

Comprehensive Characterization of the Lower Grasse River

Volume I - Main Report

Amended April 2001



Grasse River Study Area
Massena, New York



ALCOA
Massena, New York

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Volume II - Appendices

Amended April 2001



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EXECUTIVE SUMMARY CONTENTS

List of Figures

ES1.0 INTRODUCTION AND CONCLUSIONS	ES1-1
ES2.0 GRASSE RIVER HYDROLOGY	ES2-1
ES3.0 PCB TRENDS IN THE LOWER GRASSE RIVER	ES3-1
ES3.1 Resident Fish	ES3-1
ES3.2 Water Column	ES3-4
ES3.3 Sediments	ES3-6
ES4.0 PCB SOURCES TO THE LOWER GRASSE RIVER	
ES4.1 Upstream (“Background”) Inputs.....	ES4-1
ES4.2 Plant Outfalls.....	ES4-2
ES4.3 Tributaries	ES4-5
ES4.4 Groundwater.....	ES4-6
ES4.5 River Sediments	ES4-7
ES4.6 Summary of PCB Source Characterization of the Lower Grasse River	ES4-7
ES5.0 MECHANISMS AFFECTING PCB FATE AND TRANSPORT IN LOWER GRASSE RIVER SEDIMENTS	ES5-1
ES5.1 Diffusion.....	ES5-1
ES5.2 Advection via Groundwater	ES5-2
ES5.3 Resuspension.....	ES5-4
ES5.4 Burial.....	ES5-6
ES5.5 Bioturbation.....	ES5-7
ES5.6 Dechlorination.....	ES5-8
ES5.7 Summary of the Evaluation of PCB Fate and Transport Mechanisms in the Lower Grasse River.....	ES5-9
ES6.0 PCB SOURCES TO LOWER GRASSE RIVER FISH	ES6-1

LIST OF FIGURES

- Figure ES2-1. Grasse River Study Area – Location Map
Figure ES2-2. Spatial Profiles of Water Temperature and Conductivity Measurements at Several Depths in the Water Column During Stratified and Non-Stratified Periods
- Figure ES3-1. Resident Fish Sampling Locations
Figure ES3-2. Average Aroclor-based PCB Concentrations in Smallmouth Bass, Brown Bullhead and Spottail Shiner
Figure ES3-3. Water Column Sampling Locations
Figure ES3-4. Unfiltered PCB Concentrations Measured in Water Samples Collected from Shallow and Deep Water Depths at the Route 131 Bridge During Non-Stratified and Stratified Periods in 2000
Figure ES3-5. Average PCB Concentrations Measured in the Lower Grasse River During Non-Stratified Conditions Between 1995 and 1999
Figure ES3-6. Water Column PCB Concentrations Measured in the Lower Grasse River During Non-Stratified Periods
Figure ES3-7. Water Column PCBs Measured During 2000 Float Survey
Figure ES3-8. Comparison of PCB Homolog Distributions in Unfiltered Water Samples Collected During Low and High Flow Conditions
Figure ES3-9. Total PCB Concentrations in Surface Sediments of the Lower Grasse River
Figure ES3-10. Vertical Distribution of Total PCB Levels in Sediment Cores Collected from the Lower Grasse River
- Figure ES4-1. Average Annual PCB Discharges from Outfall 001
Figure ES4-2. Average PCB Homolog Distributions in SPMDs from the Grasse River and Outfall 001
Figure ES4-3. Average PCB Homolog Distributions in Water Samples Collected from the Grasse River and the Unnamed Tributary
Figure ES4-4. PCB Homolog Distributions in Field Water and SPMD Samples and Water Samples from CMU Lab Studies
Figure ES4-5. Average PCB Homolog Distributions in Water Column and Surface Sediment Samples Collected from the Lower Grasse River
- Figure ES5-1. Spatial Distribution of Net Erosion in the Lower Grasse River During a 100-Year Flood Event (Bounding Estimates)
Figure ES5-2. Comparison of Computed Particulate PCB Concentrations in Unfiltered Water Column Samples from Several SRS Surveys
Figure ES5-3. Vertical Distribution of Cesium Levels in Sediment Cores Collected from the Lower Grasse River
Figure ES5-4. ²¹⁰Pb Concentrations in Lower Grasse River Sediment
Figure ES5-5. Number of Chlorines per Biphenyl and Total PCBs in Lower Grasse River Sediments
- Figure ES6-1. Average PCB Levels in Resident Fish, Water Column and Surface Sediments
Figure ES6-2. Predicted (line) and Measured (symbols) PCB₃₊ Concentrations in Smallmouth Bass and Brown Bullhead Collected from the Grasse River

EXECUTIVE SUMMARY

ES1.0 INTRODUCTION AND CONCLUSIONS

The Supplemental Remedial Studies (SRS) Program was initiated in 1995 to provide information to support the identification and evaluation of potential remedial alternatives to address concerns related to PCB levels in fish and other biota of the lower Grasse River. Potential remedial approaches include: 1) source control; 2) sediment removal; 3) in-place containment; 4) in-place treatment; and 5) natural attenuation. The studies were undertaken based on the premise that a more fundamental understanding of PCB sources, fate and transport, and food chain transfers was necessary to support a defensible assessment of both the applicability and effectiveness of these alternatives. It also should be recognized that during the conduct of these studies, significant efforts were undertaken to control ongoing sources of PCBs from the plant site to the River in support of reducing PCB inputs to the River.

Several studies were conducted in order to achieve this overall objective, including field sampling, laboratory experiments, data evaluation and interpretation, mathematical modeling and the review of the published literature. These studies have assisted in the identification of the major PCB sources to the fish and other biota of the lower Grasse River and the processes that govern the movement of those PCBs within the River. The major conclusions produced from these studies are supported by multiple lines of evidence and are presented below:

- 1) PCB discharges from the plant facility may have provided a significant PCB load to the River prior to the extensive on-site remediation efforts that began in the late-1980s. Effluent data indicate that PCB loadings have dramatically declined since about 1990. Currently, these discharges represent a small proportion of the PCB loading to the water column observed in the River. Continuing on-site remediation will further reduce plant outfall loadings.

- 2) Contributions of PCBs to the lower Grasse River from upstream sources and the Massena Power Canal are negligible in comparison to other sources in the River. The Unnamed Tributary may have been an important source of PCBs to the River historically, but remediation efforts have virtually eliminated discharges from this area.
- 3) PCB-containing sediments are spread over an area of approximately 375 acres. The surface sediment PCB concentrations in the lower Grasse River average about 15 mg/kg. In the region between Outfall 001 (River Mile [RM] 6.3) and about RM 3.3, surface sediment PCB concentrations average about 18 mg/kg. Downstream of RM 3.3 surface sediment PCB concentrations average about 8 mg/kg. Except for several samples located between RM 1.5 and RM 1.8, surface sediment PCB concentrations in the lower 3.3 miles of the River generally are below 10 mg/kg and decline to about 1 to 2 mg/kg near the River mouth.
- 4) Analysis of water column, SPMD, and sediment data, along with laboratory tests on the Grasse River sediments and information on current sources of PCBs to the River, indicates that surface sediment is currently the principal source of PCBs to the water column.
- 5) The relatively widespread distribution of surface sediment PCBs in the lower Grasse River suggests that the PCB sediment source is diffuse and that the widespread diffusive flux from the surface sediments in the lower Grasse River is the primary source of PCBs to the water column. Sediment PCB concentrations vary greatly over short distances in the River. While there are localized regions of elevated surface PCB concentrations in some areas, most notably in the vicinity of the principal Alcoa discharge locations (Outfall 001 and the Unnamed Tributary), results of PCB fate modeling and analysis of the water column data indicate that PCB fluxes from areas of higher concentration are not the predominant source of the PCBs in the water column, although these areas may have local effects.

