Appendix I

Statistical Analysis of Chemical Parameters of Interest in Onondaga Lake

## APPENDIX I. STATISTICAL ANALYSIS OF CHEMICAL PARAMETERS OF INTEREST IN ONONDAGA LAKE

#### I.1 Introduction

This appendix presents the statistical analyses undertaken to evaluate the distribution of chemical parameters of interest (CPOIs) in Onondaga Lake sediments. Interpreting the Onondaga Lake sediment data presents several challenges. Most significantly, the contamination in the lake's sediment is quite complex, containing multiple contaminants and multiple sources, as reflected in the extensive analytical data set. Sediment was collected from more than 240 stations across the lake, and each station included samples at depths ranging from as little as 2 cm to as much as 8 m below the lake bottom. The result is that there are over 700 individual samples of sediment solids, each of which was analyzed for as many as 161 individual analytes.

Other complicating factors include widely variable sample spacing, concentrations of individual analytes that range over six orders of magnitude, and detection limits that are both highly variable and, in some cases, exceed all detected values. Because of this complexity, geostatistical modeling and a principal component analysis (PCA) were chosen as the most efficient methods for extracting usable information about the sources and distribution of CPOIs in the lake. The objectives of the statistical analyses were to:

- Assess the probability that the concentration of CPOIs (in particular mercury) in lake sediment exceed critical environmental thresholds.
- Determine the distribution of metals (other than mercury) as well as the sources and distribution of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) in the lake.

The first objective was achieved through a geostatistical assessment of lake sediment data. The results from this analysis are intended to support the feasibility study (FS), initially by assessing the adequacy of the existing sediment data for evaluating remedial alternatives, and eventually by providing a guide for any future analysis that may be required to assess the uncertainty about the value of sediment properties at unsampled locations.

The second objective was achieved through multivariate statistical analysis using sediment data from the lake. A common multivariate technique, PCA, was used to reduce the dimensionality of the data set and the results, to infer sources, and determine factors that account for observed CPOI concentrations in the lake. The CPOIs considered in the PCA analysis were metals, PAHs, and PCDD/PCDFs, as these are the CPOIs that may have multiple sources to the lake other than Honeywell. For other significant CPOIs, including mercury; benzene, toluene, ethylbenzene, xylenes (BTEX); and chlorinated benzenes, Honeywell has been determined to be the most significant source to the lake.

# I.2 Characterization and Spatial Distribution of Mercury in Onondaga Lake Sediments

This section presents the geostatistical analysis used to delineate mercury contamination in lake bottom sediments. In managing contaminated sediments it is important to evaluate the uncertainty of the spatial distribution of the contaminants so as to optimize the proposed remediation. Geostatistics provides a set of tools that allow explicit modeling of uncertainty in the form of local probability distributions for concentrations of contaminants.

The previous geostatistical assessment by Honeywell (Exponent, 2001) provided estimates of CPOI concentrations and distribution at unsampled locations using parametric kriging techniques. There is increasing awareness that such estimates are of little value in the absence of a measure of associated uncertainty (Van Meirvenne and Goovaerts, 2001). This is especially the case for prediction of environmental variables where the prediction uncertainty is required to support decision-making about further management. Because environmental variables typically display highly skewed distributions, using the kriging variance from parametric approaches as a measure of reliability of the kriging estimates is misleading. The main limitations are:

- The assumptions of normality of the distribution of prediction errors.
- Homoscedasticity (i.e., the variance of the errors is independent of the data values).

In this appendix, indicator kriging, a non-parametric approach, was used to assess the probability that mercury concentrations in the lake sediments exceed site-specific threshold criteria. This assessment serves as a preliminary analysis in the decision-making process, providing a possible basis for the delineation of remediation areas. The site-specific threshold used is the consensus probable effect concentrations (PEC) developed for Onondaga Lake using toxicity and chemistry data as described in the BERA. The PECs are site-specific and are calculated by taking the geometric mean of the apparent effects threshold (AET), threshold effect levels (TELs), probable effect levels (PELs), effects range-low (ER-L), and effects range-median (ER-M) values for each contaminant. The PEC value for mercury is 2.2 mg/kg, which is approximately the same order-of-magnitude as NYSDEC's severe effect level (SEL) of 1.3 mg/kg and approximately one order-of-magnitude greater than NYSDEC's lowest effect level (LEL) of 0.15 mg/kg.

#### I.2.1 Characterizing Mercury Contamination in Sediment

Before applying geostatistical techniques to assess the probability of exceedances of the mercury PEC at unsampled locations, it is important to first understand the phenomena influencing the characteristics and distributions of the sediments and contaminants in Onondaga Lake. Onondaga Lake is a complex environment where both natural and anthropogenic processes influence the distribution of contaminants, which in turn are important for remedial measures and pollution control.

#### I.2.1.1 Influence of Sampling Program on Spatial Complexities

Lake bottom sediment samples were collected during two events in 1992 and 2000, as follows:

- **1992:** The samples were collected along a more or less regularly spaced grid covering the entire lake bottom (Figure I-1). The 1992 samples were collected from sediment depth intervals of 0 to 0.02, 0 to 0.30, 0.30 to 0.60, 0.60 to 0.90, 0.90 to 1.2, 1.2 to 1.5, 1.5 to 1.8, and 1.8 to 2.1 meters (m).
  - **2000:** The samples were located primarily in contaminated areas, with samples clustered at the mouth of Ninemile Creek and between Ley Creek and Tributary 5A (Figure I-2). The 2000 samples were collected from sediment depth intervals of 0 to 0.02, 0 to 0.15, 0.15 to 0.30, 0.30 to 1, 1 to 2, 2 to 3, 3 to 4, 4 to 5, 5 to 6, 6 to 7, and 7 to 8 m.

As stated above, in addition to the different lateral distributions of sediment stations, the 1992 and 2000 events sampled different depth (vertical) intervals. For each sampling event, not all depth intervals were sampled at each coring location. The resulting data set is robust; however, the spatial distribution of the data is irregular both horizontally and vertically, with clustering in the more-contaminated areas. A detailed explanation of the scope of the sampling program is provided in Chapter 2 of this RI.

#### I.2.1.2 Natural Processes Affecting Contaminant Distribution

The sediments of Onondaga Lake are divided into two zones: the littoral zone (out to 9 m water depth, typically the depth of the thermocline) and the profundal zone (beyond 9 m water depth). Since the littoral zone sediments are covered by shallow, oxygenated water, they are subject to disturbance by wind-driven resuspension and bioturbation. Auer et al. (1996) described the profundal sediments as relatively undisturbed and reflective of sediment focusing (where fine-grained sediment and associated contaminants are resuspended from the littoral zone and deposited in the profundal zone). Because of the lake's depth and the formation of an anoxic hypolimnion, the profundal sediments are not subject to resuspension or bioturbation, in contrast to the sediments in the littoral zone.

The influx of suspended sediments from the tributaries also affects contaminant distribution in the lake bottom sediments. The tributaries form deltas of varying size and lateral extent, which physically impact the morphology of the lake bottom and subsequently the contaminant distribution. In addition, some of the tributaries are sources of contamination. Ninemile Creek and Onondaga Creek represent the two largest tributary inputs of water and suspended solids to Onondaga Lake.

In summary, sediment focusing, wind-driven resuspension, bioturbation, and tributary flow are among the most important natural processes that influence the distribution of contaminants in the lake bottom sediments.

#### I.2.1.3 Anthropogenic Processes Affecting Contaminant Distribution

Onondaga Lake is surrounded by industrial, commercial, and recreational areas. Most of the northern half of the lakeshore is park land, while commercial and industrial areas are concentrated around the southern end (Figure I-3). Onondaga Lake has been influenced by anthropogenic activities for over 200 years (Effler and Harnett, 1996). The varied nature and extent of these activities also influence the distribution of the CPOIs.

The historical discharge of waste into Onondaga Lake is probably the largest anthropogenic influence on contaminant distribution. The East Flume, one of the most significant discharge locations, is an excavated drainage ditch that received releases from Honeywell's plant sites. This material was discharged into the lake and formed a large delta (on the order of 3 million cubic meters [m<sup>3</sup>]) of combined waste, referred to as the Honeywell in-lake waste deposit throughout this RI report (see Chapter 4, Section 4.5). Figure I-3 illustrates some of the historic sources of contaminants to Onondaga Lake, including the East Flume and the approximate extent of the Honeywell in-lake waste deposit.

