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Preliminary Investigation of the Extent and Effects of Sediment Contamination in White Lake Near Whitehall Leather Tannery

Richard Rediske Gary Fahnenstiel Tom Nalepa Peter Meier Claire Schelske

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PRELIMINARY INVESTIGATION OF THE EXTENT AND EFFECTS OF SEDIMENT CONTAMINATION IN WHITE LAKE NEAR THE WHITEHALL LEATHER TANNERY

BY

Dr. Richard Rediske

R. B. Annis Water Resources Institute Grand Valley State University One Campus Drive Allendale MI 49401

Dr. Peter Meier

Department of Environmental and Industrial Health School of Public Health I University of Michigan Ann Arbor MI 48106

Dr. Gary Fahnenstiel

Great Lakes Environmental Research Laboratory National Oceanic and Atmospheric Administration 1431 Beach Street Muskegon MI 49441

Dr. Tom Nalepa

Great Lakes Environmental Research Laboratory National Oceanic and Atmospheric Administration 2205 Commonwealth Blvd Ann Arbor MI 48105

Dr. Claire Schelske

Department of Fish and Aquatic Sciences University of Florida Gainesville FL 32606

INTERAGENCY AGREEMENT NO. DW13947766-01

U. S. Environmental Protection Agency National Oceanic and Atmospheric Administration

PROJECT OFFICER:

Dr. Marc Tuchman U. S. Environmental Protection Agency Great Lakes National Program Office 77 West Jackson Blvd Chicago IL 60604-3590

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Project Team

EPA Project Officer

Dr. Marc Tuchman USEPA GLNPO

Principal Scientists

Consultants

Project technical assistance was provided by the following individuals:

Ship support was provided by the crews of the following Research Vessels:

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Executive Summary

By using a combination of chemistry, toxicological evaluation, ecological analysis, and radiodating, this investigation has defined the ecological effects and the nature and extent of sediment contamination in the Tannery Bay area of eastern White Lake. The sediments in Tannery Bay represent a source of chromium transport for most of the eastern basin of White Lake. The recent deposition of chromium contaminated sediments exceeding 500 mg/kg in down gradient locations shows that export processes are responsible for the movement of this material from Tannery Bay. Arsenic and mercury appear to be less mobile and are retained in the sediments of Tannery Bay. Chromium export from Tannery Bay into White Lake proper will continue as long as the contaminated sediments are influenced by hydrodynamic circulation patterns and wave action.

Chromium stratigraphy in the Tannery Bay region indicates that the top 15-20 cm of sediment are less contaminated $(2,000-4,000 \text{ mg/kg})$ than sediment located at $>30 \text{ cm}$ $(0.5,000 \text{ mg/kg})$. Radionuclide results suggest that this surface sediment layer is well mixed, however, distinct from the deeper more highly contaminated sediments. Presently this sediment layer (15-20 cm) does not physically mix with the deeper, more contaminated sediment. The 0-20 cm layer is followed by a region (30-80 cm) that contains chromium levels in excess of 20,000 mg/kg. Since the direct discharge of tannery effluent to this area ceased in 1976, evidence of the deposition of sediment with less chromium contamination should be apparent. The lack of a decreasing gradient of chromium concentration in the near surface zone sediments (0-20 cm) suggests that the processes of mixing and resuspension continue to be active in Tannery Bay. In addition, chromium transport to the 0-20 cm sediment zone may also be occurring by other mechanisms including surface runoff of contaminated soils and groundwater advection. The lack of a significant $137Cs$ horizon in the sediments indicates that groundwater is discharging in this region; however, the linkage with chromium mobility requires further investigation.

The laboratory toxicity evaluation of the Tannery Bay sediments (Ponar samples) found six of eight locations to be toxic to amphipods and two of eight locations to be toxic to midges. The amphipod toxicity was found to be dependent on the depth of the sediment. Sediments evaluated below 30 cm exhibited extreme toxicity to amphipods while some survival was observed in the region of 0-30 cm. We were unable to identify the chemical/chemicals responsible for the toxicity observed in the sediments. Amphipod populations did not reflect the laboratory sediment toxicity as *Hyalella* sp. was found at the same locations that were toxic to the test organisms. This apparent paradox can be explained by examining the natural habitat of these organisms. The native amphipod populations were primarily associated with macrophytic plants and other submerged materials. They did not appear to be associated with the sediments. Similar abundances of chironomids were found at the interior and exterior stations; however, populations of *Chironomus* sp. were significantly lower in the interior stations. The lower abundances of this genera may reflect a response to toxic chemicals in the sediment since they feed on detrital material. Even though chironomids were found in the Tannery Bay area, a majority of the genera were predators which do not ingest detritus as their primary food source. Finally, mercury bioaccumulation was not observed under laboratory or field conditions.

Chromium concentrations in all locations of Tannery Bay and in five of the six downgradient locations in eastern White Lake exceeded current sediment quality guidelines for probable adverse ecological effects. Most of the Tannery Bay stations exceeded these guidelines by an order of magnitude. Only the background station E-1P had a chromium concentration below the sediment quality guideline that would indicate no adverse effects.

1.0 Introduction

White Lake is a 2,571 acre, drowned-rivermouth lake located on the eastern shore of Lake Michigan in Muskegon County. A map of White Lake is provided in Figure 1.1. The Lake is part of the White River Watershed and discharges directly to Lake Michigan through a channel located on the western end. White Lake was designated an Area of Concern (AOC) in 1985 by the International Joint Commission because of historical discharges of heavy metals and organic chemicals. Chromium, mercury, arsenic, and animal hides have been discharged into White Lake by Whitehall Leather. The tannery began operating in Whitehall near the turn of the century and used wood bark as the original tanning agent. In 1940, the tanning agent was changed to chromic sulfate and a series of 6 waste treatment lagoons were constructed near an area of the shoreline called Tannery Bay. Effluent from these lagoons containing heavy metals and leather byproducts was discharged directly into the bay. In addition, dredged materials from the lagoons and other process wastes were disposed of in landfill areas adjacent to the shore. Process wastewater effluents from several chemical companies have also been discharged into White Lake. The former Hooker Chemical and Plastics (now Occidental Chemical) facility discharged a variety of chlorinated solvents and pesticide related materials into the lake near Dowies Point. Chlorinated organic chemicals from DuPont and Muskegon Chemical (now Koch Chemical) have also entered White Lake through groundwater and surface water discharges.