- 6) PCB levels in the lower Grasse River exhibit a distinct seasonal pattern; levels in the River increase throughout the spring, peak during the summer and decline through the fall. The enhanced PCB fluxes may be a result of biological activity at the surface or diagenetic reactions in the sediments.

- 7) Fish PCB levels have declined since 1995. This decline is likely the result of two factors: 1) the recovery from high PCB water column exposures attributable to the Non-Time-Critical Removal Action (NTCRA) activities; and 2) a downward trend in water column PCB concentrations resulting from on-site remediation efforts that have significantly reduced PCB discharges to the River over the last 10 years and deposition of solids entering the Study Area from upstream. The existing database is not sufficient to determine the relative contribution of each of these factors to the observed decline. Recent trends (1997-2000) suggest that PCB exposure levels may be declining more quickly in the upper portion of the Study Area than in the lower portion. All three trend species suggest declines in the Upper and Middle Stretches (RM 6.75 to RM 3.3) over this time period. The smallmouth bass and brown bullhead data from the Lower Stretch (RM 3.3 to RM 1.8) are exceptions to this trend, suggesting little or no reduction between 1998 and 2000.

- 8) A combination of sediment core data analyses and laboratory experimentation provide many indications that dechlorination and biodegradation are occurring in sediments of the lower Grasse River. Although the laboratory studies indicate the potential for these processes to contribute to the long-term fate of PCBs in the lower Grasse River, it does not appear that dechlorination and biodegradation of PCBs are currently important near-term processes in the River. Long-term in-River studies would be required to collect the necessary information to understand to what extent biodegradation may be an important consideration in the evaluation of the long-term fate of PCBs in the lower Grasse River.

ES2.0 GRASSE RIVER HYDROLOGY

The lower Grasse River is located along the northern boundary of New York State in the Village of Massena. This stretch of River encompasses approximately 8.5 miles, extending from Massena (immediately downstream of the Route 37 Bridge) to the confluence with the St. Lawrence River (**Figure ES2-1**). The Massena Power Canal joins the lower Grasse River from the northwest immediately upstream of the Alcoa facility (approximately 6.75 miles from the mouth). The Power Canal was constructed in the early 1900s and served as a significant power generating source to Alcoa and other industries in Massena. During its operation, water from the St. Lawrence River was conveyed through the Power Canal and discharged into the lower Grasse River. Several dredging operations were performed in both the Power Canal and the lower Grasse River to accommodate this flow. Since ceasing operations in about the 1950s, flows conveyed through the Power Canal to the lower Grasse River have been minimal.

On average, the Grasse River discharges approximately 1,100 cfs to the St. Lawrence River annually (OME, 1988). The highest River flows generally occur in the spring at levels of 2,000 to 10,000 cfs. During the summer months (June through August), flows are considerably lower, remaining relatively constant at 100 to 200 cfs. During these low flow periods, vertical stratification within the water column occurs in portions of the lower Grasse River. This stratification is evident in water temperature and specific conductivity measurements taken at several depths within the water column: surface, mid-depth and bottom (**Figure ES2-2**, River miles are designated from the confluence of the Grasse and St. Lawrence Rivers). A dye study conducted in August 1997, water quality samples from monitoring wells adjacent to the Grasse River site and a float survey conducted in June 2000 indicate the cooler, higher conductivity water observed at depth is the result of the migration of St. Lawrence River water along the bottom of the Grasse River. This stratification occurs only during low flows and when water temperature differences (4-5 degrees Celsius [$^{\circ}\text{C}$]) between the Grasse and St. Lawrence Rivers exist, principally from May to mid-August. This stratification has been consistently documented as far upstream as Transect WC007 (RM 5.30); however, on one occasion in June 1999, stratification was observed at the terminus of the Massena Power Canal (Transect WC003; RM

6.85). When the lower River is not stratified, water temperature and specific conductivity measurements throughout the water column are similar.

ES3.0 PCB TRENDS IN THE LOWER GRASSE RIVER

ES3.1 Resident Fish

Prior to the initiation of the SRS Program, two resident fish surveys were conducted in the lower Grasse River (RSI Phases I and II in 1991 and 1993, respectively). Since 1994, eleven resident fish sampling surveys have been performed: 1) Pre-Non-Time-Critical Removal Action [NTCRA] Survey in June 1995; 2) Post-NTCRA Survey in October 1995; 3) Spring 1996 SRS Survey; 4) Fall Trend Monitoring Surveys ([TMS]; 1996-2000); 5) Young-of-Year (YOY) Brown Bullhead Survey in June 1999; and 6) YOY Pumpkinseed Surveys (Fall 1998 and 1999).

The spring surveys (Pre-NTCRA and the 1996 SRS) consisted of the collection of juvenile and adult smallmouth bass and brown bullhead in the vicinity of Outfall 001 and the Unnamed Tributary (**Figure ES3-1**). The fall surveys (Post-NTCRA and TMS) focused on the collection of adult smallmouth bass and brown bullhead from three stretches adjacent to, and downstream of, the plant facility (see **Figure ES3-1**). Fish samples also were collected from a background region (upstream of the Massena Dam). In addition to smallmouth bass and brown bullhead, spottail shiners were collected during the fall surveys from four locations within the lower Grasse River (see **Figure ES3-1**). Smallmouth bass samples collected during these surveys were prepared as skin-on, scales-off fillets, while brown bullhead samples were prepared as skin-off fillets. Because of their size, spottail shiners were prepared as whole-body composite samples.

Beginning in fall 1998, YOY fish collections were added to the existing resident fish monitoring program. For these surveys, composite samples (generally consisting of 5 to 10 individual fish) were collected from the existing Background Stretch and from two newly selected near-shore sampling stretches: one adjacent to the plant facility and one further downstream in the vicinity of the Route 131 Bridge (see **Figure ES3-1**). As listed above, YOY brown bullhead were targeted in the spring and YOY pumpkinseed in the fall. The YOY fish collections were discontinued after the fall 1999 sampling.

PCB levels in fish have been quantified as concentrations of Aroclors 1242, 1254 and 1260. In addition, since 1995, a subset of the fish tissue extracts has been analyzed to determine the

concentration of individual PCB congeners. Comparisons of Aroclor-based and congener-based total PCB concentrations in these samples revealed that Aroclor-based total PCB concentrations typically were 30 to 40 percent higher than congener-based total PCB concentrations. Further investigations uncovered an apparent double-counting in the Aroclor 1254 and 1260 calculations and also indicated that PCB and lipid results were sensitive to sample preparation, handling, storage and extraction differences among laboratories. These issues were addressed, beginning in 1999, by a change in laboratories and a change in analytical procedures.

PCB levels measured in fish are presented on both wet tissue (mg/kg wet) and lipid-normalized bases (mg/kg lipid). The lipid-normalized values were calculated (i.e., wet tissue PCB concentration ÷ lipid fraction [mg/kg lipid]) in an effort to reduce PCB concentration variability resulting from differences in the lipid content of individual fish.