An example of the effect of the historical discharge of waste on the spread of contaminants is the "halo effect" observed for mercury and PCBs in the area of the East Flume (Chapter 5, Figures 5-2 and 5-23). The halo describes the area wherein sediments with higher concentrations surround sediments with relatively lower concentrations. The most likely cause of the halo effect is a combination of the history of usage of various chemicals and the ensuing industrial discharge. Honeywell used or produced several of the major CPOIs (low molecular weight PAHs [LPAHs], chlorinated benzenes, BTEX) from at least as early as 1918, but did not begin using PCBs or mercury until the 1940s (possibly in the late 1930s). Based on historical aerial photographs obtained from Cornell University's Institute for Resource Information Systems (see Chapter 4, Figures 4-6 through 4-12) (D. Ayers, pers. comm., 2001), it was found that by 1938, the East Flume had already been discharging into Onondaga Lake near the western edge of Wastebed B, and by 1951 it had moved east such that the discharge point was close to the midpoint of the wastebed's shoreline (Figure I-3).

Prior to the 1940s, a mound of Honeywell waste had formed near the point of discharge, extending along the lakeshore to the southeast. The predominant current in Onondaga Lake is counterclockwise, so the wastes would be carried along the shore (southeast) away from the East Flume. These wastes presumably contained many organic CPOIs but not mercury or PCBs, as they were not yet in use. When Honeywell began using mercury and PCBs sometime in the 1940s, the deposition of subsequent waste materials discharged via the East Flume occurred at the edges of the existing mound, forming a semicircle of mercury and PCB-contaminated sediments. The exact location of the semicircle depended upon the then-existent bathymetry and the location of the point of discharge. Other contaminants, such as dichlorobenzenes, do not exhibit a halo pattern, as they were discharged continuously since well before 1938 (Chapter 5, Figure 5-17).

Others areas of inflow to the lake have similar local variability; for example, the mouth of Tributary 5A. Mercury concentrations are quite low close to the tributary mouth, but increase dramatically farther into the lake (Chapter 5, Figure 5-2).

Other areas of the lake have similar variability due to anthropogenic activities. The distribution of mercury contamination at the Ninemile Creek delta reflects both the discharge of mercury from Honeywell facilities and dredging by Honeywell and Onondaga County in the late 1960s.

#### I.2.2 Geostatistical Assessment of Mercury in Sediment

Geostatistical analysis consists of multiple steps, each usually requiring a series of assumptions and decisions regarding the choice of approaches. Since the objective of this analysis is to estimate the probability of exceeding a critical threshold (i.e., PEC), indicator kriging was performed. The steps typically involved in this analysis include:

- Exploratory statistical analysis.
- Spatial correlation modeling.
- Spatial prediction by kriging.
- Validation of uncertainty models.

The last step, which deals with validation, was not performed in this analysis.

#### I.2.2.1 Exploratory Data Analysis

A preliminary exploration of the data is typically conducted prior to a formal modeling analysis. This preliminary exploration examined the lake sediment data for 1992 for the 0 to 2.1 m depth interval and for 2000 for the 0 to 2 m depth interval by displaying histograms and computing summary statistics. Distributions of the log-transformed data were also examined. There were very few non-detect samples for mercury and the detection limits were spatially consistent and did not influence the summary statistics.

The first analysis was to compare the 1992 and 2000 data to each other to determine whether the data sets can be combined in the geostatistical analysis. In 1992, the sampling covered the entire lake bottom, while the 2000 sampling focused on source areas. For this reason, comparison of the 1992 and 2000 data was limited to the littoral zone only, where most of the 2000 data were collected (Figure I-2). The resulting histograms and summary statistics for all sediment concentrations between 0 to 2 m (Figure I-4) showed little discernable differences in the distribution and magnitude of mercury concentrations in both years. However, it should be noted that the 2000 data included more littoral zone samples at depth than the 1992 data.

The entire lake bottom was divided into two regions for further analysis and kriging: the profundal zone and the littoral zone. The profundal zone was analyzed using only the data for 1992. The area in the southwestern littoral zone from Ley Creek to the Ninemile Creek delta was analyzed using only the 2000

data. The remaining area of the littoral zone (i.e., the northeastern area) was not analyzed because there were very few data points, and these had large separation distances. Any analysis done on the northeastern littoral zone would result in poor resolution and large uncertainties. Based on the low levels of mercury observed in the samples from the northeastern area, it is clear that this area does not accumulate substantive levels of contamination, unlike the littoral region from Ley Creek to the Ninemile Creek delta. Both the profundal zone and the southwestern littoral zone region were analyzed using the depth intervals of the samples for which the data were collected. Summary statistics and histograms were prepared for each depth interval and each region (Figures I-5 to I-6). This exploratory statistical analysis suggests that:

- The data are highly positively skewed and in some cases the distribution is bimodal, which indicates the presence of hot spots or zones of high contamination.
- The log transformation in most cases did little to improve the departures from normality.

Based on these observations, indicator kriging was selected for the geostatistical approach. It is important to note that indicator kriging makes no assumption about the underlying distribution of the data.

#### I.2.2.2 Spatial Correlation Modeling

Geostatistical estimations are based on a model of spatial continuity or correlation. Spatial correlation is measured using a tool known as the semivariogram. Before constructing the semivariogram, the mercury concentrations were first transformed into an indicator variable (w), which is a binary variable that takes the values 1 and 0 only as follows:

$$w(x) = \begin{cases} 1 & if Hg(x) > PEC \\ 0 & if otherwise \end{cases}$$

where:

w(x) is the indicator value at location x. Hg(x) is the mercury concentration at location x.

The expectation of this indicator (E [Hg(x)>PEC]) is the probability that the mercury concentration at location x exceeds the PEC value.

Because earth science data sets typically exhibit spatial continuity, the basic premise in geostatistical modeling is that data from locations close together are more likely to have similar values than data from locations that are far apart. There are two steps involved in modeling the spatial correlation. As mentioned above, the first step is to estimate the spatial variance of the data via a semivariogram, and the second step is to fit this semivariogram with a mathematical model. The semivariogram ( $\gamma$ ) is defined as half the expected

squared difference between paired random functions separated by the distance and direction vector called lag **h**:

$$\gamma(h) = \frac{1}{2}E\left[\left\{w(x) - w(x+h)\right\}^2\right]$$

In practice, an experimental semivariogram in which data points separated by a particular lag vector **h** are paired is estimated as follows:

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left\{ w(x_i) - w(x_i + h) \right\}^2$$

where:

 $N(\mathbf{h})$  is the number of pairs of data points separated by the lag vector  $\mathbf{h}$ .

The geostatistical software GS+ (http://www.geostatistics.com; accessed August 2002) was used for constructing semivariograms in this kriging analysis. Because the data are not regularly spaced, each pair of observations is separated by a potential unique lag in both distance and direction. Directional variograms can be constructed by grouping the separations by direction as well as by distance. Isotropic or omnidirectional variograms, as well as variograms corresponding to the directions 0°, 45°, 90°, and 135° (measured from the north) were constructed for each region and sediment depth interval (Figures I-7 and I-8). The lag tolerance was set at 50 percent of the lag distance, and the angular tolerance was 22.5°. The directional semivariograms indicate that anisotropy exists in some depth intervals, but the scatter of the points in these variograms is too large to allow for the modeling of this anisotropy. Isotopic semivariograms were, therefore, used for further analysis.

The isotopic semivariograms were fitted by a combination of nugget effect and a spherical or exponential model (Figures I-7 and I-8). The parameters for the fitted models, which are summarized in Table I-1, are:

- The nugget, which represents the local variance among points with little separation (typically the variability of co-located field duplicates).
- The sill (also the *a priori* variance of the process), which is the upper bound at which the semivariograms remain after their initial increase.
- The range, which is the distance of separation or lag beyond which pairs of values are uncorrelated.

In the profundal zone (Figure I-7 and Table I-1), the effective ranges modeled were similar for the 0 to 0.3 m and 0.3 to 0.6 m depth intervals, with values of 1,500 and 1,800 m, respectively. At 0.9 to 1.2 m, the

effective range decreased to 900 m. These results are consistent with the distribution of mercury concentrations with depth as shown in Chapter 5, Figures 5-2 and 5-3. Shallower sediments in the profundal zone show consistent levels of contamination over large areas, which is indicative of a high degree of correlation and large range values. The deeper sediments show more lateral variation, and hence a smaller range. In the littoral region (Figure I-8 and Table I-1), the effective ranges were smaller (> 550 m) and decreased with depth.

