	g/cm3			0.39			NYSDEC recommended value - Based on Hairston 1997 core, percent moisture and assumed SG value (2.7) for 4-10 cm.		
In-situ Density Post Aeration Mixed Layer	Pb	g/cm3			0.34			NYSDEC recommended value - Based on Hairston 1997 core, percent moisture and assumed SG value (2.7) for 0 - 10 cm.		

INPUT PARAMETERS AND SOURCE INFORMATION FOR STANDARD NATURAL RECOVERY MODELING OF TOTAL MERCURY
TABLE N.8 INPUT PARAMETERS AND SOURCE INFORMATION FOR FLUX MODELING OF METHYL MERCURY

		Units	Input Values						
Parameter	Symbol		Low		Mid		High	Information Sources	
Initial Mixed Layer Concentration	C_{LT}	mg/kg	0.002	0.015	0.030	0.045	0.060	Range of values found in profundal and deep littoral sediments throughout lake (TAMS, 2002).	
Initial Buried Layer Concentration	C_{BT}	mg/kg	0.002	0.075	0.010	0.015	0.020	Range of values found in profundal and deep littoral sediments throughout lake (TAMS, 2002).	
Settling Sediment Concentration	<i>B</i> ₀	mg/kg	0.001		0.060		0.167	Mininum, average, and maximum from 1992, 1996, and 2000 non-littoral sediment traps.(TAMS, 2002).	
Partition Coefficient, Mixed Layer	K _d	L/kg	604		2,681		4,863	Porewater data from profundal cores (2000) 0-4 cm samples, RI Table B1-49. See Section 4.2.1 for review.	
Partition Coefficient, Buried Layer	K _d	L/kg	2,250		13,829		21,870	Porewater data from profundal cores (2000) >12 cm samples, RI Table B1-49. (TAMS, 2002). See Section 4.2.1 for review.	
Molecular Diffusion Coefficient	D ₀	cm ² /yr			193			Calculated per DiToro <i>et al.</i> , 1981 ($D_0 = 6935*MW^{-2/3}$)	
Mixed Layer Porosity	j	unitless			0.75			Based on a variety of informational sources, including Effler, 1996 Fig. 8.14 on surface sediment types for profundal sediments.	
Buried Layer Porosity	j	unitless			0.75			Same as mixed layer porosity. Porosity not expected to change substantially in first few centimeters below mixed layer.	
Biodiffusion Coefficient	<i>D</i> _{<i>b</i>}	cm ² /yr			11.89			Boudreau, 1997, Equation 4.148. $D_b = 15.7 * s^{0.69}$ and $s = w / ((1-i)*SG)$	
Velocity of Porewater	и	cm/yr	0.04		0.72		1.4	Values based on lines of evidence presented in Section 4.1.4.	
Settling Sediment Flux	W	g/cm ² /yr	0.072		0.451		0.951	See review Section 4.1.2. NYSDEC (2003) suggested 0.3 based on fewer data points.	
Depth of Mixed Layer	L	cm			4-10			Assumed rapid increase in bioturbation from 4 cm to 10 cm deep due to hypolimnetic oxygenation and/or recovery of sediments in year 2004 of the model.	
Specific Gravity of Dry Sediment	SG	g/cm ³			2.7			Typical value.	

TABLE N.9

TOTAL MERCURY - PROFUNDAL NATURAL RECOVERY MODELING, PREDICTED CONCENTRATION PROJECTED 22 YEARS FROM 1992 CONDITIONS (mg/kg in surface mixed layer sediments at end of modeling period)

		Post Capping Concentration ^a					
Scenario	1.5	2.5	2.59 (SWAC)	4	7.5	20	0
Natural Recovery (10 cm post-remediation mixed layer depth) ^b							
with Current Souces							
Reasonable mid-point values	1.25	1.47	1.49	1.81	2.60	5.42	0.21
"Worst-case" values ^c	1.58	1.79	1.81	2.19	3.14	6.50	0.33
with Source Controls							
Reasonable mid-point values	0.93	1.17	1.19	1.53	2.38	5.42	0.04
"Worst-case" values ^c	1.06	1.41	1.44	1.84	2.84	6.42	0.07
Natural Recovery (4 cm post-remediation mixed layer depth) ^d							
with Current Souces							
Reasonable mid-point values	1.43	1.48	1.49	1.57	1.76	2.46	NA
"Worst-case" values ^c	1.86	1.94	1.94	2.05	2.32	3.28	NA
with Source Controls							
Reasonable mid-point values	0.65	0.70	0.71	0.79	1.00	1.74	NA
"Worst-case" values ^c	0.89	0.98	0.98	1.10	1.38	2.39	NA
Thin-Layer Cap Placement (15 cm) with Current Sources							
Reasonable mid-point values	0.36	0.41	0.41	0.48	0.66	1.28	NA
"Worst-case" values ^c	0.49	0.53	0.53	0.59	0.77	1.50	NA
Thin-Layer Cap Placement (10 cm) with Current Sources							
Reasonable mid-point values	0.44	0.50	0.51	0.60	0.82	1.63	NA
"Worst-case" values ^c	0.59	0.64	0.65	0.72	0.98	1.91	NA