Average wet tissue, Aroclor-based PCB concentrations in samples collected within the site during RSI Phases I and II and each of the SRS Program fish surveys are presented in **Figure ES3-2**. PCB levels in fish collected upstream of the site in the Background Stretch are not presented because PCBs were not detected in over seventy percent of the samples. Detected concentrations ranged from 0.05 mg/kg to 0.16 mg/kg, with two exceptions at PCB levels of about 1.4 mg/kg.

PCB levels in smallmouth bass exhibit little variation across the three River stretches. For brown bullhead, average PCB concentrations are generally highest in the Middle Stretch of the River; however, differences among the three Stretches are not statistically significant. PCB levels in spottail shiners exhibit consistent differences among locations. Average PCB levels measured in spottail shiners captured near Outfall 001 and the Unnamed Tributary are similar and higher than those observed at the mouth of the River. This spatial trend is evident in each survey except for fall 1995, where PCB levels in samples collected near Outfall 001 were about 3 times higher than those observed near the Unnamed Tributary. The elevated PCB levels observed near Outfall 001 during this survey are likely related to the NTCRA dredging program conducted during summer 1995.

Changes in PCB levels over time are evident for all three fish species. Average wet tissue PCB concentrations in smallmouth bass have ranged over about a factor of ten from about 2.5 mg/kg in 1991 to about 20 mg/kg in 1993 (see **Figure ES3-2**). Between 1993 and 1997, a general, though variable, decline in average PCB levels is observed, with 1997 concentrations averaging 4 to 5 mg/kg. After 1997, no consistent trend is apparent. Average lipid-normalized PCB concentrations (expressed as mg/kg lipid) in smallmouth bass exhibit patterns that are somewhat different from those of the wet tissue concentrations (see **Figure ES3-2**). Declines in average lipid-normalized PCB levels between 1993 and 1997 are evident throughout the entire lower River. Levels in the Upper and Middle Stretches continue to decline through the remaining years and the 2000 values are the lowest on record. However, average levels in the Lower Stretch have remained relatively unchanged since 1998.

PCB concentrations in brown bullhead exhibit less spatial and temporal variability than those observed in smallmouth bass. Average concentrations in wet tissue vary only by about a factor of two between 1993 and 2000 (see **Figure ES3-2**). Declines between 1993 and 1997 are evident; however, PCB levels from 1998 to 2000 are similar to those observed in 1993. Lipid-normalized PCBs in brown bullhead exhibit greater variability than wet tissue PCB levels, ranging from about 180 to 900 mg/kg lipid throughout the River (see **Figure ES3-2**). Although year-to-year variability confounds the interpretation of temporal trends in the brown bullhead, a general decline in lipid-normalized PCB levels between 1993 and 2000 is evident at all locations.

In 1993, average wet tissue PCB levels in spottail shiners collected near Outfall 001 and the Unnamed Tributary are relatively similar, averaging 11 mg/kg and 13 mg/kg, respectively, while those collected at the mouth of the River are much lower (4.5 mg/kg; see **Figure ES3-2**). In October 1995, PCB levels in spottail shiners near Outfall 001 increase to about 42 mg/kg, while levels measured near the Unnamed Tributary and the mouth of the River remain similar to the levels observed in 1993. This increase is likely a result of the NTCRA dredging operations. Since 1995, PCB levels have declined to about 3 mg/kg and 2 mg/kg in the Upper and Middle Stretches, respectively. At the mouth of the River, continual declines in spottail shiner PCBs are observed (from about 4 mg/kg in 1995 to about 0.7 mg/kg in 2000). Similar trends are exhibited in the lipid-normalized PCB concentrations (see **Figure ES3-2**).

ES3.2 Water Column

Since 1995, 73 routine and high-flow water column surveys have been conducted in the lower Grasse River, resulting in over 1500 samples collected and analyzed for PCB congeners. In addition, an array of conventional water quality parameters have been measured (i.e. water temperature, specific conductivity and suspended solids). Routine water column surveys typically are conducted between April and November and include the collection of samples from transects upstream and downstream of the plant facility (**Figure ES3-3**). High-flow events were conducted during spring runoff events (March through April), with the exception of one survey in September/October 1996.

Between 1995 and 1999, water samples consisted of composites of nine discrete, unfiltered samples at each targeted transect: three samples (0.2, 0.5 and 0.8 times the total water depth) collected at three locations along a single transect perpendicular to River flow. Prior to 2000, routine monitoring surveys conducted at times when the River was stratified resulted in composite samples that contained lower Grasse River water and St. Lawrence River water in unknown proportions. In 2000, this issue was addressed by collecting discrete samples from the middle of the River channel at the Route 131 Bridge (Transect WC131) at depths equal to 0.2 and 0.8 times the total water depth and analyzing each separately for PCBs.

The PCB data collected from the Route 131 Bridge in 2000 illustrate the effects stratification has on PCB concentrations in the lower Grasse River. When the River is not stratified, PCB levels measured in surface water samples (0.2 times the water depth) and deeper water samples (0.8 times the water depth) are similar (**Figure ES3-3, panel a**). However, during periods of stratification, PCB levels in the deeper samples are greater than those observed in the surface samples (**Figure ES3-3, panel b**). The effects of stratification complicate the interpretation of the composited water column data and SPMD data collected during previous years. Therefore, composited data collected during stratified periods were not used in the assessment of spatial and temporal trends in water column PCBs.

PCB levels in the lower Grasse River exhibit a distinct seasonal pattern; highest levels occur during the summer and lowest levels occur in the late fall (note that no data are collected during winter due to ice formation in the River). Superimposed on this seasonal pattern is an overall decline in levels over the period of record. These temporal patterns are partially explained by seasonal and year-to-year variations in River flow. However, the patterns also are evident in PCB mass flux (i.e., the product of PCB concentration and River flow), indicating that PCB sources to the River vary seasonally and have declined over time.

Typical seasonal trends observed in water column PCB concentrations in the lower Grasse River are presented in **Figure ES3-5**. At water column Transect WC007 (River mile 5.3), PCB concentrations increase from about 20 to 50 ng/L during the spring (April and May), peak at 100 to 200 ng/L in the summer (June through August) and decline to 10 to 20 ng/L during the fall (September through November) (**Figure ES3-5, top panel**). This pattern also is evident in the PCB mass flux data. Similar seasonal patterns are observed at Transects WC007A and WC011, although absolute PCB concentrations (and, thus, mass fluxes) are higher at these downstream locations (**Figure ES3-5, middle and bottom panels**, respectively).

An overall downward trend in the water column PCB levels over the last 5 to 6 years is more evident when the PCB data are plotted on a logarithmic scale (**Figures ES3-6, top panel**). For example, at Transect WC007 maximum summertime PCBs decline from 200 to 260 ng/L in 1995 to about 60 ng/L in 1999. At water column Transect WC007A, PCB levels decline from about 300 ng/L in 1995 to about 40 ng/L in 2000 (2000 samples collected from Route 131 Bridge located about 500 feet upstream of Transect WC007A; **Figure ES3-6, middle panel**). Finally, PCB levels measured at water column Transect WC011 in summer 1999 are about a factor of 2 times lower than those observed in summer 1995 (**Figure ES3-6, bottom panel**).