#### I.2.2.3 Spatial Prediction by Kriging

The semivariogram models discussed in Section I.2.2.2 were used to produce kriged probability maps for the Onondaga Lake bottom sediments. These maps portray the probability that sediments in a particular location and depth interval will exceed the PEC concentration of 2.2 mg/kg. (Note that use of the PEC value in this appendix is for example only; remedial action objectives (RAOs) in the FS may be the same or different than this value and other CPOIs will also need to be evaluated.) Figures I-9 through I-12 present the probability maps for the profundal zone and Figures I-13 through I-16 present the probability maps for the profundal zone and Figures I-13 through I-16 present the probability maps for the the profundal zone and Figures I-13 through I-16 present the probability maps. These defined according to Garcia and Froidevaux (1997), were used to interpret the probability maps. These two probability thresholds delineate three types of areas:

- Clean areas (probability < 0.2).
- Contaminated areas (probability > 0.8).
- Unclassified areas (probability between 0.2 and 0.8).

In the profundal zone, much of the sediments in the 0 to 0.3 m (Figure I-9) and 0.3 to 0.6 m (Figure I-10) intervals are highly contaminated relative to the mercury PEC, with the exception of areas off of Ninemile Creek and Bloody Brook, which are likely affected by the deltas from those streams. Below 0.6 m (Figures I-11 and I-12), areas of contamination relative to the mercury PEC are limited to the southern basin, especially between Harbor Brook and Ley Creek, although some areas in the Ninemile Creek delta also have a high probability of exceedance. The high contamination in the profundal zone's shallow sediments suggests the gradual accumulation of mercury-contaminated sediments over the entire hypolimnion, perhaps via calcite precipitation and sediment focusing. The deeper profundal sediments show higher contamination near source areas, suggesting local settling of contaminated sediments, perhaps due to a high rate of discharge at the time of discharge. Because of their proximity to the source areas, these regions of the profundal zone have also accumulated thicker deposits of contaminated sediments relative to the rest of the profundal zone.

The probability maps for the littoral zone between Ley Creek and Ninemile Creek (Figures I-13 through I-16) delineate three areas contaminated with mercury, including:

• From the mouth of Harbor Brook extending out to the boundary of the profundal zone (note the halo effect previously discussed).

- In the vicinity of the loading dock or causeway.
- At the mouth of Ninemile Creek.

As expected due to lack of upland sources of mercury, the area between Tributary 5A and the southern edge of the Ninemile Creek delta (near Lakeview Point) is unlikely to exceed the PEC for mercury. The 0 to 0.15, 0.15 to 0.3, 0.3 to 1, and 1 to 2 m depth maps (see also Chapter 5, Figure 5-2) all show extensive areas of contamination in the southern littoral zone, but at 2 m the mercury contamination is primarily around Harbor Brook and in some areas in the Ninemile Creek delta, suggesting historically high rates of deposition in these areas due to their proximity to Honeywell sources.

#### I.2.3 Summary

The results of this exploratory statistical analysis support the maps in Chapter 5, suggesting that the littoral zone around Harbor Brook, the Ninemile Creek delta, and much of the top 0.6 m of the profundal zone are highly contaminated with mercury. In this analysis only a single threshold was used in the indicator kriging (i.e., the PEC), which is appropriate, given that this is a preliminary analysis intended to provide a guide for an FS. In practice, because the estimate of individual probability from a single threshold is crude, Goovaerts (1997) stated that at least five thresholds are required to provide a reasonable discretization of the local distribution. Notably, the NYSDEC risk-based sediment screening criteria, which include the LEL and SEL criteria for metal CPOIs (NYSDEC, 1999), could also be used. The NYSDEC screening criteria, including the LEL (0.15 mg/kg) and SEL (1.3 mg/kg), are lower than the Onondaga Lake mercury PEC (2.2 mg/kg), based on site-specific data, suggesting that these NYSDEC screening criteria would indicate more contamination than the areas shown in the kriging maps based on the PEC.

### I.3 Sources and Distributions of Metals, PAHs, and PCDD/PCDFs in Onondaga Lake Sediments: Multivariate Statistical Analysis

In addition to mercury, there are other metals (cadmium, chromium, copper, lead, nickel, and zinc) that exceed NYSDEC risk-based sediment screening criteria in the lake bottom sediments shown in Chapter 5, Figures 5-4 through 5-9. In order to determine patterns of distribution of these metal CPOIs, a correlation analysis and PCA were performed on the concentrations of the non-mercury metals (cadmium, chromium, copper, lead, nickel, and zinc) detected in Onondaga Lake sediment samples collected in 1992 and 2000.

Among the more important classes of organic compounds present in Onondaga Lake are the PAHs and PCDD/PCDFs. These compound classes represent a relatively large number of similarly structured compounds with comparable geochemistries and sources. Although the compounds themselves are similar, the mixtures of these compounds will vary from source to source; for example, one source may contain primarily one or two compounds, with the remainder of the class absent, while a second source may contain a significant contribution from all compounds in the group. Because of their similar geochemistries, the proportions observed in the sources are often preserved to some degree in the environment. Thus, by

examining the patterns present in the samples collected from the lake, the source of the compounds can often be identified. Such analysis was performed for both PAHs and PCDD/PCDFs.

As previously discussed, a standard statistical approach used to examine patterns in data is the PCA. The PCA reduces a set of potentially co-varying parameters (in this case, concentrations of individual compounds) to a minimum number of independent variables (i.e., principal components). These components represent vectors derived from the data such that each vector is uncorrelated and, therefore, orthogonal to the other vectors. The vectors themselves are simply linear combinations of the data. Each vector is derived so as to contain (or "explain") the maximum amount of variance in the data set. Thus, the direction representing the strongest correlation within the data becomes the direction of the first principal component. The vectors are derived sequentially, with each successive component explaining subsequently smaller portions of the variance while still being orthogonal to all previously derived vectors. Once constructed, these vectors are used to transform the data so that it can be plotted against the principal component axes, as follows:

 $z_{1} = \alpha_{1}x_{1} + \alpha_{2}x_{2} + ... + \alpha_{n}x_{n}$   $z_{2} = \beta_{1}x_{1} + \beta_{2}x_{2} + ... + \beta_{n}x_{n}$  $z_{n} = \eta_{1}x_{1} + \eta_{2}x_{2} + ... + \eta_{n}x_{n}$ 

where:

z <sub>i</sub>	=	the coordinate value for the data point along principal component axis i
n	=	the number of parameters in the data set
$\mathbf{x}_{i}$	=	the value of the original parameter i for the sample
$\alpha_{i}$	=	the coefficient for parameter i in the first principal component
$\beta_i$	=	the coefficient for parameter i in the second principal component
$\eta_i$	=	the coefficient for parameter i in the n <sup>th</sup> principal component

Note that the magnitude of the coefficients  $\alpha_i$ ,  $\beta_i \dots \eta_i$ , reflects the importance of a given parameter to the principal component. These coefficients can be negative or positive, depending on whether the principal component is negative or positively correlated with the parameter.

Typically, a significant fraction of the variance is explained by the first two to three principal components, with subsequent components explaining only small fractions of the total variance. Essentially, these components represent the two or three most significant correlations within the data set. For PAHs and PCDD/PCDFs in Onondaga Lake, these components can be expected to correspond to differences in source patterns. In the discussions that follow, the analyses presented are based exclusively on the first two principal components derived for both compound classes.

To aid in the identification of possible source patterns in lake sediment contamination, the PCA is performed on the mass fractions of the analytes within their respective compound class. For example, the individual PAH concentrations within a sample are divided by the total PAH concentration for that sample. Thus, for the PCA analysis, the sum of PAH mass fractions for an individual sample is unity. In this manner, the pattern information is not weighted by absolute concentration and all samples are treated equally in the analysis. As a result, samples with similar patterns of contamination will fall close together on the principal components plots, regardless of the absolute concentrations in the samples. This in turn creates data clusters for each source, with samples containing mixtures from several sources to fall midway between the clusters.

## I.3.1 Principal Component Analysis for Non-Mercury Metals

This section presents the results of the correlation analysis and PCA performed on Onondaga Lake nonmercury metals; specifically, cadmium, chromium, copper, lead, nickel, and zinc. The results from the correlation analysis showed that nickel and chromium have a strong correlation with a coefficient determination of 0.91 (Table I-2). Zinc and copper also have a strong correlation with a coefficient determination of 0.71. Zinc-cadmium, copper-cadmium, and lead-cadmium have a moderate correlation with coefficients of determination of about 0.5 to 0.6.

The results of the PCA showed that the metals can be divided in two groups, based on similarities in their distributions (Figure I-17), with lead, cadmium, zinc, and copper as the first group, and chromium and nickel as the second group (presented in Chapter 5, Figures 5-4 through 5-9. The correlations and similar spatial distributions suggest that these metal groups represent classes of contaminant discharges with similar point sources and similar geochemistries within the lake.