a Assumes clean cap material is placed, and has an initial mercury concentration of zero. Provides a value for comparison of natural recovery and active remediation scenarios. Concentration projected 20 years after installation of the cap

b For these model runs the the mixed layer (bioturbation) depth is set at 4 cm for the pre-remediation period (1992-2004) and 10 cm for the postremediation period (2004-2014). This assumes that, once implemented, aeration (oxygenation) would cause increased bioturbation in the profundal c "Worst-case" is that combination of parameters from Table 7 that produces the slowest decrease (or greatest increase) in mixed layer

concentrations.

d For these model runs the the mixed layer (bioturbation) depth is set at 4 cm for the entire pre-remediation (1992-2004) and post-remediation (2004-2014) periods. This assumes that aeration (oxygenation) or similar technologies are not implemented and minimal bioturbation would continue to occur in the anoxic profundal sediments.

NA Not Applicable or run not conducted.

SWAC - The Surface Weighted Average Concentration of the entire profunal area.

TABLE N.10

TOTAL MERCURY - PROFUNDAL NATURAL RECOVERY MODELING, STARTING CONCENTRATIONS THAT ACHIEVE TWO SEC VALUES, PROJECTED 22 YEARS FROM 1992 CONDITIONS (mg/kg in top 10 cm of sediments at end of modeling period)

	Starting Concentration (mg/kg)		
	Meets PEC of 2.2	Maata AET of 12 mg/kg	
Scenario	mg/kg	Meets AET of 15 mg/kg	
Current sources using reasonable mid-values	5.7	>30	
Current sources using "worst-case" values ^a	4.0	>30	
Assumed source controls using reasonable mid-values	6.7	>30	
Assumed source controls using "worst-case" values*	5.2	>30	
Thin cap placement (15 cm) using reasonable mid-values	>30	>30	
Thin cap placement (15 cm) using "worst-case" values ^a	>30	>30	
Thin cap placement (10 cm) using reasonable mid-values	28.9	>30	
Thin cap placement (10 cm) using "worst-case" values ^a	23.7	>30	

a "Worst-case" is that combination of parameters from Table 7 that produces the slowest decrease (or greatest increase) in mixed layer concentrations.

PEC - Probable Effects Concentration.

AET - Apparent Effects Threshold.

Note - all results shown assume a post-remediation (2004-2014) mixed layer depth of 10 cm.

Standard Model		Result at End MNR	Sensitivity	
Input Parameter	Input Value	Period (mg/kg Total Mercury)	Ratio	
Settling Sediment Flux (g/cm2/yr)				
Minimum	0.072	3.41		
Maximim	0.951	1.36		
Relative Percent Difference	-172%	86%	0.50	
Settling Sediment Mercury Concentration (mg/kg)				
Minimum	0.65	1.20		
Maximim	1.90	2.24		
Relative Percent Difference	-98%	-60%	0.62	
Partition Coefficient, Mixed Layer (L/kg)				
Minimum	81081	1.70		
Maximim	961765	1.71		
Relative Percent Difference	-169%	-0.6%	0.00	
Partition Coefficient, Buried Layer (L/kg)				
Minimum	386,332	1.71		
Maximim	1009146	1.70		
Relative Percent Difference	-89%	0.6%	0.01	
Buried Layer Mercury Concentration (mg/kg)				
Minimum	1.50	1.70		
Maximim	20.00	1.71		
Relative Percent Difference	-172%	-0.6%	0.00	
Porewater Velocity (cm/yr)				
Minimum	0.04	1.71		
Maximim	1.40	1.71		
Relative Percent Difference	-189%	0.0%	0.00	
Mixed Layer Depth (cm) ^a				
Minimum	4	1.34		
Maximim	10	1.89		
Relative Percent Difference	-86%	-34.1%	0.40	
Porosity Mixed Layer (unitless)				
Minimum	0.65	1.99		
Maximim	0.85	1.44		
Relative Percent Difference	-27%	32.1%	1.20	

TABLE N.11 sensitivity analysis of model variables

a Parameter held at the value shown throughout model period.

APPENDIX N

FIGURES





