Water column PCBs vary spatially throughout the lower Grasse River. In each survey conducted between 1996 and 1999, PCB mass fluxes increase from upstream to downstream. This pattern of continual increase was confirmed by intensive sampling during a float survey conducted in June 2000. In this survey, PCB levels exhibited a continual increase from about 10 ng/L at Transect T23 to 20-40 ng/L at Transect T50 (**Figure ES3-7**). PCB concentrations in samples

collected upstream of Transect T23 were reported below the nominal detection limit (10 ng/L) while those collected downstream of Transect T50 decline due to the effects of stratification that was noted in this stretch of the River. Although the magnitude of these PCB increases vary during the course of the year, the increases observed with distance downstream is consistent with a diffuse, surface sediment PCB source.

PCB composition in water column samples is similar during low- and high-flow events. For example, the PCB homolog distributions observed in water samples collected during low-flow conditions in 1997 (about 160 cfs, August - September, 1997) are similar to those observed during the 1998 spring high flow event (about 7561 cfs, March 1998; **Figure ES3-8**). Although some variability in the PCB homolog patterns exists, di- and tri-PCBs consistently dominate the homolog distributions observed at most water column transects located downstream of the plant facility (approximately 60 to 85 percent of total PCBs).

ES3.3 Sediments

Several sampling surveys have been conducted to characterize PCB levels in lower Grasse River sediments. Low-resolution core surveys were performed in 1991 (River and Sediment Investigation [RSI] Phase I), 1993 (RSI Phase II), and in 1995 prior to and immediately after the NTCRA activities. In 1997, surface grab sample and high-resolution core surveys were conducted as part of the SRS Program. Finally, a focused sediment sampling program consisting of the collection of sediment core samples was initiated in 2000, with an expected completion date of spring 2001. In total, about 500 cores/grabs have been collected throughout the lower River, resulting in over 1100 sediment samples analyzed for PCBs.

PCB concentrations in surface sediments¹ are highly variable and range over several orders of

¹ Although an extensive database has been compiled for PCBs in lower Grasse River sediments, the analysis of the data is complicated by the different segmentation schemes employed during each of the surveys. For example, sediment cores collected in 1991 were divided into 0 to 3-inch, 3 to 12-inch, 12 to 24-inch and 24 to 36-inch slices (when possible). In 1993, cores were generally divided into 12-inch slices, while cores in 1995 were segmented into 0 to 1-inch, 1 to 6-inch and 6 to 12-inch slices. In 1997, sediment cores were segmented into 1-centimeter slices (to depth of core) while grab samples represented the top 3 inches of sediment. Finally, sediment cores collected in 2000 were divided into the same depth intervals as in 1991 (0 to 3-inch, 3 to 12-inch, 12 to 24-inch and 24 to 36-inch slices). In an attempt to make use of the entire data set, samples collected within the top 3 inches of the sediment surface during the 1991, 1995, 1997 and 2000 surveys and all samples from the 1993 survey were considered "surface sediments."

magnitude, even for closely spaced samples (**Figure ES3-9**). The average PCB concentration in surface sediments of the lower Grasse River is about 15 mg/kg dry (area-weighted average using polygon analysis; see below). Between River miles 6.3 and 3.3, surface sediment PCB concentrations average about 18 mg/kg dry. Downstream of River mile 3.3, the average surface sediment PCB concentration is about 8 mg/kg dry. Except for several samples collected between River miles 1.5 and 1.8, surface sediment PCB concentrations in the lower 3 miles generally are below 10 mg/kg dry and decline to about 1-2 mg/kg dry near the mouth of the River. In general, the higher PCB levels tend to be found in areas with deeper water depths (i.e., closer to the middle of the channel).

Sediment core data collected in 1991, 1997 and 2000 indicate that maximum PCB concentrations tend to be buried in the River sediments. In the sediment cores collected in 1991, peak PCB levels are, on average, found about 1 to 3 feet below the sediment-water interface. In 1997, peak PCB concentrations in Core 30S were measured about 50 centimeters (1.6 feet) below the sediment-water interface; peak PCB levels in the other four cores occurred between 85 to 105 centimeters (2.8 to 3.5 feet) below the sediment-water interface (**Figure ES3-10**). Average PCB levels in sediment cores collected in 2000 generally increase with sediment depth, with maximum PCB levels observed about 2 to 3 feet below the sediment-water interface.

ES4.0 PCB SOURCES TO THE LOWER GRASSE RIVER

Potential PCB sources to the River include any sources upstream of the site that enter the upper Grasse River, plant outfalls, the Unnamed Tributary, groundwater discharges to the River and River sediments. A combination of data analyses, laboratory experiments and modeling studies were performed to determine the relative importance of each potential PCB source. In several cases, PCB loading to the River was estimated from available data and compared to PCB mass transport in the lower Grasse River.

ES4.1 Upstream (“Background”) Inputs

Two potential upstream sources exist: the Grasse River upstream of the Massena Dam and the Massena Power Canal. Water column samples collected upstream of the Massena Dam (at water column Transect WC001 between 1995 and 1997 and at the Main Street Bridge in 1998 and 2000, see **Figure ES2-1**) were generally below the 20 ng/L method detection limit for PCB congeners. These estimated PCB concentrations are similar to PCB levels measured in rain collected in the Great Lakes region during the late 1980s and 1990s (1 to 8 ng/L; Eisenreich and Strachan, 1992; 1 to 12 ng/L, USEPA [undated]; 1 to 3 ng/L, Simcik *et al.*, 2000). Low PCB levels also were measured in SPMDs deployed at Transect WC001 in 1995, 1996 and 1997 (averaging 0.12 :g compared to 32.8 :g downstream at Transect WC007). Sediment samples collected between the Route 37 Bridge and water column Transect WC001 during RSI Phase I activities all yielded PCB results below the contract required quantitation limit (CRQL = 0.08 mg/kg). PCB results from sediment samples collected during RSI Phase I activities between WC001 and the Power Canal again were below the CRQL, except for two samples (1.2 mg/kg, 0-3”; 0.38 mg/kg, 12-24”).

PCB concentrations measured in water column, SPMD and surface sediment samples from the Power Canal are low, suggesting the PCB flux from the Power Canal to the River also is negligible. For example, water samples collected from the Power Canal in June 1995 averaged 7.9 ng/L total PCBs, a value not significantly different from the upstream “background” sample collected at the same time at Transect WC001 (3.9 ng/L), both below the 20 ng/L detection limit for PCB congeners. In 1999, all water samples collected from the Massena Intake Dam

(Transect WC002; see **Figure ES3-3**) were below the 20 ng/L detection limit, except for one sample collected in September which contained 87 ng/L. PCB levels measured in SPMDs deployed in the Power Canal in 1995 also were low (about 0.50 :g). Surface sediment samples collected in the Power Canal during RSI Phase I activities contained relatively low levels of PCBs, with concentrations ranging from non-detect to 2 mg/kg for most samples. Two samples collected during this survey contained slightly higher PCB concentrations (5.4 mg/kg and 5.9 mg/kg). Finally, further support is provided by investigations conducted during RSI Phase II, which indicated that the contribution of water from the Power Canal to the lower Grasse River is minor (based on conductivity measurements, BBL, 1994).

Further support that the Grasse River upstream of the Massena Dam and the Power Canal are not important PCB sources to the lower Grasse River is provided by comparisons of PCB levels measured in paired SPMDs deployed at two sampling transects: one immediately upstream of the facility (but downstream of the confluence with the Power Canal [Transect WC004]), and at a transect one mile downstream of Outfall 001 (Transect WC007). Because SPMDs were deployed in the River for a two-week period, PCB levels measured in SPMD samples represent time-weighted averages of PCB concentrations in the River. PCB levels measured in SPMDs collected from upstream of the Alcoa facility were about 20-fold lower than levels observed in SPMD samples collected one mile downstream of Outfall 001, except for samples collected in June 1995 and 1997 where upstream samples were 5 to 10-fold lower. Stratification has been observed at Transect WC007 during the summer months and may have affected PCB levels in these samples. Based on these data, PCBs from the upper Grasse River and the Massena Power Canal are negligible in comparison to the rest of the River.