Recent and historical studies have indicated extensive contamination of sediments in White Lake. Elevated levels of chromium, lead, arsenic, and mercury were detected in the northeastern section of the lake in 1982 during a U.S. Environmental Protection Agency (U.S.EPA) funded study conducted by the West Michigan Shoreline Regional Development Commission (WMSRDC 1982). This study also found evidence of heavy metal contamination in several locations along the northwest shore. In a more recent study conducted in the summer of 1994 by U.S.EPA/Michigan Department of Environmental Quality (MDEQ), elevated concentrations of these metals were detected in an area of the northeast shore of White Lake (Bolattino and Fox 1995). This area was the historical discharge point for tannery effluent from Whitehall Leather. The area near the Whitehall Leather Tannery where the U.S.EPA/MDEQ conducted the 1994 sampling will be referred to the Tannery Bay area. The chromium levels found in the sediments of this area were some of the highest reported from any site in the Great Lakes.

The current extent of sediment contamination in the area near Tannery Bay is unknown with respect to spatial and vertical distribution. Since the direct discharge of effluent to Tannery Bay was discontinued in 1976, vertical depositional patterns may reflect changes in the flux of chromium into the system. The stability of the sediments in this region is also unknown. Without more information on sediment stability and accumulation rates, it is difficult to determine the residence time of contaminants within any specific region of the sediments. Whether historical levels of metals are being covered by less contaminated material or being resuspended by physical events are critical questions that need to be answered before evaluating remediation options.

FIGURE 1.1 WHITE LAKE

Since previous studies have focused only on chemical contamination, the ecological effects of the heavy metal contamination have not been evaluated. Because this site has extremely elevated levels of several heavy metals (Bolattino and Fox 1995), questions of both toxicity and bioaccumulation arise. The toxicological effects of heavy metals in the Tannery Bay area on benthic organisms and the potential for bioaccumulation at several trophic levels are critical questions that merit further examination. Also, important information on the present condition of benthic invertebrate community within and near Tannery Bay is lacking.

1.1 Project Objectives And Task Elements

The objectives of this investigation were to define the ecological effects of the heavy metal contamination in Tannery Bay and to conduct a preliminary assessment of heavy metal contamination in eastern White Lake. In addition, a preliminary assessment of chromium depositional patterns and sediment stability was performed to assist in the analysis of the ecological effects data and in the evaluation of remediation alternatives. Specific objectives and task elements are summarized below:

- Determine the extent of sediment contamination in eastern White Lake, including the Tannery Bay area.
	- A preliminary investigation was conducted to expand the sediment core sampling previously performed by U.S.EPA/MDEQ. The investigation included more spatial coverage outside of the Tannery Bay area and the analysis of a background location for control purposes. Arsenic, chromium, and mercury were analyzed in all core samples. Two core samples were also analyzed for selected semi-volatile compounds related to adjacent CERCLA and RCRA sites.
	- Surface sediments were collected in the Tannery Bay area with a Ponar dredge to provide heavy metal concentration information for the toxicity evaluations. The data from the Ponar samples was also used to describe the chemical composition of the surface zone sediments (approximately 0-15 cm).
	- Two core samples were collected in the Tannery Bay area for detailed stratigraphy analysis and radiochemical dating. These samples were collected to provide a preliminary assessment of historical chromium deposition patterns and sediment stability.
	- All sediment samples were analyzed for chromium, arsenic, mercury, total organic carbon, and grain size. Samples for radiodating were analyzed for ²¹⁰Pb, ²²⁶Ra ¹³⁷Cs.
- Determine the abundance and diversity of benthic invertebrates in eastern White Lake and in the Tannery Bay area*.*
	- Sediment samples were collected with a petite Ponar in eastern White Lake and Tannery Bay.
	- Analysis of the abundance and composition of the benthic invertebrate communities at these locations was conducted. The benthic invertebrate data for Tannery Bay was compared to the sites in eastern White Lake and the control location to determine if the invertebrate community structure had been impacted by sediment contamination related to the Tannery.
- Evaluate the toxicity of sediments from sites in the Tannery Bay area.
- Sediment toxicity evaluations were performed with *Hyalella azteca* and *Chironomus tentans*. (10 day acute toxicity).
- Toxicity measurements in Tannery Bay sediments were evaluated and compared to the control location. These measurements determined the presence and degree of toxicity associated with sediments from Tannery Bay.
- The survival of the test organisms was measured in the toxicity tests along with water quality indicators during exposure (ammonia, dissolved oxygen, temperature, conductivity, pH, and alkalinity).
- Evaluate the bioaccumulation of mercury from sediments in the Tannery Bay area.
	- The bioaccumulation of mercury was evaluated using laboratory and *In-situ* experiments. Two stations and one control were used for bioaccumulation measurements. Laboratory studies involved assays with *Lumbriculus variegatus*. *Insitu* experiments were conducted in mesocosms with *Pimephales promelas* and *Ictalurus punctatus*.
	- Initial and final mercury concentrations in the organisms exposed to Tannery Bay sediment were compared to the control station to determine if a potential impact from bioaccumulation exists.

1.2 Experimental Design

The project elements for the White Lake Sediment Investigation are shown in Figure 1.2. Assessment protocols for the evaluation of sediment contamination commonly utilize three components:

- Chemical analysis
- Laboratory toxicity assessment
- Ecological assessment using an analysis of the benthic macroinvertebrate community

Chemical analysis provided information related to the nature and extent of sediment contamination. Chemistry data was then supplemented by laboratory toxicity studies that utilize standardized exposure regimes to evaluate the effects of contaminated sediment on test organisms. These exposures were performed on sediments that are representative of approximately 0-15 cm in depth. Since most benthic invertebrates inhabit the top 2 cm, a survey of this community needed to be performed to evaluate current conditions. The benthic community will also reflect a longer term exposure to the sediments that the 10 day (acute) toxicity tests. The results of laboratory toxicity tests have been shown to be correlated with impacts to the benthic macroinvertebrate community (Bailey et al. 1995).