## I.3.2 Principal Component Analysis for Polycyclic Aromatic Hydrocarbons

The section presents the results of the PCA performed on Onondaga Lake PAH-contaminated sediments. PAHs are a class of compounds that consist of two or more fused aromatic rings. They are produced mainly by incomplete combustion of organic matter. Major sources include emissions from wood and coal burning, coke ovens, automobile exhaust, heat and power generation, and refuse burning. PAHs are also associated with petroleum refining, and are typically found in the distillate bottoms. Some of the lighter PAH compounds, particularly naphthalene, are used in manufacturing. Naphthalene was produced in the benzene, toluene, and xylenes manufacturing process at the Honeywell Main Plant and the Willis Avenue facility. Large amounts of naphthalene from this process are found in waste tars at the Semet Residue Ponds site and in wastes at the Wastebed B/Harbor Brook site.

I-11

#### I.3.2.1 Site Data

For this analysis, PAH data from the 1992 and 2000 lake sediment investigations conducted by Honeywell formed the main data set. The data available include 105 samples collected in 1992 and 409 samples collected in 2000, for a total of 514 sediment samples from Onondaga Lake. Seventeen PAH compounds are typically included on the Target Compound List (TCL), as specified through USEPA's Contract Laboratory Program (CLP). All of the samples from 2000 were analyzed for all 17 of these PAH compounds. However, 46 of the 105 lake samples collected in 1992 were only analyzed for 16 PAHs (2-methylnaphthalene was not analyzed).

In order to use both the 1992 and 2000 data sets together and reflect the entire set of PAH compounds, only those samples analyzed for all 17 PAH compounds were considered, reducing the available 1992 samples to 59 and the total number of samples in the PCA to 468. An analysis (provided in Section I.3.2.2) examining the impact of excluding 2-methylnaphthalene showed this exclusion to have little impact on the PCA outcome. This PCA provides a way of relating the PAH mass fraction patterns from the probable source sites to the Onondaga Lake samples. Other available PAH data include over 600 samples from surrounding sites, including Wastebed B/Harbor Brook.

#### I.3.2.2 Polycyclic Aromatic Hydrocarbon Principal Component Analysis Results

For this PAH PCA, the data were normalized to mass fractions based on the total PAHs (the sum of 17 PAH concentrations). All non-detects were assigned a value of zero in the PCA to avoid the potential for distortion of the PAH ratios by assuming a single value for a PAH. The goal was to identify the first three principal components because they would describe the majority of the variance in the following analyses. These three principal components, PC 1, PC 2, and PC 3, explained 35 percent, 16 percent, and 11 percent of the total variance, respectively. However, as previously mentioned, only the first two principal components are discussed in detail in this section.

#### **Principal Component 1**

The first principal component, PC 1, yielded positive loadings, or factors, for the majority of the heavy, or high molecular weight, PAH (HPAH) compounds, including the following:

- Acenaphthylene.
- Acenaphthene.
- Anthracene.
- Phenanthrene.
- Pyrene.
- Fluoranthene.
- Benz[a]anthracene.
- Chrysene.
- Benzo[a]pyrene.

- Benzo[b]fluoranthene.
- Benzo[k]fluoranthene.
- Benzo[g,h,i]perylene.
- Iindeno[1,2,3-cd]pyrene.
- Dibenz[a,h]anthracene.

The LPAHs (i.e., fluorene, naphthalene, and 2-methylnaphthalene) had negative loadings (Figure I-18). Individual PAH concentration loadings revealed a prominent split between fluorene and acenaphthylene, or between LPAHs and HPAHs, for PC 1 (Figure I-18).

A similar scale of loading factors within the LPAH and HPAH compound clusters indicated that some samples were dominated by LPAHs and others by HPAHs. From this analysis, it can be inferred that 35 percent of the variability in the sediment samples can be explained by examining the ratio of the LPAHs and HPAHs.

It is important to note that two characteristic PAH patterns based on mass fraction were identified from the Onondaga Lake sediment data (Figure I-19). The first pattern, Pattern 1, is comprised of the LPAHs; predominantly naphthalene. Pattern 2 samples are primarily comprised of the HPAHs. These results are consistent with the PCA results discussed above.

#### **Principal Component 2**

The source of the variance associated with PC 2 may be associated with petroleum spills and other uncombusted fuels. The main PAHs associated with PC 2 include two- and three-ring PAH compounds, specifically:

- Fluorene.
- 2-methylnaphthalene.
- Acenaphthylene.
- Acenaphthene.
- Anthracene.
- Phenanthrene.

These PAHs had positive loadings, while most of the other PAHs had negative or minor loadings. Notably, compounds that had the largest factors in PC 1 (e.g., naphthalene, benz[a]anthracene, benzo[k]fluoranthene) had much smaller factors in PC 2. This suggests that a second source of variance arises among the more central PAH compounds, presumably those that are less important to the overall PAH inventory. This is further discussed below.

#### **Graphic Examination of Principal Component Analysis**

The PCA results were examined graphically by plotting the principal component scores. The axis with the greatest variance is the first PCA axis, and the second PCA axis is perpendicular to the first. Thus, these two PCA axes represent the greatest amount of variation in the data set and theoretically contain some patterns of significance. The PCA results for the lake sediments are provided in Figure I-20, in which the results for both the data set with 17 PAHs (468 samples) and the results for the data set with 16 PAHs (516 samples) are presented. The general distribution of samples is the same in both instances, suggesting that the exclusion of the 46 1992 samples without 2-methylnaphthalene does not affect the interpretation of the data.

Using the data set with 17 PAHs, the Onondaga Lake PAH sediment concentrations were examined from two perspectives: distance from the East Flume (Figure I-21) and total PAH concentration in the sample (Figure I-22). When PC 1 and PC 2 were plotted, a spread of points was observed between two dense clusters of points at the far left and far right of the diagram (i.e., near values of +4 and -3.5 for PC 1). By comparing Figures I-21 and I-22, it can be seen that the samples closest to the East Flume exhibit the highest PAH concentrations. These samples exhibit PAH Pattern 1 (i.e., naphthalene-dominant). The samples farthest from the East Flume exhibit the lowest PAH concentrations. These samples exhibit PAH Pattern 2 (i.e., high-molecular-weight-dominant).

The spread of the points between the dense clusters may be the result of mixing the two sources within the lake, additional minor sources, weathering effects, or, most likely, some combination of these factors. It is important to point out that the formation of the two dense clusters identifies these patterns as characteristic of two major sources to the lake. The region between these clusters contains a scattering of points with no clear focus, suggesting that sources that may be characterized by patterns from this area have not contributed substantively to lake contamination, since there are relatively few samples with these patterns. Note that Figures I-20 to I-22 are based on lake sediment data alone. The principal components described above are derived exclusively from the patterns within the sediment.

In attempting to identify the sources, it is useful to plot possible sources to the lake on the same basis; that is, PC 1 and PC 2 values for PAH results from possible source samples were determined using the loading factors given in Figure I-18 and plotted on the upper diagram of Figure I-20. Note that the source data were not included in the determination of the principal components themselves. Thus, coincidence between the patterns seen in the lake and patterns seen in the possible sources would implicate the coinciding source as a possible major contributor to the lake's PAH contamination. The large number of possible sources required that several figures of this type be generated (Figures I-23 to I-26).

In Figure I-23, sample results for four possible sources are plotted on the lake sediment PCA diagram, including Ninemile Creek sediments (from the Honeywell Geddes Brook/Ninemile Creek RI), other tributary sediments as collected by NYSDEC, Sawmill Creek sediments, and soils from the Town of Salina Landfill. These materials are considered representative of possible PAH patterns present in the watershed (for the tributaries) or on an upland site (Town of Salina Landfill). In this instance, nearly all the data cluster

near the far right of the diagram, suggesting that these potential sources may be related to the Pattern 2 contamination present in the lake.

In Figure I-24, data from soil samples from the Honeywell Willis Avenue site, the Niagara Mohawk Power Corporation Hiawatha Boulevard facility, and the Honeywell Solvay Wastebeds, as well as sediments from Harbor Brook, are presented. In general, these samples also tend to cluster to the right side of the diagram, but also contain patterns that scatter across the diagram, similar to the lake sediments. These results suggest that some of these sites may be partially responsible for some of the lake contamination. However, the lack of a substantive cluster coinciding with the Pattern 1 cluster would suggest that these sources are only minor contributors to the large mass of PAH contamination characterized by Pattern 1.

Figure I-25 shows the PAH data for the General Motors – former Inland Fisher Guide (GM–IFG) facility (including adjacent Ley Creek sediment), the Niagara Mohawk Erie Boulevard facility, the Honeywell LCP Bridge Street site, and sediments from Geddes Brook and Ninemile Creek superimposed on the lake sediment data PCA results. Results for both the LCP Bridge Street site and Geddes Brook/Ninemile Creek cluster around the right side of the diagram, which is characteristic of Pattern 2. Thus, PAH contamination from these sources is consistent with the low concentration of PAH contamination found in the lake at distances greater than 1,000 m from the East Flume.