ES4.2 Plant Outfalls

The Plant currently has five permitted outfalls discharging a mixture of treated wastewaters and storm waters. The outfalls are routinely monitored, with permits requiring Aroclor-based PCB analyses in addition to other monitoring/analytical requirements. Some of the outfalls have been subject to special, short-term, high-flow studies that have included analyses of PCBs by

congener (BBL, 1998b). The contribution of PCBs from each outfall to the River is discussed below.

Until November 1998, PCBs were discharged from the plant to the River primarily through Outfall 001, and to a lesser extent Outfall 004. Effluent data collected under the permit issued through the New York State Pollution Discharge Elimination System (SPDES) were used to estimate PCB loadings to the lower Grasse River. Although plant facility discharges may have been important contributors to lower Grasse River PCBs in the past, on-site remediation efforts have dramatically reduced PCB discharges to River. For example, PCB discharges from Outfall 001 have declined from about 60 grams/day in 1990 to about 1.7 grams/day in 1997 (**Figure ES4-1**). In 1998, PCB discharges from Outfall 001 were slightly higher at about 6.3 grams/day; the increase in 1998 relative to previous years was likely the result of sewer cleaning activities undertaken in the fall 1998, as well as the lowering of the detection limit for reporting PCBs by the Alcoa Massena Operations ChemLab². PCB discharges from Outfall 001 in 1999 and 2000 averaged 2.1 grams/day and 1.4 grams/day, respectively. Currently, a portion of the effluent previously discharged to Outfall 001 is directed to the new 005 Impoundment and thereafter pumped to Building 156 for treatment via dual media filtration, followed by activated carbon adsorption, and discharged to Outfall 004. Because effluent from Outfall 004 undergoes carbon treatment prior to discharge, PCBs are not discharged during “dry weather.” However, stormwater can bypass treatment during large rainfall events (greater than a 19-year return period storm event). The SPDES monitoring program generally does not characterize releases during storm events. Therefore, to evaluate potential PCB discharges during storm events, water samples were collected at Outfalls 001 and 004 during six rainfall events in 1997 and analyzed for PCBs (for details on Storm Sampling Program, see Section 2.2). During these events, PCB discharges to the River averaged about 12 and 6 grams/storm for Outfalls 001 and 004, respectively (BBL, 1998b). It should be noted that additional source control efforts have been implemented at the plant following the collection of these data.

² The Alcoa Massena Operations ChemLab detection limits for PCB Method 608 were lowered in October 1998. The method detection limit was lowered from 0.175 :g/L for Aroclors 1242, 1248 and 1254 and 0.125 :g/L for Aroclor 1260 to 0.065 :g/L for all Aroclors.

The significance of Outfalls 001 and 004 as PCB sources to the River was assessed by comparing estimates of annual PCB mass discharges from the outfalls and annual PCB mass flux in the River. Using paired measurements from the SPDES and SRS data, relationships between PCB concentration and effluent flow were developed for each outfall. Annual PCB mass discharges were estimated using these relationships and effluent flow records from October 1, 1996 to September 30, 1997. A similar approach was taken to estimate PCB mass flux in the River; a relationship between PCB concentrations at Transect WC007 and River flows was developed and applied to the River hydrograph for the same time period. Results indicate that for this period, Outfalls 001 and 004 discharged about 1.5 kg and 0.1 kg of PCBs to the River, representing about 11 percent of the PCB mass flux past Transect WC007 (14.3 kg), less than 11 percent for locations downstream of Transect WC007. On-going plant facility remedial efforts will continue to reduce PCB discharges from these outfalls. Mass balance calculations performed by the PCB fate model for the four-year calibration period (1997-2000) confirm the relatively minor contribution of PCBs from the outfalls to the River; the model estimates that PCBs from Outfalls 001, 004, 005 and 007 represent less than 5 percent of the PCBs mass discharges to the River during this period.

PCB homolog distributions in SPMDs deployed in the Outfall 001 mixing basin are significantly different than those observed in SPMDs deployed in the River, further supporting that Outfall 001 is not a significant contributor to water column PCBs (**Figure ES4-2**). PCBs from Outfall 001 contain a greater amount of higher chlorinated congeners than samples from the River, indicating (based on compositional differences) that the outfalls are not a significant source of PCBs to the River.

SPDES monitoring data collected for Outfalls 003 (discharging to the Power Canal) and 007 indicate these outfalls contribute negligible PCB mass discharges to the lower Grasse River. However, occasional PCBs have been observed in the Outfall 007 discharge. PCB discharges from the former Outfall 002 (which discharged to the Unnamed Tributary) are described below in Section ES4.3.

Alcoa initiated a land-based remediation program in 1991 that aimed to eliminate or mitigate any off-site migration of hazardous constituents, especially to the Grasse River. Many elements of this remediation program have been completed, including: 1) remediation of numerous on-site lagoons, landfills and disposal areas containing PCBs; and 2) remediation of a major portion of the Unnamed Tributary. Concurrently with the land-based remediation program, Alcoa made several site improvements as part of the SPDES permit, including the construction of three new stormwater/wastewater impoundments and cleanup of several underground utilities. Through these efforts, Alcoa has dramatically reduced PCB discharges to the lower Grasse River. The PCB discharges are expected to be further reduced following the completion of Alcoa's on-site remediation program.

Although not a plant outfall, the Town of Massena sewage treatment plant is a potential source of PCBs to the lower Grasse River. No data from direct monitoring of the discharge are available, but data from a sample (June 1995) taken in the discharge plume's zone of initial dilution showed only 8.9 ng/L total PCBs, a value consistent with values obtained at the same time from nearby Transect WC004 (14.0 ng/L) and from the background sample at Transect WC001 (3.9 ng/L). PCB data from SPMDs located within the discharge plume's zone of initial dilution also have been low (1.5 :g).

ES4.3 Tributaries

Several tributaries enter the lower Grasse River, the most notable being the Unnamed Tributary. Since 1995, the Unnamed Tributary has been sampled several times. Based on data from the storm sampling in 1997 (BBL, 1998b), the storm-related discharges of PCBs from the Unnamed Tributary to the lower Grasse River were calculated to range from 0.01 to 0.06 kg/yr (average ~ 0.03 kg/yr). In addition, PCB homolog distributions in these samples are much different than those observed in the River. Samples collected from the Unnamed Tributary during these storm events contained greater levels of hexa- and hepta-PCBs relative to those observed in the River (**Figure ES4-3**).

As discussed above, Alcoa completed a major remedial action on the Unnamed Tributary in 1998. This effort included the removal of significant amount of sediments containing PCBs, as well as the rerouting of all Outfall 002 discharges (except for flows greater than the 50-year, 24-hour storm) to the Area III Impoundment. In turn, these waters are pumped to the Central Impoundment before being discharged to the River through Outfall 001. PCB levels in water samples collected from the Unnamed Tributary in August and October 2000 ranged from non-detect to 1.2 ng/L. PCB concentrations in sediment samples collected during the same period ranged from non-detect to 1.4 mg/kg.

No data are available for the four other small tributaries that enter the lower Grasse River. However, there is no reason to believe these tributaries contribute PCBs in the lower Grasse River based on their locations and drainage areas.