FIGURE 1.2. WHITE LAKE SEDIMENT INVESTIGATION TASK ELEMENTS

In this project, a combination of core and Ponar samples were used for sediment chemistry analysis. A series of eight core samples were collected in eastern White Lake to evaluate the migration of the heavy metals related to the tannery discharge outside of Tannery Bay. One sample in this series was collected in an area upstream from the tannery discharge that was not heavily influenced from anthropogenic sources. This location was used as a control station. These sampling stations were designated as exterior stations E-1 through E-9 (Figure 1.3). The sediment cores were collected with a VibraCore device with core lengths ranging from 6-8 ft. The core samples were then sectioned in three equal lengths for chemical analysis. Ponar samples were also collected at these locations to provide an assessment of the near surface zone sediments. In Tannery Bay, eight Ponar samples were collected. These locations were designated as interior stations I-1 through I-7 (Figure 1.4). The interior stations were also used to provide data on the composition of the surface zone sediments and to supplement the core samples previously collected by U.S.EPA/MDEQ. All sediment

samples were analyzed for arsenic, chromium, mercury, total organic carbon (TOC), and grain size. In addition, two of the exterior sediment cores were analyzed for selected xenobiotic organic compounds. These analyses included measurement of chlorinated hydrocarbons in the vicinity of Occidental Chemical (E-9) and the measurement of chlorinated ethers and benzenes near the mouth of Mill Pond Creek (E-7). These core samples were analyzed for semivolatile compounds using Gas Chromatography/Mass Spectrometry (GC/MS). Analytical methods were performed according to the protocols described in SW-846 3rd edition (EPA 1994a).

FIGURE 1.3. TANNERY BAY EXTERIOR SAMPLING STATIONS.

FIGURE 1.4. TANNERY BAY INTERIOR SAMPLING STATIONS

In this project, standard EPA methods (1994b) using *Chironomus tentans* and *Hyalella azteca* were used to determine the acute toxicity of sediments from eight interior sites in the Tannery Bay area and the control site. Ponar samples were used for the toxicity experiments in the fall of 1996. Eight replicate assays were conducted with each organism from each site. After exposure, standard statistical tests were used to determine whether significant differences existed between treatments and controls. Based on the results of the fall 1996 toxicity testing, a limited series of core and Ponar samples were collected in April 1997. Sediment toxicity studies using *Hyalella azteca* were performed to confirm previous results and to determine if there was a variation in toxicity with depth.

The abundance and composition of the benthic invertebrate community are valuable tools for assessing the impact of anthropogenic perturbations. Benthic macroinvertebrate samples were collected at all exterior and interior locations using a petite Ponar (Flannagan 1970 and Nalepa 1978). After collection, the samples were elutriated using the technique of Powers and Robertson (1965) and then preserved with 5% formalin. Each invertebrate was identified to the lowest practical taxonomic level. Standard statistical methods were used to determine whether the populations in Tannery Bay differed from the exterior stations and the control. Samples were initially collected in October 1996. Due to the heavy growth of aquatic vascular plants in the Tannery Bay area, an additional benthic invertebrate collection was made in April 1997.

In order to provide additional information related to ecological effects of the contamination in Tannery Bay, the traditional approach described above was augmented with experiments that focused on evaluating the dynamics of sediment deposition and the potential for bioaccumulation. A combination of radiodating and chromium stratigraphy analysis was used to evaluate sediment deposition. A piston corer (Fisher et al. 1992) was used to obtain the samples for stratigraphy and radiodating since the VibraCore causes some degree of internal mixing in the core tube. Two core samples from Tannery Bay were radiodated using the ²¹⁰Pb method (Robbins et al. 1978). Radiodating using ²¹⁰Pb provides a continuous sequence of dates from a single core utilizing the natural decay of ^{210}Pb . This technique has been widely used in limnology and has been independently verified by comparisons with other techniques (e.g., Robbins et al. 1978; Appleby et al. 1979; and Wolfe et al. 1994). ²¹⁰Pb is a naturally occurring radioisotope that enters lakes through wet and dry deposition following the decay of atmospheric 222 Rn. Once in the lake, 210 Pb is rapidly scavenged by particles and settles to the bottom. The concentration of ²¹⁰Pb can then be analyzed at a series of depths in the cores from the surface to the depth where excess ^{210}Pb is no longer measurable, approximately 5-8 half-lives or 150 years. From this ^{210}Pb profile, dates and sediment accumulation rates are calculated using one of several mathematical models, such as the constant rate of supply method. Using a combination of ^{210}Pb dating and detailed metal stratigraphy, critical information related to contaminant profiles and sediment stability was obtained. Because of the effluent diversion that occurred in 1976, chromium flux into Tannery Bay has changed dramatically over the last 20 years. If the sediments are stable and not subject to resuspension, lower levels of chromium should be encountered in the surface strata. Also, the pattern of 210 Pb deposition was used to determine the stability of these sediments and the accumulation rates. This information along with the biological and toxicological studies discussed previously provides a technically sound basis for the development of remediation alternatives for the site.

Since elevated levels of mercury were encountered in the sediments from Tannery Bay, the potential for bioaccumulation needed to be evaluated. The bioaccumulation of mercury was determined using laboratory and *in-situ* experiments. For laboratory bioaccumulation studies, the standard chemical accumulation study using *Lumbriculus variegatus* was performed (EPA 1994b) using sediment from two locations in Tannery Bay and at a control site (I-5M, I-7M, and E-1; Figures 1.3 and 1.4). Sediment samples for bioaccumulation studies were collected with a Ponar sampler. The bioaccumulation experiments were performed in a

manner similar to the acute toxicity experiments described above. Five replicates were performed for each exposure using adult organisms. A twenty-eight day exposure period was used for the experiments. Bioaccumulation was measured by chemical analysis at the end of the test.