The other two possible sources shown in Figure I-25 lie primarily outside the lake sediment cloud of points. Samples from the GM-IFG facility lie to the upper right, while samples from the Niagara Mohawk Erie Boulevard facility lie to the upper left. While these possible sources represent PAH patterns that are not extensively found in the lake sediments, they also represent the kinds of patterns required to cause the scatter observed in the lake sediment patterns. That is, relatively small contributions from these sources to the lake will serve to create the scatter observed in the data. The contributions from these sources can be characterized as "small," based on their relative distance from the main clusters of data and the fact that there are no dense clusters of sediment samples close to the source centers. Such clusters would be expected in sediments close to the sources, if they were major contributors of PAHs to the lake.

The last figure representing possible PAH source patterns is Figure I-26. This figure presents preliminary data from Honeywell's Wastebed B/Harbor Brook and Willis Avenue Ballfield site investigations, including samples from the Penn-Can property, the CSX Railroad Area, and the Wastebed B lakeshore areas. One of the more important characteristics of these sites is the presence of a dense non aqueous phase liquid (DNAPL) plume comprised primarily of naphthalene in the aquifer below the Penn-Can property within the Wastebed B/Harbor Brook site. With the primary hydraulic gradient to the lake, it is likely that this DNAPL plume is discharging to the lake directly or via overlying groundwater. In either case, this area represents a likely source for the naphthalene-dominated Pattern 1 source.

The preliminary data from the Wastebed B/Harbor Brook site and related areas contain both Pattern 1 and Pattern 2 samples. However, these sites show the largest number of samples consistent with the Pattern 1 source. Additional data are currently being obtained by Honeywell as part of the RI for both upland sites.

I-15

#### I.3.2.3 Polycyclic Aromatic Hydrocarbon Pattern Interpretation

Lake sediment samples exhibit a range of PAH patterns, predominantly derived from two distinct patterns that can be related to the molecular weight of the mixture. PAH Pattern 1 is naphthalene-dominated and has its highest concentrations in the vicinity of the East Flume, which is located just offshore from the Honeywell facilities. Pattern 2 is dominated by HPAH compounds that are generally associated with combustion or petroleum-product spills. Uncombusted sources (e.g., oil seeps, petroleum spills) contain predominantly two- and three-ring compounds, whereas combustion (e.g., vehicle exhaust, domestic heating with coal, forest fires) results in predominantly four- and five-ring species. Within the list of PAH compounds examined here, petroleum-related PAHs would include naphthalene through phenanthrene, as identified in Figure I-18. The PAHs from combustion include pyrene through indeno[1,2,3-c,d]pyrene (Van Metre et al., 2000). Thus, as shown in Figure I-19, Pattern 2 is dominated by HPAHs.

The variation of lake sediments between the two main PAH patterns is primarily captured by PC 1. The variability expressed in PC 2 appears to be related to the amount of three-ring PAH compounds relative to the rest of the sample. Given the association between three-ring PAHs and petroleum-based fuels, it is likely that this component is derived from the presence of petroleum-related contamination in the samples. Given the ubiquitous use of petroleum products, it is not surprising that this material is identified by the PCA analysis. The historical presence of Oil City on the lake's perimeter near Onondaga Creek is a likely source of petroleum fuels to the lake as well. Notably, PAH concentrations are also elevated in the nearshore sediments off Oil City, although these concentrations are not as high as those observed off the East Flume (see Chapter 5, Figure 5-22, which illustrates the distribution of HPAHs in lake sediments).

Besides the identified source possibilities, other sources and weathering of PAHs undoubtedly affect the principal components as well. Possible sources such as the GM–IFG facility and the Niagara Mohawk Erie Boulevard site represent patterns capable of explaining some of the observed variations in PAH patterns.

In support of the impact of weathering on PAH patterns, Arzayus et al. (2001) found that factors controlling PAH distribution in Chesapeake Bay surface sediments include PAH sources (combustion versus petroleum) and partitioning differences (volatile versus particle-reactive or low-volatility PAHs). Although this study did not measure naphthalene, it can be concluded that differences in the physical-chemical properties of PAH compounds are a likely source of variance in the Onondaga Lake PCA. Similarly, in support of the combustion and fuel-related PAH patterns discussed above, Yamashita et al. (2000) performed such an analysis based on individual PAH pairs, identifying combustion and fuel-related sources.

#### **I.3.2.4 Identification of Likely Sources**

Taken alone, the results of this PCA analysis are not conclusive since the analysis only notes correlation and not causation. However, the observations made from the PCA, taken with other data, provide a very credible link between lake contamination and Honeywell-related discharges. In particular, the following factors implicate the Honeywell facilities in this regard:

- The predominance of Pattern 1 PAH contamination in sediments closest to the East Flume (see Figure I-21).
- The occurrence of maximum observed PAH concentrations in the area off the East Flume.
- The presence of a DNAPL plume of almost pure naphthalene in the aquifer beneath the Wastebed B/Harbor Brook site and related sites.
- The close match between PAH patterns observed in sediments near the East Flume with a number of soils and sediment samples obtained from the Wastebed B/Harbor Brook site and related sites.

On this basis, it can be concluded that the Honeywell facilities are the likely source of the naphthalene-based PAH contamination present in the lake.

In addition to the likely naphthalene source associated with the Honeywell facilities, a second source pattern was also observed, as noted previously, to be associated with combustion byproducts. This pattern was noted in many areas of the lake near potential sources. The ubiquitous nature of the pattern suggests that the source is a common area-based phenomenon, probably resulting from atmospheric deposition of combustion byproducts onto the lake surface and the surrounding soils of the watershed. In this instance it may be that there is no single source, but rather a wide, area-based source delivered to the lake sediments via direct deposition on the lake's surface as well as via transport from the watershed by the lake's tributaries.

A third, less well defined source pattern is suggested by PC 2. This source may be the result of petroleum fuel spills on the lake's perimeter as well as within the lake itself. This pattern is not well defined and may in fact represent a combination of fuel spills (perhaps from past or historical Oil City operations), as well as contributions from sites such as the GM-IFG facility and the Niagara Mohawk Erie Boulevard facility. Weathering of PAHs may also add to the overall variability in PAH patterns observed in the lake.

#### I.3.2.5 Historical and Current Polycyclic Aromatic Hydrocarbon Loads

Having established the likelihood of a Honeywell-related source of PAHs, as well as the possibility of other PAH sources, it is now useful to examine the current status of PAH loads to the lake. An analysis of loads was described in Chapter 6 of this RI. However, the analysis in this appendix will focus on the historical versus current loads of PAHs to the lake as recorded by the sediments. Figures I-27 and I-28 present the results from two cores: one near the East Flume (Station S312; Figure I-27) and one near Oil City (Station S319; Figure I-28). These cores document concentrations of PAHs in the sediments with depth. By assuming that depth is a rough surrogate for time, the shallowest, most recently deposited sediments can be compared with those at greater depth. In both cores, surface concentrations are about 4 to 10 times

lower than sediments at greater depths. Thus, in both locations, PAH deposition has declined substantially from prior conditions, implying that input of PAHs to the lake has probably greatly declined as well.

A closer examination of the core profiles yields information on the nature of the PAH mixtures being deposited over time. For Station S312, near the East Flume (Figure I-27), the amounts of total PAH and naphthalene deposited over time have varied in parallel, such that the proportion of naphthalene in the PAHs at this location has remained constant over time (see the third diagram in Figure I-27).

The core obtained from Station S319 (near Onondaga Creek; see Figure I-28) tells a different story. At this location, naphthalene is only a small fraction of the total PAH mixture, but its percentage varies over time. As shown in the figure, the naphthalene fraction varies from much less than 0.01 to about 0.10, or an order-of-magnitude. Notably, the maximum naphthalene fraction is coincident with the maximum concentration. These results suggest that the contribution of the naphthalene-dominant source increased during the period of maximum PAH accumulation at the site, raising the proportion of naphthalene in the mixture. These results in turn suggest that the naphthalene-dominant source may have had a larger area of impact during its peak period of discharge than it currently does. This is consistent with the data presented in Chapter 5, Figure 5-20.