ES4.4 Groundwater

PCB data collected from several groundwater monitoring wells indicate groundwater is not a significant source of PCBs to the lower Grasse River. As part of Alcoa's bedrock monitoring program, groundwater samples have been collected from several shallow and deep (i.e., bedrock) monitoring wells over the past decade. This program was performed at the request of NYSDEC and initiated prior to the installation of the Dennison Road public water supply line. PCB levels ranging from non-detect to 0.60 µg/L were measured in groundwater samples collected between 1990 and 1992 from four of the sampled wells (MW-089D, MW-090D, MW-091D and MW-092D). PCBs were not detected in the other shallow and bedrock wells sampled during this period. Except for a single sample collected from MW-091D in September 1994 (4.4 µg/L), no detectable concentrations of PCBs have been measured in any of the 28 samples taken from these wells since 1992. This information, coupled with the limited groundwater discharge to the lower Grasse River (as indicated by the modeling and data analyses), indicates that groundwater advection from the plant site is an insignificant source of PCBs to the River.

ES4.5 River Sediments

PCB concentrations in surface sediments of the Grasse River vary over several orders of magnitude (see **Figure ES3-9**). This relatively random distribution of surface sediment PCBs suggests that the surface sediment source is diffuse and widespread. The increases observed in the water column PCB data collected downstream of the facility are consistent with patterns expected from such a diffuse source. This pattern is exemplified by the results of the June 2000 float survey (see **Figure ES3-7**). In addition, data collected during this survey indicated that, although areas of elevated surface sediment PCB concentrations may have local effects, these areas are not the predominant source of the PCBs in the water column.

The composition of the PCBs in water column provides evidence that these PCBs were derived principally from the surface sediments. PCB homolog distributions in the water column closely match those observed in water samples from batch aqueous extraction of River sediments and column studies of PCB flux from River sediments (**Figure ES4-4** and Nadal, 1998). This similarity indicates that surface sediment pore water is a significant source of PCBs to the water column. In contrast, PCB homolog distributions in water samples and surface sediment are different, suggesting water column PCBs are not derived from resuspended sediments (**Figure ES4-5**). This difference is maintained even during high flow events, providing a further indication that the source of PCBs to the water column is pore water, not resuspended sediments (see **Figure ES3-8**). Further support is provided by the similarity between PCB homolog distributions in water column and SPMD samples that reflect only soluble PCBs, which suggests a soluble PCB source (**Figure ES4-5**).

ES4.6 Summary of PCB Source Characterization of the Lower Grasse River

Analysis of water column, SPMD and sediment data collected in the lower Grasse River indicate that a widespread flux from the surface sediments is the principal source of PCBs to the water column. While there are localized regions of elevated surface PCB concentrations in some areas, most notably in the vicinity of the principal Alcoa discharge locations (Outfall 001 and the Unnamed Tributary), results of PCB fate modeling and analysis of the water column data

indicate that PCB fluxes from areas of higher concentration are not the predominant source of the PCBs in the water column, although these areas may have local effects.

Results of data analyses indicate contributions from upstream point sources, the Massena Power Canal, the Unnamed Tributary and groundwater discharges from the plant site are insignificant. Finally, data collected as part of SPDES monitoring and during high-flow events in 1997 indicate PCB discharges from plant facility outfalls are not significant relative to other sources and efforts have continued at the facility since the 1997 sampling effort to further reduce PCB discharges to the River.

ES5.0 MECHANISMS AFFECTING PCB FATE AND TRANSPORT IN LOWER GRASSE RIVER SEDIMENTS

Several mechanisms may affect the fate and transport of PCBs in the lower Grasse River sediments, including diffusion, advection, resuspension, burial, bioturbation, dechlorination and microbial degradation. Each mechanism was evaluated using site-specific field data, laboratory experiments and/or modeling studies.

ES5.1 Diffusion

The SRS data indicate that the PCB flux from surface sediments is the predominant source of the PCBs in the water column of the lower Grasse River. Further, the PCBs originate primarily from the pore waters of the sediments. Pore water PCBs can be transported to the water column via numerous mechanisms. By virtue of the concentration gradient between surface sediment pore water and the overlying water, diffusion contributes to transport. Diffusive mechanisms include molecular diffusion and dispersion (and/or advection) caused by hydrodynamic pressure gradients at the rough surface of the sediment and the respiratory activity of benthic organisms.

The seasonal cycle of water column PCB levels (see Section ES3.2) indicates that the processes responsible for the flux from pore water vary over the year. The extent of the variation and the magnitude of the mass transfer coefficients that quantify the flux were empirically derived through a mass balance calculation using observed water column and sediment data collected from the lower Grasse River between water column monitoring Transects WC004 and WC007 (details provided in Appendix C). To reproduce the seasonality observed in water column PCBs, sediment-water mass transfer coefficients of 1 to 2 cm/d and 4 to 5 cm/d were required for the winter (September through May) and summer (June through August) months, respectively. The mass transfer rates of 1 to 2 cm/d (winter) compare well with estimates from column studies performed by Carnegie Mellon University. In these studies, rates of 2 to 3 cm/d were estimated for simple diffusion from pore water (Nadal, 1998). The higher rates needed to reproduce PCB levels during summer months imply additional transport mechanisms may be operative during these periods.

The relative contribution of sediment areas with higher PCB concentrations was assessed during the modeling studies. Specifically, the PCB fluxes from surface sediments were estimated for the following regions: 1) sediments within the NTCRA area (post-remediation); 2) sediments in Areas 2, 3 and 4 (as defined during the RSI Phase II); and 3) sediments throughout the remaining portions of the River. The modeling results indicate that PCB fluxes from these isolated areas with higher surface sediment PCBs contribute a minor fraction of the total diffusive PCB flux to the water column (about 10 percent). Although these areas contribute only a relatively small fraction to the overall PCB levels observed in the Grasse River water column, data collected during the June 2000 float survey suggest that areas with elevated surface sediment PCB concentrations may have effects on local water column PCB levels. PCB flux from surface sediments throughout the rest of the River account for about 90 percent of the total PCB flux to the water column, indicating that the widespread, diffusive flux from the surface sediments is the primary source of PCBs to the water column. This is consistent with a number of observations:

- 1) water column PCB fluxes exhibit a continual increase from upstream to downstream across the site;
- 2) PCBs are present in all surface sediments at concentrations that vary in a somewhat random pattern;
- 3) PCB composition in water column samples is similar to that estimated for sediment pore water (using sediment data and equilibrium partitioning concepts); and
- 4) PCB composition in water samples collected from the River is similar to that observed in water samples collected during laboratory column flux and batch aqueous extraction studies performed using lower Grasse River sediments.

ES5.2 Advection via Groundwater

Groundwater could enter the lower Grasse River in several ways: 1) through the banks (i.e., local groundwater discharge); 2) in a preferential, highly localized manner from fractured bedrock which does exist at the River bottom in the upper end of the Study Area (i.e., upstream of Outfall 001); and/or 3) in a diffuse manner through the soft sediments and underlying till which cover most of the River bottom downstream of Outfall 001.