A specific bioaccumulation study for White Lake was conducted *in-situ* using mesocosms with standard test fish. Mesocosms, large enclosures placed *in-situ*, have been used extensively in limnology to examine the impact of a specific perturbation (Heath et al. 1995). The enclosures employed were 1 m in diameter and 3 m deep and constructed of Fabrene, a heavy-duty, inert, flexible, and clear plastic material. The mesocosms were open to the sediments. A double ringed floatation collar was located at the surface and the mesocosm was secured to the sediments by a weighted ring. The mesocosms were open to the air surface at the top and the sediment surface at the bottom. Because these enclosures were flexible on the sides, yet floating on the surface, the contents of the enclosures remained wellmixed. Thus, natural benthic and plankton communities from shallow littoral environments can be enclosed for several weeks to months under natural conditions. To these enclosures, six fathead minnows (*Pimephales promelas*) and six channel catfish (*Ictalurus punctatus*) were added. Duplicate mesocosms were placed near the I-7M site in Tannery Bay and at the control site E-1 in White Lake. The mesocosms were deployed for one month and monitored twice weekly. At the end of the experiments, the test fish were removed and analyzed for mercury accumulation.

1.3 References

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2.0 Sampling Locations

The Tannery Bay area is located on the south shore near the eastern end of White Lake. This region of White Lake is relatively shallow with a mean depth of 3.7 m. In an initial survey of chemical contamination conducted in 1994 by the U.S.EPA and MDEQ, 22 sites were sampled in this area. Eight of these same sites that represent the range of chemical concentrations found in the Bay were selected for this investigation (Figure 1.4). These sites are referred to as interior stations (I-1 through I-8). Two of the eight sites were identified as master stations (I-5M and I-7M). At these stations, detailed stratigraphy and bioaccumulation studies were performed in addition to the chemical, benthic macroinvertebrate, and toxicity studies. These stations were located near historical discharge locations for tannery wastes. Station I-5M is located near the historical discharge point of the waste treatment lagoons. Station I-7M is located near the solid waste disposal site. The previous U.S.EPA/MDEQ study identified these locations as areas with high concentrations of heavy metals. Standard and petite Ponar samples were collected at all interior stations. In addition, piston core samples were collected at the master stations.

Eight sites were also selected outside the Tannery Bay area, in order to characterize the possible spread of contamination and to extend the previous work conducted by the U.S.EPA/MDEQ. At these eight sites, heavy metals and other selected chemical analyses and benthic invertebrate studies were performed (Figure 1.3). These stations will be referred to as exterior stations (E-2 through E-9) because they are outside the initial studied area of Tannery Bay. A control station for toxicity and bioaccumulation studies was selected at the northeast corner of White Lake near the river mouth. This location (E-1) should not be influenced by historical anthropogenic activities related to heavy metals and organic pollutants. VibraCore and Ponar samples were collected at the exterior stations. Core samples were used for chemical analysis. Ponar samples were used for benthic macroinvertebrate identification and chemical analysis. The locations of the exterior stations are illustrated in Figure 1.3.

The initial sampling of White Lake was conducted October 1 through October 5, 1996. Due to a water leak that developed during extrusion of the piston core from station I-5M, a second core was collected on October 29, 1996. Loran coordinates were used to locate the station. An additional sampling of White Lake was performed on April 2, 1997 to collect a second set of benthic invertebrate and toxicity evaluation samples. GPS and Loran were used to locate sampling stations during the October 1996 collection. The samples collected in April 1997 were located by standardizing the GPS to a reference monument west of Tannery Bay. Locations and descriptions of the sampling stations are given in Table 2.1

Table 2.1

White Lake Sampling Locations

3.0 Methods

3.1 Sampling Methods

Sediment and benthos samples were collected using the U.S. EPA Research Vessel *Mudpuppy* and the NOAA Research Vessels *Shenehon* and *Remorse*. Vibra Core methods were used to collect sediment cores for chemical analysis. A 4 inch aluminum core tube with a butyrate liner was used for collection. A new core tube and liner was used at each location. The core samples were measured and sectioned into three equal segments corresponding to top, middle, and bottom. Each section was then homogenized in a polyethylene pan and split into sub-samples. The visual appearance of each segment was recorded along with the water depth and core depth.

A piston core device was used to collect core samples for radiodating and toxicity testing. A clean 4 inch lexan core tube was used for each sample. For samples requiring radiodating, the cores were extruded by water pressure and cut into 2 cm intervals. The sections were then dried and weighed in the laboratory. For toxicity evaluations conducted during the spring sampling, the cores were split into 0-30 cm and 30-70 cm sections. The individual sections were transferred to 2 L amber bottles for shipment to the laboratory.

Ponar samples were collected for toxicity testing, sediment chemistry, and benthic macroinvertebrates. For sediment chemistry and toxicity testing, a standard Ponar sample was deposited into a polyethylene pan and split into sub-samples. The Ponar was washed with water in between stations. A petite Ponar was used for the collection of benthic macroinvertebrates. Three replicate grabs were taken at each of the sites. All material in the grab was washed through a nitex screen with 500 μm openings, and the residue preserved in buffered formalin containing rose bengal stain.

3.1.2 Sample Containers, Preservatives, And Volume Requirements

Requirements for sample volumes, containers, and holding times are listed in Table 3.1. All sample containers for sediment chemistry and toxicity testing were purchased precleaned and certified as Level II by I-CHEM Inc.

TABLE 3.1 SAMPLE CONTAINERS, PRESERVATIVES, AND HOLDING TIMES

3.2 Chemical Analysis Methods

A summary of analytical methods is provided in Table 3.2.1. Instrumental conditions and a summary of quality assurance procedures are provided in the following sections.

TABLE 3.2.1 ANALYTICAL METHODS AND DETECTION LIMITS

SEDIMENT MATRIX

1 - SW846 3rd. Ed. EPA 1994.

3.2.2 Sample Preparation For Metals Analysis

For arsenic and total chromium analysis, sediment samples were digested according to EPA SW-846 method 3051 "Microwave Assisted Asid Digestion of Sediments, Sludges, Soils and Oils". Samples were air-dried prior to digestion. A Questron (Mercerville, NJ) Q-4000 microwave system was used. The system provided a controled temperature and pressure in each digestion vessel. Approximately 0.5 g of sediment was weighed into a teflon liner and 10 mL of concentrated nitric acid was added. Vessels then were capped and placed into the microwave cavity. The program was set to raise the temperature inside the vessels to 175°C

over a 5.5 minutes time period and keep this temperature for 4.5 minutes. After completion of the run, vessels were cooled and vented. The contents were transferred into 50 mL centrifuge tubes and brought up to 50 mL with Type I deionized water. Samples were centrifuged for 5 minutes at 3000 rpm before analysis.