#### I.3.2.6 Summary

In this analysis, principal components were used to examine PAH contamination in lake sediments and identify two main source patterns, as well as suggest the presence of a third source, as follows:

- The single most important PAH source to the lake, in terms of yielding the highest PAH concentrations, is the Honeywell facilities, and in particular the Wastebed B/Harbor Brook site and associated areas. PAH patterns associated with this source have a characteristically high proportion of naphthalene relative to the other PAHs in the mixture. The combination of PAH pattern match, known contamination, and proximity to the maximum concentrations in the lake implicates these Honeywell facilities as the likely source.
- A second PAH pattern is evident in lake sediments, possibly due to combustion-related PAH inputs via shoreline sources and tributaries. Sediments with combustion-related PAH patterns are characterized with higher proportions of four- and five-ring PAH compounds and are typically low in concentration.
- The last identified pattern is less well defined, but is consistent with a petroleum fuel source or sources. This pattern typically has higher proportions of the three-ring PAH compounds. Sediments with this pattern generally have higher concentrations, similar in scale to those with the naphthalene-dominant pattern.

## I.3.3 Principal Component Analysis for PCDD/PCDFs

PCDD/PCDFs have been detected in the sediment of Onondaga Lake, the sediment of several tributaries to the lake, and in soil from sites in the vicinity of the lake. A PCA of the sediment and soil samples serves to identify the source of the contamination in the lake. This analysis reduces the number of effective variables (mass fraction of each contaminant), allows for the detection of the relationship between these variables, and provides a way of relating the mass fraction patterns from the sites to the samples from the lake.

The chemical structure of PCDD/PCDFs, which are a group of related compounds, is shown in Figure I-29. Dioxins consist of two benzene molecules connected at two points with oxygen bridges. Furans are similarly constructed, with one oxygen bridge and one carbon bond. Each of the numbered locations can have either a hydrogen or chlorine molecule, depending on the congener. There are eight dioxin homologs and eight furan homologs. There are 75 dioxin congeners, but 135 furan congeners due to the lack of symmetry.

PCDD/PCDFs are among the most toxic compounds known. The toxicity of each of the homologs was measured against the toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), and the toxicity equivalence (TEQ) was calculated using the factors developed by the World Health Organization (WHO) (Van den Berg et al., 1998). Exposure to PCDD/PCDFs is associated with cancer, severe reproductive and developmental problems, immune system damage, and interference with regulatory hormones. The compounds are persistent in the environment, showing little tendency to degrade in soil or sediment. PCDD/PCDFs are also known to bioaccumulate in the food chain (Agency for Toxic Substances and Disease Registry [ATSDR], 1998).

Numerous activities produce PCDD/PCDFs, although they are not intentionally produced for any purpose. Incineration is commonly the source of PCDD/PCDF contamination in the atmosphere. The manufacturing of chlorinated compounds, including chlorine gas, chlorobenzenes, metal chlorides, and PCBs, may produce these compounds, leaving PCDD/PCDFs present in the mixture as byproducts (ATSDR, 1998). Based on their presence in soil and/or sediment samples, PCDD/PCDF-producing activities have occurred at a site or sites in the vicinity of Onondaga Lake.

#### I.3.3.1 Site Data

In sediments, PCDD/PCDF concentrations were measured for Onondaga Lake, Geddes Brook, Ninemile Creek, Ley Creek, and the East Flume. In soils, PCDD/PCDF concentrations were measured for the Geddes Brook and Ninemile Creek areas, the Honeywell Willis Avenue Chlorobenzene site, and the GM – IFG facility.

The concentrations of other CPOIs, such as mercury, chlorobenzene, and PCBs, at the potential source sites may provide an additional means of determining the source of the PCDD/PCDF contamination,

I-19

assuming the PCDD/PCDFs and the other CPOIs may have entered the lake in the same waste stream. Table I-3 lists the sites, number of measurements, and range of concentrations for the PCDD/PCDFs and some of the CPOIs for the potential source sites.

#### I.3.3.2 PCDD/PCDF Mass Fractions in the Sediment, Soil, and Source Material

Typical mass fraction patterns for the lake sediment, tributary sediment, and soil from potential source sites are presented in Figure I-30. There are two distinct homolog patterns in the lake. Each is dominated by one homolog, one having the highest fraction of octachlorodibenzodioxin (OCDD), the other having the highest fraction of 2,3,7,8-tetrachlorodibenzofuran (TCDF). The homolog with the second highest fraction is more variable, though for the samples with highest fraction of OCDD, many of the samples have heptachlorodibenzodioxin (HpCDD) as the second largest component and, for the TCDF patterns, many of the samples have pentachlorodibenzofuran (PeCDF) as the second largest component. A breakdown of the sediment and soil samples follows:

- For the Willis Avenue Chlorobenzene site samples, most of the soil samples have TCDF as the highest fraction, with significant fractions of PCDF.
- For the sediment samples from the lower East Flume (also part of the Willis Avenue Chlorobenzene site data), eight of the 14 samples have TCDF as the highest fraction, with lesser amounts of PCDF. In the upper East Flume, all of the samples have TCDF as the highest fraction, with lesser amounts of HpCDD (Figure I-30).
- The six soil samples from the GM-IFG facility show no consistent patterns, but most of the samples have substantial amounts of OCDD or TCDF.
- The sediment samples collected from Ley Creek near the GM-IFG facility were more consistent, with 12 of the 13 samples having the highest fraction of OCDD and lesser amounts of HpCDD (Figure I-30).
- Sediment samples from Ninemile Creek, downstream from the Honeywell LCP Bridge Street site, all had OCDD as the homolog with the highest fraction, with lesser amounts of either HpCDD or TCDF.
- From Geddes Brook, downstream from the Honeywell LCP Bridge Street site, all five sediment samples had OCDD as the highest fraction, with a smaller fraction of TCDF.
- Of the 15 soil samples for Ninemile Creek, downstream from the Honeywell LCP Bridge Street site, all of the samples had OCDD as the homolog with the highest

fraction, 13 samples had a lesser fraction of HpCDD, and two samples had a lesser fraction of TCDF (Figure I-30).

Mass fractions from pure source material were found in the literature (USEPA, 2000), as discussed below; these are depicted in Figure I-31. Atmospheric samples are composed of approximately 80 percent OCDD. The discharge from incinerators is composed of several dioxin and furan homologs. Sludge from chlorine gas manufacture has the highest fraction of PCDF, with significant fractions of TCDF and hexachlorodibenzofuran (HxCDF). Patterns for PCDD/PCDFs in tri-, tetra-, penta-, and hexachlorobenzene were found in the literature, but not mono- and dichlorobenzenes, which were the products manufactured at the Willis Avenue Chlorobenzene site. The pattern for each chlorobenzene is quite different from the others, with the PCDD/PCDF pattern in the mixed trichlorobenzenes being most similar to the Willis Avenue Chlorobenzene site soil and sediment samples that have the highest fraction of TCDF and a lower fraction of PCDF. The PCDD/PCDFs in the Aroclor samples are predominantly furans, with most of the Aroclor 1254 samples having HxCDF as the highest fraction.

#### **I.3.3.3 PCDD/PCDF Principal Component Analysis Results**

Principal components were calculated for all sediment samples with PCDD/PCDF measurements collected in Onondaga Lake. As was done in Eltzer (1993), the PCA was performed on the mass normalized homolog data. The loading factors are presented in Figure I-32. PC 1 and PC 2 together account for 64 percent of the total variance. For PC 1, all of the loading factors are positive, except HpCDD and OCDD, which are strongly negative. For PC 2, all of the loading factors are positive, except OCDD, TCDF, and PCDF, with TCDF and PCDF being more negative than OCDD.

PC 1 and PC 2 are plotted in Figure I-33 with the highest fraction of homologs for each sample point. The samples to the right of zero have patterns most similar to the sediment and soil samples from the Willis Avenue Chlorobenzene site. The samples to the left of zero are similar to the Geddes Brook, Ninemile Creek, and Ley Creek samples.

Superimposing the concentration ranges of the CPOIs from the potential source sites over the PCA results was not successful in separating the samples. An example of this, as performed for PCBs, is shown in Figure I-34. There are high and low concentrations in each section of the graph. Grouping the data based on concentration of PCDD/PCDF also did not separate the data, as can be seen in Figure I-35.

Using the mass fractions for the pure source material and the loading factors from the lake sediment samples, the source samples could be mapped on the lake sediment samples, as can be seen in Figure I-36. The atmospheric samples fell to the left of zero, along with the other samples with the highest fraction of OCDD. Most of the Aroclor samples fell far to the right of the samples. The incinerator and chlorobenzene samples had PC 2 values higher than most of the sediment samples, except the hexachlorobenzene source material that fell near the atmospheric samples.

The tributary sediment and site soil samples are plotted in Figure I-37 on the PC 1 and PC 2 graph using the loading factors from the lake sediment samples. The soil samples from Ninemile Creek and Geddes Brook and the sediment samples from Ley Creek near the GM – IFG facility are grouped to the left of zero. The Willis Avenue Chlorobenzene site soil samples are grouped to the right of zero. Some of the samples with PC 2 values higher than most of the Willis Avenue Chlorobenzene site soil samples were collected near the building that burned in the 1920s. This coincides with the mass fractions for the higher chlorinated chlorobenzenes (Figure I-36). Most other sediment and soil samples are scattered between the predominantly Ninemile Creek/Geddes Brook soil and sediment samples and the Willis Avenue Chlorobenzene site soil samples.