Although the piezometric heads in monitoring wells along the River are higher than the elevation of the River, discharge through the banks is likely to be severely limited by the low hydraulic conductivity of the soils (clay and till, mostly). Also, any such discharge is not expected to be significant because of the limited amount of PCB-containing sediments found on the steep banks. Discharge from fractured bedrock is also not believed to be an important pathway since: 1) there is minimal to no PCB-containing sediments in much of the area where bedrock located near or at the bottom of the River; and 2) only a small sediment surface area would be involved where PCB-containing sediments did exist. Thus, the largest effect of any groundwater discharges would be from flow through the soft sediments on the bottom of the River.

To determine the diffuse discharge through underlying till, an initial order-of-magnitude estimate of the groundwater flux to the River was calculated (based on work performed for the Alcoa/Massena facility). The calibrated, numeric (three dimensional, finite element) model DYNFLOW was used to estimate discharge (flux per unit length of River) through the overburden and shallow bedrock from the plant (north) side of the River in the region between the Power Canal and the confluence with the St. Lawrence River. Flow through deep bedrock was not modeled. Discharges to the River from the south side were assumed to be the same as from the north side. The resulting estimate for total groundwater flux (from the north and south sides) was approximately 1 cubic foot per day per linear foot of River ($1 \text{ ft}^3/\text{d-ft}$), which is approximately equal to 100 liters per day per meter (100 L/d-m). A discharge flux per unit area may be estimated by factoring in the width of the River. Assuming a typical width of 100 m, a discharge flux estimate of $1 \text{ L/m}^2\text{-d}$ is obtained. The equivalent Darcy velocity is 0.1 cm/d . This is more than an order-of-magnitude lower than the estimated PCB mass transfer velocity from sediments (see discussion of PCB flux below).

In addition to the modeling, groundwater seepage rates were measured in the lower Grasse River during two surveys; one in fall 1998 and one in spring/summer 1999. For each survey, seepage meters were placed into the sediments by SCUBA divers at three sediment probing transects with soft sediment bottoms (transects T6, T13 and T28). A total of twelve meters were deployed during each survey, 4 at each transect. Results from the two surveys showed no significant discharge in the areas monitored. Overall area-wide average fluxes of $-0.004 \text{ L/m}^2\text{d}$ and 0.014

L/m²-d were determined for the 1998 and 1999 surveys, respectively (with the negative sign implying flow from the River into the sediments). The lowest and highest individual meter measurements from 1998 were -0.23 L/m²d and +0.25 L/m²d, respectively. The flux numbers (length³/length²time) can also be expressed as a velocity (length/time). Multiplying L/m²d by 0.1 yields cm/d, and thus, for example, the lowest and highest seepage velocities (ignoring porosity effects) were -0.023 cm/d and +0.025 cm/d, respectively. In 1999, the lowest and highest individual meter measurements were -0.623 L/m²d and +0.411 L/m²d, corresponding to seepage velocities (ignoring porosity effects) of -0.062 cm/d and +0.041 cm/d, respectively.

The weight-of-evidence data, from multiple and fundamentally different characterization approaches, supports a conclusion that there is no significant amount of groundwater being discharged - in a broad, diffuse pattern - through the soft sediments present in areas downstream of Outfall 001. However, the available data do not rule out the possibility of some locally-significant groundwater discharges through the banks of the River or through bedrock fractures where bedrock lies at or near the River bottom.

ES5.3 Resuspension

The lower Grasse River was deepened in the early 1900s to accommodate water flow from the Massena Power Canal. Since flows from the Power Canal ceased (in 1950s), velocities in the River have decreased significantly and the River has functioned as an efficient trap for sediment transported in from upstream. During the dye study conducted in the lower Grasse River (July/August 1997), when River flows were at the common summertime lows (95-105 cfs), the average water velocities, based on dye concentration measurements, were estimated to be on the order of 0.02 ft/s. At these low flows, the travel time between Outfall 004 and the River's mouth is close to 21 days. During extreme flow conditions, flow velocities still are relatively low. A hydrodynamic model developed for the lower Grasse River predicted maximum flow velocities during a storm flow of 15,600 cfs (similar in magnitude to a 100-year flood event) in the River to be about 3 to 4 ft/s.

The in-situ resuspension potential (i.e., eroded sediment mass per unit area) of lower Grasse River cohesive sediments was measured during sediment shaker studies and SedFlume testing that were conducted between 1998 and 2000. Using these data, bounding erosion potential functions³ were developed and applied to the hydrodynamic model to provide conservative estimates of sediment scour in the lower Grasse River during a 100-year flood event. The hydrodynamic model predicts that, on average, about 0.2 cm of erosion occurs during a flood of this magnitude, with about 99 percent of the cohesive sediments in the River experiencing less than 1 cm of erosion (**Figure ES5-1**). The maximum erosion predicted during the 100-year flood was about 1.4 cm. Thus, even under extreme flow conditions, little sediment resuspension is expected within the River.

The conclusions from the erosion potential studies and the modeling simulations are supported by data collected during the SRS Program, suggesting resuspension of River sediments is not a significant source of PCBs to the water column. First, water samples collected from several transects within the lower Grasse River exhibit little change in suspended solids concentrations, even during seasonal high flows. TSS concentrations remain relatively low (about 20 mg/L) even during the high flow events such as the one monitored in March 1998. Second, particulate PCB concentrations computed using paired unfiltered PCB and TSS measurements (PCBs in ng/L ÷ TSS in mg/L) collected at the Route 131 Bridge during the March 1998 high flow survey were very low (ca. 0.5 to 1 mg/kg; **Figure ES5-2**). If significant resuspension were occurring in the River during these high-flow surveys, computed particulate PCB concentrations would be similar to those observed in surface sediments (about 10 to 30 mg/kg). Third, PCB homolog distributions in water samples are different than those observed in the surface sediments (see **Figure ES4-4**). Specifically, surface sediment PCBs are dominated by tri-PCBs and contain greater proportions of the higher-chlorinated PCBs (tetra- through octa-PCBs) relative to those found in the water column. Finally, the vertical profiles of ¹³⁷Cs levels in several of the high-resolution cores collected in 1997 show well-defined, apparently undisturbed, cesium peaks,

³ Bounding estimates of several key model parameters were used in the analysis of sediment scour during a 100-year flood event in the River. These upper bound estimates were selected such that reasonable maximum estimates of sediment erosion and reasonable minimum estimates of natural recovery were achieved. Multiple simulations were performed with several sets of bounding parameters so that a conservative estimate of sediment scour during an extreme flood event could be attained. Results of these simulations indicated that, for a variety of bounding parameters values, the extent of sediment scour during an extreme flood did not change appreciably.

suggesting that little resuspension of sediment occurred historically in these areas (**Figure ES5-3**).

ES5.4 Burial

Historic sediment deposition rates in the lower Grasse River were examined through the analysis of ^{137}Cs levels in finely sliced sediment samples from high-resolution cores collected from the River in 1997. Cesium in sediments is derived from atmospheric nuclear weapons testing. The first occurrence of cesium in sediments generally marks the year 1954, while peak concentrations correspond to 1963, the year maximum atmospheric fallout from testing was observed. Using this information and the ^{137}Cs levels measured in the sediment cores, long-term average deposition rates of 2 to 3 cm/yr have occurred historically in the River, except for Core 30S where a lower deposition rate of 1.2 cm/yr was estimated. Cesium peaks were not evident in the 7 remaining cores. However, ^{137}Cs levels in these cores are relatively constant with depth (1-2 pCi/g dry) at levels similar to the levels observed in the post-1970 sections of sediment cores with distinct cesium peaks, suggesting that only post-1970 sediments were collected. If this is the case, deposition rates for the remaining cores would be greater than those estimated for Cores 7M, 13M, 18M, 23N and 30S.