For every 10 samples at least one set of the following quality control samples was prepared:

Method Blank (10 mL of nitric acid); Laboratory Cotrol Spike (Blank Spike); Matrix Spike; Matrix Duplicate.

For determining total mercury the samples were prepared by EPA SW-846 method 7471A "Mercury in Solid and Semisolid Waste". Between 0.6 and 1 g of wet sediment was weighed into a 50 mL centrifuge tube. 2.5 mL of Type I deionized water and 2.5 mL of aqua regia were then added to the tube. Samples were heated in a water bath at 95°C for 2 minutes. After cooling, the volume of the samples was brought up to 30 mL with Type I deionized water. Then 7.5 mL of 5% potassium permanganate solution was added to each sample, samples were mixed, and the centrifuge tubes were returned in the water bath for a period of 30 minutes. Three mL of hydroxylamine chloride solution was added to each sample after cooling. Finally, the samples were mixed and centrifuged for 5 minutes at 3,000 rpm.

Calibration standards were digested along with the samples. Quality control samples were prepared as stated previously for every batch of 10 samples or less.

3.2.3 Arsenic Analysis

Arsenic was analyzed in accordance with the EPA SW-846 method 7060A utilizing Graphite Furnace technique. The instrument employed was Perkin Elmer 5100ZL atomic absorption spectrophotometer. An arsenic Electrodless Discharge Lamp was used as a light source at wavelength of 193.7 nm. The instrument utilized a Zeeman background correction which reduces the non-specific absorption caused by some matrix components. The temperature program is summarized below:

A Pd/Mg modifier was used to stabilize As during pirolysis step. The calibration curve was constructed from four standards and a blank. Validity of calibration was verified with a check standard prepared from a secondary source. This action was taken immediately after calibration and after every 10 samples. At least 1 postdigestion spike was performed for every analytical batch of 20 samples.

3.2.4 Chromium Analysis

Chromium was analyzed in accordance with EPA SW-846 method 6010A by Inductively Coupled Plasma Atomic Emission Spectroscopy. Samples were analyzed on a Perkin Elmer P-1000 ICP Spectrometer with Ebert monochromator and cross-flow nebulizer. The following settings were used:

Wavelength: 267.716 nm RF Power: 1300 W

Matrix interferences were supressed with internal standartization utilizing Myers-Tracy signal compensation. Interelement interference check standards were analyzed in the beginning and at the end of every analytical run, and indicated absence of this type of interferences at the given wavelength. The calibration curve was constructed from four standards and a blank and was verified with a check standard prepared from a secondary source.

3.2.5 Mercury

After the digestion procedure outlined in 3.2.2, sediment samples were analyzed for total mercury by cold vapor technique according to SW-846 Method 7471. A Perkin Elmer 5100ZL atomic absorption spectrophotometer with FIAS-200 flow injection accessory was used. Mercury was reduced to an elemental state with stannous chloride solution, and atomic absorption was measured in a quartz cell at an ambient temperature and a wavelength of 253.7 nm. A mercury electrodeless discharge lamp was used as a light source. The calibration curve consisted of four standards and a blank and was verified with a check standard prepared from a secondary source.

3.2.6 Total Organic Carbon

Total Organic Carbon anlysis of sediments was conducted on a Shimadzu TOC-5000 Total Organic Carbon Analyzer equipped with Solid Sample Accessory SSM-5000A. An air dried sample was first placed in the oven at 900°C, where all the carbon is cataliticly converted to $CO₂$ (Total Carbon Analysis). A different portion of the sample was treated with phosphoric acid at 250° C to displace $CO₂$ from carbonates and bicarbonates (Inorganic Carbon Analysis). CO_2 is measured in the infra-red cell. Total Organic Carbon content was determined by difference between results of the two analyses.

Calibration curves for both analyses were constructed from three standards and a blank. Glucose was used as a standard compound for Total Carbon Analysis (44% carbon by weight). For Inorganic Carbon Analysis, sodium carbonate was used (11.11% of carbon by weight).

3.2.7 Grain Size Analysis

Grain size was performed by wet sieving the sediments. The following mesh sizes were used: 2mm (granule), 1 mm (very coarse sand), 0.5 mm (coarse sand), 0.25 mm (medium sand), 0.125 mm (fine sand), 0.063 (very fine sand), and 0.031 (coarse silt).

3.2.8 Semivolatiles Analysis

Sediment samples were extracted for semivolatiles analysis using SW-846 Method 3050. The sediment samples were dried with anhydrous sodium sulfate to form a free flowing powder. The samples were then serially sonicated with 1:1 methylene chloride/acetone and concentrated to a 1 mL volume.

The sample extracts were analyzed by GC/MS on a Finnigan GCQ Mass Spectrometer. Instrumental Conditions are itemized below:

MS operating conditions:

A list of analytes and detection limits is given in Table 3.2.2. Surrogate standards were utlilzed to monitor extraction efficiency. Acceptance criteria for surrogate standards are given in Table 3.2.3. The GC/MS was calibrated using a 5 point curve. Instrument tuning was performed by injecting 5 ng of Decafluorotriphenylphosphine and meeting method acceptance criteria. The MS and MSD samples were analyzed at a 5% frequency.

3.2.9 Quality Assurance/Quality Control Program

A detailed description of the Quality Assurance/Quality Control program for this project was described in the Quality Assurance Project Plan.

TABLE 3.2.2 ORGANIC PARAMETERS AND DETECTION LIMITS

TABLE 3.2.3 METHOD SPECIFIC DATA QUALITY OBJECTIVES SURROGATE COMPOUND PERCENT RECOVERY CONTROL LIMITS

3.3 Radiochemistry

Wet samples were initially frozen upon receipt. Sample preparation consisted of freeze drying the sediment and the grinding the sample to a homogenous mixture. Sub samples were then packed and sealed with an epoxy resin in polypropylene tubes in preparation for radiometric analysis. Radiometric analysis and calculation of ^{210}Pb ages followed the procedures outlined below.