#### I.3.3.4 OCDD/TCDF Ratio

The PCA did not separate the samples with atmospheric contamination from lake sediment samples that have high OCDD mass fractions. Plotting the ratio of OCDD to TCDF against the total PCDD/PCDF concentration for each lake sediment sample separates the atmospheric contamination from site-associated contamination, as presented in Figure I-38. Three groupings are clear on the map:

- High OCDD mass fraction samples with low mass (1 to 10 ng/kg).
- High OCDD mass fraction samples with high mass (100 to 100,000 ng/kg).
- High TCDF mass fraction samples (1 to 10,000 ng/kg).

The OCDD low mass samples are mostly located in the deeper sediment, further suggesting that these samples are from atmospheric deposition.

The tributary and surrounding site sediment and soil samples were plotted in Figure I-39. Three groupings are also seen here, with the Willis Avenue Chlorobenzene site samples in the TCDF grouping; the Ninemile Creek/Geddes Brook soil samples and the Ley Creek sediment samples in the OCDD high mass grouping; and a small group of Ninemile Creek/Geddes Brook samples in the OCDD low mass grouping.

To examine the depositional history and relative magnitude of contamination, mass percent in cores from each section of the lake are presented in Figures I-40 to 45, with each segment classified as either OCDD high mass, TCDF, or atmospheric (OCDD low mass). A breakdown of the segments follows:

- At Ninemile Creek, most of the sediment segments are OCDD high mass, with only the deepest sediment sample predominantly TCDF (Figure I-40).
- Near the East Flume, all of the sediment segments are predominantly TCDF (Figure I-41).
- Near the Interstate 690 (I-690) drainage system outfall on the Willis Avenue site, the sediment segments are mixed between TCDF and OCDD high mass, with the TCDF sediment segments deeper in the core (Figure I-42).

1

- The core nearest the Metropolitan Syracuse Sewage Treatment Plant (Metro) (S316) appears to be mostly atmospheric deposition, with TCDF segments in the top 102 cm (Figure I-43, left side).
- Core S315, which is west of the deep Metro outfall and north of the East Flume and Harbor Brook, is mixed between OCDD high mass samples from 0 to 300 cm and TCDF samples from 300 to 600 cm. This shows that the TCDF material was deposited prior to the OCDD high mass samples (Figure I-43, right side).
- The core near Ley Creek is entirely OCDD high mass (Figure I-44).

The depositional history is consistent with the TCDF material originating at the Willis Avenue Chlorobenzene site and the OCDD high mass material originating at the LCP Bridge Street site or the GM - IFG facility. The core results are also consistent with the fact that the Willis Avenue Chlorobenzene site was in operation more than 30 years prior to the opening of the other sites.

Because the toxicity of OCDD is 1,000 times less than TCDF it might be expected that the areas of the lake with contamination composed mostly of OCDD would be considerably less toxic than the areas with TCDF contamination. However, the level of toxicity does not exactly match the distribution of TCDF. The distribution of the TEQs for PCDD/PCDFs is mapped in Chapter 5, Figures 5-26 and 5-27 for each depth interval down to 2 m. Cores from the East Flume area were composed of TCDF and have the highest TEQ concentrations in the lake. At Ley Creek, an area with OCDD high mass contamination, the TEQ concentrations near the I-690 outfall, an area of combined OCDD high mass and TCDF contamination. The Ninemile Creek delta, an area of OCDD high mass contamination, has lower TEQ concentrations, but still exceeds NYSDEC wildlife bioaccumulation criteria at several depths. The core taken near the Metro outfall showed a mix of atmospheric and TCDF contamination but is the only core with all TEQ concentrations less than the NYSDEC wildlife standard.

#### I.3.3.5 Summary

The PCA was successful in identifying three distinct types of contamination: TCDF, OCDD high mass, and OCDD low mass. Sources for each type of contamination were identified using soil and sediment samples from the surrounding sites. The spatial distribution and the deposition history for these types of contamination are consistent with the relative years of operation for each of the identified sources.

The predominantly TCDF contamination is similar to the soil samples collected from the Willis Avenue Chlorobenzene site and sediment samples from the East Flume. This type of contamination appears to radiate from the East Flume delta, further indicating that the Willis Avenue Chlorobenzene site soils and East Flume sediments are the sources of this contamination. OCDD high mass contamination seems to come from two sources: Geddes Brook and Ninemile Creek sediments, downstream from the LCP Bridge Street site and the sediments of Ley Creek in the vicinity of the GM – IFG facility. Although no samples collected at the LCP Bridge Street site were measured for PCDD/PCDFs, the sediments and soils from Ninemile Creek and Geddes Brook have been affected by this site and show the OCDD high mass pattern of contamination. Cores from the Ninemile Creek delta and the I-690 storm drain outfall also have this pattern, although the cores from the I-690 storm drain outfall also have this pattern, although the cores from the I-690 storm drain outfall also have the pattern of contamination in the core collected near Ley Creek was indistinguishable from the pattern of contamination seen at the Ninemile Creek delta and the I-690 storm drain outfall (Station S336), the source of the contamination can only be inferred, based on the spatial distribution of the contaminant patterns in the lake. There is OCDD high mass throughout the studied portion of the lake with the exception of the East Flume-related contamination. The East Flume area seems to be a divide in the lake between the OCDD high mass contamination emanating from Ninemile Creek and from the contaminated sediments of Ley Creek.

The OCDD low mass contamination appears to be deposition from the atmosphere. Atmospheric deposition samples typically are high in OCDD contamination relative to the other homologs. The concentrations in the sediment characterized as OCDD low mass were 1 to 10 ng/kg, much lower than the other samples. Core segments with OCDD low mass were located in the deepest portions of the core, below site-associated contamination.

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## **List of Figures**

Figure I-1	1992 Sediment Sample Locations, Excluding the 0 to 0.02 m Stations
Figure I-2	2000 Sediment Sample Locations, Excluding the 0 to 0.02 m Stations
Figure I-3	Natural and Anthropogenic Site Features
Figure I-4	Comparison of Histograms and Summary Statistics for Mercury Concentrations in the Littoral Zone of Onondaga Lake from 1992 and 2000
Figure I-5	Histograms and Summary Statistics for Mercury Concentrations in the Profundal Zone of Onondaga Lake (1992)
Figure I-6	Histograms and Summary Statistics for Mercury Concentrations in the Littoral Zone of Onondaga Lake (Ley Creek to Ninemile Creek Delta - 2000)
Figure I-7	Experimental Isotropic and Directional Indicator Semivariograms of Mercury (data points) and Model Fits (continuous line) for the Profundal Zone Sediments of Onondaga Lake in 1992
Figure I-8	Experimental Isotropic and Directional Indicator Semivariograms of Mercury (data points) and Model Fits (continuous line) for the Littoral Zone (Ley Creek to Ninemile Creek) Sediments of Onondaga Lake in 2000
Figure I-9	Mercury Probability Map for the Profundal Zone, 0 to 0.30 m Depth Interval
Figure I-10	Mercury Probability Map for the Profundal Zone, 0.30 to 0.60 m Depth Interval
Figure I-11	Mercury Probability Map for the Profundal Zone, 0.60 to 0.90 m Depth Interval
Figure I-12	Mercury Probability Map for the Profundal Zone, 0.90 to 1.2 m Depth Interval
Figure I-13	Mercury Probability Map for the Littoral Zone Between Ley Creek and Ninemile Creek, 0 to 0.15 m Depth Interval
Figure I-14	Mercury Probability Map for the Littoral Zone Between Ley Creek and Ninemile Creek, 0.15 to 0.30 m Depth Interval
Figure I-15	Mercury Probability Map for the Littoral Zone Between Ley Creek and Ninemile Creek, 0.30 to 1 m Depth Interval

I-26

Figure I-16	Mercury Probability Map for the Littoral Zone Between Ley Creek and Ninemile Creek,
	1 to 2 m Depth Interval