Contemporary sedimentation rates were estimated using ^{210}Pb profiles in the surface sediments of three high-resolution cores (Cores 7M, 13M and 18M) and a one-dimensional contaminant transport model (see **Appendix C** for details). Results of the modeling analysis indicate that contemporary sedimentation rates are on the order of 0.2 cm/yr, a rate much lower than those discerned from the ^{137}Cs profiles.

Contemporary sedimentation rates also were estimated through the evaluation of solids loadings currently entering the Study Area from upstream. For this analysis, River flow and TSS measurements collected from the Main Street Bridge in Massena were used to develop a functional relationship between solids loading and River flow (i.e., a solids rating curve). Using this solids rating curve and the River hydrograph for 1997 and 1998, the annual solids loading to the lower Grasse River from upstream was estimated to be about 7,800 metric tons (MT). This

solids loading could support a maximum average deposition rate of 0.4 cm/yr if all solids that enter the lower Grasse River from upstream are deposited on the River bottom. This current sedimentation rate estimate is more consistent with that discerned from the ^{210}Pb data, and lower than the average rates indicated by the cesium data. Crop rotation and other soil conservation practices within the Grasse River watershed have significantly increased since the mid-1980s and may be responsible for the apparent reduced solids loadings to the River at present compared to the 1960s and 1970s (Howard, 1998).

ES5.5 Bioturbation

Chironomids and oligochaetes were the predominate organisms measured during the benthic community studies performed in the lower Grasse River. Most of the available studies of the effects of these organisms on sediment bed mixing have been conducted in lake sediments. These studies indicate that chironomids and oligochaetes generally burrow to depths of 8 to 10 cm (Matisoff and Wang, 2000; McCall and Tevesz, 1982; Ford, 1962). However, several studies suggest most of the population of benthic organisms is found closer to the surface than the maximum depth of occurrence (Milbrink, 1973; Ford, 1962; Matisoff and Wang, 2000; Krezoski *et. al*, 1978; Charbonneau and Hare, 1998). Based upon these studies, some mixing is likely to be occurring to at least a depth of about 5 cm.

The vertical profiles of ^{210}Pb levels in surface sediments of three of the twelve high-resolution cores collected in 1997 were examined to assess the extent of biological mixing in the lower Grasse River sediments. ^{210}Pb is a decay product of radon that enters natural systems via atmospheric deposition (dry and wet deposition). Because the atmospheric flux of ^{210}Pb is relatively constant and ^{210}Pb decays in the sediment with a half-life of about 22 years (Robbins 1978), vertical profiles of ^{210}Pb levels in sediments provides an estimate of the depth to which organisms burrow into the sediments.

In all three cores, ^{210}Pb levels range from about 1.6 to 2.6 pCi/gram dry weight at the surface and decline exponentially to values of about 0.5 pCi/gram dry weight (at 30 centimeters below the sediment-water interface; **Figure ES5-4**). ^{210}Pb levels are expected to be relatively constant

throughout the active depth of mixing and to decline exponentially below this depth. The existence of large gradients in ^{210}Pb levels within the top few centimeters of each core suggest little bioturbation is occurring in surface sediments of the lower Grasse River. The depth and intensity of biological mixing in the surface sediments of these three cores were determined through the calibration of a one-dimensional contaminant transport model (see **Appendix C** for details). Results of this modeling analysis indicate that limited mixing (both depth and intensity) is required to reproduce the ^{210}Pb profiles observed in the three cores.

It is important to note this analysis was only performed for three high-resolution cores and that lack of information for some of the model parameters introduces uncertainty into the analysis. However, the ^{210}Pb data are consistent with other information for the site, and suggest that significant bioturbation on the lower Grasse River sediments is restricted to the upper few cm.

ES5.6 Dechlorination

Analysis of the PCB congener data from the high-resolution cores provides several indications that microbially-mediated reductive dechlorination (from anaerobic biodegradation) is occurring in the lower Grasse River sediments. For example, reductions in the total number of chlorines per biphenyl are observed in the high-resolution core data (**Figure ES5-5**). In addition, strong relationships between dechlorination by-products BZ 4 (2,2') and BZ 19 (2,2',6) and the total number of chlorines exist, suggesting the production of these congeners during the dechlorination process. The lack of accumulation of BZ 1 in sediments containing PCBs dominated by BZ 4 and BZ 19 suggests the existence of some mechanism for the destruction of BZ 1.

Additional evidence of microbial degradation is seen in the ratios of biphenyl to total PCBs measured in sediment samples; the ratios are 1 to 3 orders of magnitude greater than those observed in pure Aroclors 1242 and 1248 (0.02 and 0.03 percent, respectively). Microcosm experiments using lower Grasse River sediments spiked with dichloro-orthonated PCB congeners suggest the potential for PCB destruction under anaerobic conditions. In these

experiments, a 25 percent reduction in congener mass was observed. In addition, small amounts of biphenyl (equaling 2.7 percent of the spiked congeners were produced).

Although the laboratory studies indicate the potential for these processes to contribute to the long-term fate of PCBs in the lower Grasse River, it does not appear that dechlorination and biodegradation of PCBs are currently important near-term processes in the River. Long-term in-River studies would be required to collect the necessary information to understand to what extent biodegradation may be an important consideration in the evaluation of the long-term fate of PCBs in the lower Grasse River.

ES5.7 Summary of the Evaluation of PCB Fate and Transport Mechanisms in the Lower Grasse River

The continual increases observed in water column PCB data collected downstream of the facility are consistent with patterns expected from a widespread PCB flux from the surface sediments. The migration of PCBs from the surface sediment to the water column appears to be mainly due to processes occurring at the sediment surface that transport pore water PCBs to the water column (i.e., diffusion and bioturbation). Other processes that affect the deeper sediments in the lower Grasse River (i.e., groundwater advection, resuspension and deep mixing) appear to be limited, based on the available data. Natural mechanisms such as burial and microbially-mediated dechlorination and degradation of PCBs are occurring in the River, although the importance of these processes for the long-term fate of PCBs in the lower Grasse River cannot be ascertained from the available information.

ES6.0 PCB SOURCES TO LOWER GRASSE RIVER FISH

The water column, sediment, and fish data collected from the lower Grasse River together suggest that PCBs in resident fish originate from sediments, and are accumulated primarily through a water-column based food web. That is, PCBs enter the water column from the sediments, accumulate in water column-based food resources such as filter-feeding chironomids and phytophilus macroinvertebrates, and ultimately accumulate in fish feeding on these organisms. This is based, in part, on the observation that fish PCB levels are relatively uniform up and down the length of the River while PCB levels in sediment vary by over a factor of ten or greater (**Figure ES6-1**). In contrast, the water column PCB gradient is small, generally varying by a factor of two to four. In addition, the food web model applied to smallmouth bass and brown bullhead of the lower Grasse River, which includes both benthic and pelagic components to each species' diets, generally reproduces the temporal trends of PCB levels observed in these species over the past several years (**Figure ES6-2**).

Although the data and modeling studies suggest the food webs of lower Grasse River resident fish are largely pelagic, the conclusion is not definitive. Chironomids were the predominate species identified in the benthic community studies. Chironomids feed on water column particulates or on the top few millimeters of the sediment bed (Pennak 1978). The relative contributions of water column particulates, freshly deposited detritus and surface sediments to their diet are unknown. This uncertainty at the base of the food web propagates to the smallmouth bass and brown bullhead.