Radiometric measurements were made using low-background gamma counting systems with well-type intrinsic germanium detectors (Schelske et al. 1994). To prepare samples for radiometric analysis, dry sediment from each section was packed to a nominal height of 30 mm in a tared polypropylene tube (84 mm high x 14.5 mm outside diameter, 12 mm inside diameter). Sample height was recorded and tubes were weighed to obtain sample mass. Samples in the tubes were sealed with a layer of epoxy resin and polyamine hardener, capped, and stored before counting to ensure equilibrium between 226 Ra and 214 Bi. Activities for each radionuclide were calculated using empirically derived factors of variation in counting efficiency with sample mass and height (Schelske et al. 1994). Total ^{210}Pb activity was obtained from the 46.5 kev photon peak, and 226 Ra activity was obtained from the 609.2 kev peak of 214 Bi. 226 Ra activity was assumed to represent supported 210 Pb activity. Excess 210 Pb activity was determined from the difference between total and supported 210 Pb activity and then corrected for decay from the coring date. The 661.7 kev photon peak was used to measure 137 Cs activity. The peak in 137 Cs activity was measured to evaluate its usefulness as an independent time marker for the peak period of fallout from nuclear weapons testing in 1962-63.

Sediments were aged using measurements of the activity of naturally occurring radioisotopes in sediment samples. The method is based on determining the activity of total ^{210}Pb (22.3 yr half-life), a decay product of 226 Ra (half-life 1622 yr) in the 238 U decay series. Total 210 Pb represents the sum of excess ^{210}Pb and supported ^{210}Pb activity in sediments. The ultimate source of excess ²¹⁰Pb is the outgassing of chemically inert ²²²Rn (3.83 d half-life) from continents as 226 Ra incorporated in soils and rocks decays. In the atmosphere, 222 Rn decays to ²¹⁰Pb which is deposited at the earth's surface with atmospheric washout as unsupported or excess ²¹⁰Pb. Supported ²¹⁰Pb in lake sediments is produced by the decay of ²²⁶Ra that is deposited as one fraction of erosional inputs. In the sediments, gaseous 222 Rn produced from ²²⁶Ra is trapped and decays to ²¹⁰Pb. By definition, supported ²¹⁰Pb is in secular equilibrium with sedimentary 226 Ra and is equal to total 210 Pb activity at depths where excess 210 Pb activity is not measurable due to decay. Because the decay of excess ^{210}Pb activity in sediments provides the basis for estimating sediment ages, it is necessary to make estimates of total and supported ^{210}Pb activities so excess ^{210}Pb activity can be determined by difference. Excess²¹⁰Pb activity was calculated either by subtracting ²²⁶Ra activity from total 210 Pb activity at each depth or by subtracting an estimate of supported 210 Pb activity based on measurements of total 210 Pb activity at depths where excess 210 Pb activity is negligible.

Sediment ages were calculated using a CRS model (Appleby and Oldfield 1983). This model calculates ages based on the assumption that the flux of excess ^{210}Pb to the lake was constant

and therefore that variation in ²¹⁰Pb activity from a pattern of exponential decrease with depth depends on variation in rate of sedimentation. The age of sediments at depth x is given by:

$$
t = (1/k) [\ln (Ao/A)]
$$

where t is time in yr, k is 0.03114 (the ²¹⁰Pb decay constant), Ao is the total residual excess 210 Pb activity in the sediment core, and A is the integrated excess 210 Pb activity below depth x. Calculations for each depth provide a continuous profile of ages as a function of depth. Mass sedimentation rate (MSR) at depth x is given by :

$MSR = m/t$

where m is dry mass of sediment (g /cm²) for the sampling interval. Errors in age and mass sedimentation rate were propagated using first-order approximations and calculated according to Binford (1990).

3.4 Sediment Toxicity

The evaluation of the toxicity White Lake sediments was conducted using the ten day survival test for the amphipod *Hyalella azteca* and the dipteran *Chironomus tentans*. The procedures followed are contained in EPA/600/R-94/024, Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Fresh Water Invertebrates. All sediments were stored at 4°C prior to analysis.

3.4.1 Laboratory Water Supply

A moderately hard water for *H. azteca* and *C. tentans* cultures and maintenance was employed. Preparation of the reconstituted moderately hard laboratory water is outlined in EPA/600/4-91/002. This water was made up in volumes of 200 L on which water quality parameters were run to check for consistencies between batches. This moderately hard water was utilized as the culture water as well as the overlying renewal water.

3.4.2 Test Organisms

The original stocks were obtained from the U.S.EPA laboratory in Columbia, Missouri. The *H. azteca* culture was maintained in a 36 L glass aquarium using maple leaves as a substrate and YCS as a food source, which was supplemented with a suspension of Tetrafin® goldfish food. The culture of *C. tentans* was also maintained in a 36 L glass aquarium using shredded paper toweling as a substrate and was fed a suspension of Tetrafin[®] goldfish food.

3.4.3 Experimental Design

For the November testing, eight replicates per sediment were set up for both *H. azteca* and *C. tentans* exposures, with the sediment from site E-1P designated as the control. The testing done in April was conducted with *H. azteca* only and the paper toweling used in maintaining laboratory cultures was used as a surrogate control sediment. In all tests, moderately hard laboratory water was utilized as the overlying water. The experimental conditions outlined in Tables 3.4.1 and 3.4.2 were used for the toxicity evaluations.