- Figure I-17 PCA Loadings for Non-Mercury Metals in Onondaga Lake Sediments
- Figure I-18 PAHs Loadings on Principal Components (Lake Sediment Data Only)
- Figure I-19 Typical PAHs Mass Fraction of Lake Sediment Data
- Figure I-18 PAHs Loadings on Principal Components (Lake Sediment Data Only)
- Figure I-20 Results of Principal Component Analysis of PAHs in Onondaga Lake Sediment
- Figure I-21 PAH Principal Component Analysis Results for Lake Sediment Data Grouped by Distance to East Flume
- Figure I-22 PAH Principal Component Analysis Results for Lake Sediment Data Grouped by Concentration
- Figure I-23 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Surrounding Sites Data (I)
- Figure I-24 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Surrounding Sites Data (II)
- Figure I-25 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Surrounding Sites Data (III)
- Figure I-26 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Wastebed B/Harbor Brook and Willis Ave Ballfield Sites
- Figure I-27 Naphthalene and the Sum of PAH Profiles in Sediment Cores of Onondaga Lake from 2000 (Pattern 1)
- Figure I-28 Naphthalene and the Sum of PAH Profiles in Sediment Cores of Onondaga Lake from 2000 (Pattern 2)

I-27

- Figure I-29 Chemical Structure of PCDD/PCDFs
- Figure I-30 Representative PCDD/PCDFs Mass Fractions for Soils and Sediment
- Figure I-31 Mass Fraction of PCDD/PCDFs from Pure Source

Figure I-32	Loading Factors for Principal Component Analysis of PCDD/PCDFs in Onondaga Lake
Figure I-33	Scatter Plot of Highest PCDD/PCDFs Homologues Concentrations on Principal Components for Onondaga Lake Sediments
Figure I-34	Scatter Plot of PCB Concentrations on PCDD/PCDFs Principal Components for Onondaga Lake Sediments
Figure I-35	Scatter Plot of PCDD/PCDFs Concentrations on PCDD/PCDFs Principal Components for Onondaga Lake Sediments
Figure I-36	Scatter Plot of Mass Fraction of Lake Sediment and Source Material on PCDD/PCDFs Principal Components for Onondaga Lake
Figure I-37	Scatter Plot of PCDD/PCDFs Principal Components for Sediment and Soil Samples
Figure I-38	Scatter Plot of OCDD/TCDF vs. Total Concentration of PCDD/PCDFs for Onondaga Lake Sediments
Figure I-39	Scatter Plot of OCDD/TCDF vs. Total Concentration of PCDD/PCDFs for Tributary and Surrounding Site Sediment and Soils
Figure I-40	OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near Ninemile Creek
Figure I-41	OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near East Flume
Figure I-42	OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near I-690 Outfall
Figure I-43	OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near Metro
Figure I-44	OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near Ley Creek
Figure I-45	OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs in Onondaga Lake

## List of Tables

Table I-1	Parameters Used in Semivariance Model for Data from 1992 and 2000
Table I-2	Coefficient of Determination Matrix for Linear Relations of Non-Mercury Metals in Onondaga Lake Sediments
Table I-3	Data Available to Determine the Source of PCDD/PCDFs









Figure I-4 Comparison of Histograms and Summary Statistics for Mercury Concentrations in the Littoral Zone of Onondaga Lake from 1992 and 2000





**Figure I-5** Histograms and Summary Statistics for Mercury Concentrations in the Profundal Zone of Onondaga Lake (1992)



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Figure I-6 Histograms and Summary Statistics for Mercury Concentrations in the Littoral Zone of Onondaga Lake (Ley Creek to Ninemile Creek Delta - 2000)




Figure I-7 Experimental Isotropic and Directional Indicator Semivariograms of Mercury (data points) and Model Fits (continuous line) for the Profundal Zone Sediments of Onondaga Lake in 1992



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Figure I-8 **Experimental Isotropic and Directional Indicator Semivariograms of Mercury (data points)** and Model Fits (continuous line) for the Littoral Zone (Ley Creek to Ninemile Creek) Sediments of Onondaga Lake in 2000



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Figure I-17 PCA Loadings for Non-Mercury Metals in Onondaga Lake Sediments



Figure I-18 PAHs Loading on Principal Components (Lake Sediment Data Only)



Figure I-19 Typical PAHs Mass Fraction of Lake Sediment Data



## **Onondaga Lake Sediment – 17 PAHs PCA**

## **Onondaga Lake Sediment – 16 PAHs PCA**





Figure I-21 PAH Principal Component Analysis Results for Lake Sediment Data Grouped by Distance to East Flume



Figure I-22 PAH Principal Component Analysis Results for Lake Sediment Data Grouped by Concentration



Figure I-23 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Surrounding Sites Data (I)



Figure I-24 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Surrounding Sites Data (II)



Figure I-25 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Surrounding Sites Data (III)



Figure I-26 PAH Principal Component Analysis Results for Lake Sediment Data Plotted with Wastebed B/Harbor Brook and Willis Ave Ballfield Sites



Naphthalene and the Sum of PAH Profiles in Sediment Cores of Onondaga Lake from 2000 (Pattern 1)



Figure I-28 Naphthalene and the Sum of PAH Profiles in Sediment Cores of Onondaga Lake from 2000 (Pattern 2)



Figure I-29 Chemical Structure of PCDD/PCDFs



Figure I-30 Representative PCDD/PCDFs Mass Fractions for Soils and Sediment



Figure I-31 Mass Fraction of PCDD/PCDFs from Pure Source



Loading Factors for Principal Component Analysis of PCDD/PCDFs in Onondaga Lake



Figure I-33 Scatter Plot of Highest PCDD/PCDFs Homologues Concentrations on Principal Components for Onondaga Lake Sediments



Figure I-34 Scatter Plot of PCB Concentrations on PCDD/PCDFs Principal Components for Onondaga Lake Sediments



Figure I-35 Scatter Plot of PCDD/PCDFs Concentrations on PCDD/PCDFs Principal Components for Onondaga Lake Sediment



Figure I-36 Scatter Plot of Mass Fraction of Lake Sediment and Source Material of PCDD/PCDFs Principal Components for Onondaga Lake



Figure I-37 Scatter Plot of PCDD/PCDFs Principal Components for Sediment and Soil Samples



Figure I-38 Scatter Plot of OCDD/TCDF vs. Total Concentration of PCDD/PCDFs for Onondaga Lake Sediments



Figure I-39 Scatter Plot of OCDD/TCDF vs. Total Concentration of PCDD/PCDFs for Tributary and Surrounding Site Sediment and Soils



Figure I-40 OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near Ninemile Creek



Figure I-41 OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near East Flume



Figure I-42 **OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs** for Cores Near I-690 Outfall


Figure I-43 OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near Metro

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Figure I-44 OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs for Cores Near Ley Creek

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Figure I-45 OCDD/TCDF vs. Mass Groupings of PCDD/PCDFs in Onondaga Lake

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Depth Interval (m)	Model Type	Nugget	Range (m)	Sill
Profundal Zone - 1992 data				
0-0.3	Spherical	0.02	1,515	0.11
0.3-0.6	Spherical	0.02	1,877	0.08
0.6-0.9	Spherical	0.05	922	0.16
0.9-1.2	Exponential	0.0002	313	0.11
South Littoral Zone - 2000 data				
0-0.15	Spherical	0.12	502	0.25
0.15-0.30	Spherical	0.0001	380	0.30
0.30-1	Exponential	0.12	77	0.28
1-2	Exponential	0.10	63	0.26

Table I-1. Parameters Used in Semivariance Model for Data from 1992 and 2000

	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Cadmium	1					
Chromium	0.05	1				
Copper	0.58	0.32	1			
Lead	0.13	0.30	0.51	1		
Nickel	0.01	0.91	0.18	0.12	1	
Zinc	0.60	0.11	0.71	0.33	0.05	1

 

 Table I-2. Coefficient of Determination Matrix for Linear Relations of Non-Mercury Metals in Onondaga Lake Sediments

	Number of Samples	Mean	Minimum	Median	Maximum
Dioxin+Furans (ppt)					
GB Sediment	15	1,863	130	640	17,724
NM Sediment	22	431	2	316	1,510
Allied Soil	24	1,616	4	1,357	4,965
GM Sediment	13	3,450	26	3,501	9,575
GM Soil	6	6,675	151	759	34,283
Willis Sediment	26	6,985	2,140	6,178	14,186
Willis Soil	76	271,077	37	7,642	6,157,140
Mercury (ppm)					
LCP Soil	180	424	0	5.45	19,200
Chlorobenzenes (ppb)					
Willis Soil	88	1,115,955	0	2,048	44,473,000
PCBs (ppb)					
GM Soil	166	409,839	122	840	14,000,000
Chromium (ppm)					
GM Soil	156	803	7.1	21.55	34,900
Willis Soil	14	248	0	35.45	2,380
Selenium (ppm)					
GM Sediment	33	1.85	0	0.58	43
LCP Sediment Note: ppt - ng/kg, ppb - ug/kg, ppm - mg	12 /kg	1.06	0	1.045	2

## Table I-3. Data Available to Determine the Source of PCDD/PCDFs

TAMS Consultants, Inc.

December 2002