One day prior to the start of the test (day -1), the sediment from each site was mixed thoroughly and 100 mL s were transferred to each of the eight test chambers. Additionally, visual observations of the sediments were made. Moderately hard laboratory water was also added at this time. On day 0, the overlying water was renewed once before the test organisms were introduced into each of the glass beakers. Measurement of water quality parameters was also initiated on this day. Ten, 7-14 day old *H. azteca* and 10 third instar *C. tentans* larvae were randomly added to their respective test chambers. At this time the organisms were fed, 1.5 mL YCS for the *H. azteca* and 1.5 mL Tetrafin[®] for the *C. tentans*. The glass beakers were placed in a rack and transferred to a temperature controlled room $(23 + 1^{\circ}C)$. The light cycle was 16 hours on and 8 hours off. Temperature and dissolved oxygen measurements were taken from one randomly selected beaker for each sediment sample every 12 hours, after which the overlying water was renewed in all the beakers. Feeding occurred after the morning renewal. This procedure was repeated daily through day 10, at which point

TABLE 3.4.1 TEST CONDITIONS FOR CONDUCTING A TEN DAY SEDIMENT TOXICITY TEST WITH *HYALELLA AZTECA*

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Test Method 100.1. EPA Publication 600/R-94/024 (July 1994).

TABLE 3.4.2 RECOMMENDED TEST CONDITIONS FOR CONDUCTING A TEN DAY SEDIMENT TOXICITY TEST WITH *CHIRONOMUS TENTANS*

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Test Method 100.2. EPA Publication 600/R-94/024 (July 1994).

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the test was terminated. On day 0, the overlying water from the beakers was composited from each sediment sample and 250 mLs were retained for alkalinity, hardness and ammonia analysis. On the last day the same procedure was carried out. On day 10, the sediments were sieved, and the surviving test organisms were removed and counted. The biological endpoint for these sediment tests was mortality. The validity of the test was based on greater than 80% survival in the control treatment for *H. azteca* and greater than 70% survival in the control treatment for the *C. tentans*. In addition, it was recommended that the hardness, alkalinity, pH, and ammonia in the overlying water within a treatment should not vary by more than 50% over the duration the test.

3.4.4 Statistical Analysis

Survival data for the November testing were analyzed first for normality and homogeneity employing Kolmogorov and Bartlett's Tests. If necessary, the data were transformed prior to analysis. The data were then examined using Dunnett's Procedure to determine whether there was a significant difference in survival between the designated control sediment and those sediments containing pollutants. For the testing conducted in April, data were evaluated for normality using Shapiro-Wilk's Test and homogeneity using Bartlett's Test. Since no transformations were able to yield normally distributed, homogeneous data, the nonparametric Steel's Many-One Rank Test was used to evaluate the survival data for significant differences between the control and test sediments. In addition, these data were also examined employing Kruskal-Wallis' Test. This analysis performed a pair-wise comparison of the survival data from the April testing of sites I-2, I-5M, I-5T, I-7M and I-7T in order to determine if there was a significant difference in survival between the sites. The TOXSTAT[®] 3.5 Program was used in these evaluations.

3.4.5 Quality Assurance

Sodium chloride was used as a reference toxicant to calibrate the toxicity tests. The results are provided in Appendix D.

3.5 Laboratory Bioaccumulation Studies With *Lumbriculus variegatus***.**

The laboratory evaluation of the bioaccumulation of mercury in White Lake sediments was conducted using the 28 day test with *Lumbriculus variegatus*. The samples that were analyzed for bioaccumulation were from the control station E-1 and master stations I-5M and I-7M. An initial four day toxicity screening test was performed to determine if the sediment would exhibit toxic effects. The results of the four day screening test produced no observable toxic effects. Based on these results, the 28 day bioaccumulation test was performed. The procedures followed are contained in EPA/600/R-94/024, Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Fresh Water Invertebrates. All sediments were stored at 4°C prior to analysis.

3.5.1 Laboratory Water Supply

Moderately hard water for *Lumbriculus variegatus* culture and maintenance was employed. Preparation of the reconstituted moderately hard laboratory water is outlined in EPA/600/4- 91/002. This water was made up in volumes of 200 L on which water quality parameters are run to check for consistencies between batches. This moderately hard water was utilized as the culture water as well as the overlying renewal water.

3.5.2 Test Organisms

The original stocks were obtained from the U.S.EPA laboratory in Columbia, Missouri. The L. variegatus culture was kept in a 6 L glass aquarium using shredded paper toweling as a substrate and food source, which was supplemented with Salmon Starter®.

3.5.3 Experimental Design For The Four Day Toxicity Screening Test

For the toxicity screening test, three replicates per sediment were set up for *Lumbriculus variegatus* exposures, with the sediment from site E-1P designated as the control. In all tests, moderately hard laboratory water was utilized as the overlying water. The experimental conditions outlined in Table 3.5.1 were used for the toxicity evaluations.

One day prior to the start of the test (day -1), the sediment from each site was mixed thoroughly and 100 mL s were transferred to each of the eight test chambers. Additionally, visual observations of the sediments were made. Moderately hard laboratory water was also added at this time. On day 0, the overlying water was renewed once before the test organisms were introduced into each of the glass beakers. Measurements of water quality parameters were also initiated on this day. Ten adult *Lumbriculus variegatus* organisms were randomly added to their respective test chambers. The behavior of the oligochaetes was observed to assure that they were burrowing into the sediment. The glass beakers were placed in a rack and transferred to a temperature controlled room $(23 + 1^{\circ}C)$. The light cycle was 16 hours on and 8 hours off. Temperature and dissolved oxygen measurements were taken from one randomly selected beaker for each sediment sample every 12 hours, after which the overlying water was renewed in all the beakers. This procedure was repeated daily through day 10, at which point the test was terminated. On day 0, the overlying water from the beakers was composited from each sediment sample, and 250 mLs were retained for alkalinity, hardness, and ammonia analysis. On the last day the same procedure was carried out. On day four, the
sediments were sieved, and the surviving test organisms were removed and counted. The biological endpoint for these sediment tests was mortality. The validity of the test was based on greater than 80% survival in the control treatment for *Lumbriculus variegatus*.

3.5.4 Statistical Analysis

Survival data for the toxicity screening were analyzed first for normality and homogeneity employing Shapiro-Wilk's and Bartlett's Tests. The data were then examined using Dunnett's Procedure to determine whether there was a significant difference in survival between the designated control sediment and those sediments containing pollutants. The TOXSTAT[®] 3.5 program was used in this evaluation.

3.5.5 Experimental Design For The 28 Day Bioaccumulation Test

For the bioaccumulation test, eight replicates per sediment were set up for *Lumbriculus variegatus* exposures, with the sediment from site E-1P designated as the control. In all tests, moderately hard laboratory water was utilized as the overlying water. The experimental conditions outlined in Table 3.5.2 were used for the toxicity evaluations.

On day -1, the sediment from sites E-1P, I-5M and I-7M were individually mixed and 1 L of sediment was added to each of the five glass test chambers. In addition, 2 L of moderately hard laboratory water was also added. The following day (day 0) the overlying water was renewed once before the introduction of the oligochaetes. Measurement of water quality parameters was also initiated on this day. A minimum of five grams of adult *L. variegatus* were randomly added to the test chambers, which were then placed in a fume hood. The light cycle was 16 hours on and 8 hours off. Temperature and dissolved oxygen measurements were taken from 1 randomly selected glass jar for each sediment sample every 12 hours, after which the overlying water was renewed in all the chambers. This procedure was repeated daily through day 28, at which point the test was terminated. On day 0, the overlying water from the test chambers was composited from each sediment sample and 250 mL s were retained for alkalinity, hardness, and ammonia analysis. This procedure was repeated on day 7, 14, and 28 of the test. On day 28, the sediments were sieved. The surviving test organisms were removed and placed in a 1 L beaker containing moderately hard laboratory water without sediment. The organisms were held for 24 hours to eliminate their gut contents. At the same time, approximately five grams of *L. variegatus* from the laboratory culture were placed in a 1 L beaker for gut content purging. This provided a baseline for the chemical analysis. After 24 hours, the oligochaetes were removed from the beakers, placed in a tarred weigh boat, blotted dry, and weighed. The test organisms were then frozen and analyzed for mercury by Method 7140.

TABLE 3.5.1 TEST CONDITIONS FOR CONDUCTING A FOUR DAY SEDIMENT TOXICITY TEST WITH *LUMBRICULUS VARIEGATUS*

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Test Method 100.3. EPA Publication 600/R-94/024 (July 1994).

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TABLE 3.5.2 TEST CONDITIONS FOR CONDUCTING A 28 DAY SEDIMENT BIOACCUMULATION WITH *LUMBRICULUS VARIEGATUS*

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Test Method 100.3. EPA Publication 600/R-94/024 (July 1994).

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3.6 Mesocosms

The mesocosms were constructed as described by Heath et al. 1995. The enclosures were constructed of fabrene and were 1 meter in diameter and 3 meters deep. Two-inch nylon webbing and six steel hoops were used for internal support. The bottom was fastened to a large stainless steel ring one meter in diameter that provided weight to anchor the mesocosms. Double 4-inch polyurethane flotation collars rested on the surface to extend the mesocosm through the water. The fabrene extended three meters from the steel ring to the bottom of the flotation collars. Together the ring and collar allowed the mesocosms to be open to the sediments and the air. The mesocosms were deployed on June 23, 1997. A large mooring buoy was secured to the lake floor with chain and an eighty pound cement weight. Attached to the buoy was a mast that supported an amber flashing light for navigation and an owl to repel water fowl. Three mesocosms were placed around the buoy in a triangular fashion at each of the two sites and were labeled A, B, and C. Each mesocosm was placed in approximately 8-9 feet of water to allow slack in the material. Since the mesocosms were flexible yet floated on the surface, the enclosed contents remained well mixed. Internal water was not allowed to exchange with the external environment to maximize the potential for bioaccumulation. The mesocosms were secured to reduce their movement with the water currents and wind using 3/8-inch nylon line and 40 pound steel bricks. An additional halfinch line was laced through a nylon loop at the top of each mesocosm and connected with a carabiner to prevent the collars from drifting apart.

On June 24, 1997, eight fathead minnows (*Pimephales promelas*) and eight channel catfish (*Ictalurus punctatus*) were introduced into each mesocosm. Both the control and experimental sites were visited every three days for the duration of the project. On July 23, 1997, the fish were collected using electro-shocking and an extended fishing net. The fish were frozen until analysis was performed. On August 5, 1997, the mesocosms and buoys were removed from the water.

3.7 References

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- Binford, M. W. 1990. Calculation and uncertainty analysis of 210Pb dates for PIRLA project lake sediment cores. J. Paleolim. 3:253-267.
- Schelske, C. L., A., Peplow, M. Brenner, and C. N. Spencer. 1994. Low-background gamma counting: Applications for 210Pb dating of sediments. J. Paleolim. 10:115-128.

4.0 Results And Discussion

The results and discussion of each project element are presented in the following sections. In addition, a summary of the complete project data set is also included in Appendix A.

4.1 Sediment Chemistry

The results of core and Ponar samples collected from the Tannery Bay interior and exterior stations are summarized in Tables 4.1.1 and 4.1.2 respectively. The results for chromium

Station	Depth	Arsenic	Chromium	Mercury	% Solids	TOC
	(inches)	(mg/kg)	(mg/kg)	(mg/kg)		$\%$
E-1 Top	$0 - 20$	6.9	37	0.18	17	16
E-1 Mid	20-40	2.5	6	< 0.10	50	5
E-1 Bot	$40 - 60$	3.5	13	< 0.10	45	$\overline{8}$
E-2 Top	$0 - 27$	7.9	512	0.39	18	16
E-2 Mid	27-54	5.5	19	0.11	29	14
E-2 Bot	54-82	9.2	30	< 0.10	22	17
E-3 Top	$0 - 23$	13	381	0.66	16	15
E-3 Mid	23-46	11	21	< 0.10	18	12
E-3 Bot	46-69	11	24	< 0.10	19	12
E-4 Top	$0 - 23$	10	184	0.55	17	15
E-4 Mid	23-47	7.6	24	< 0.10	21	15
E-4 Bot	47-71	8.3	26	< 0.10	18	18
E-5 Top	$0 - 20$	9.4	385	0.68	15	15
$E-5$ Mid	$20 - 40$	8.5	27	< 0.10	17	16
E-5 Bot	$40 - 60$	9.7	21	< 0.10	17	15
E-6 Top	$0 - 29$	12	445	0.77	12	20
E-6 Mid	29-58	8.2	26	0.15	18	15
E-6 Bot	58-87	8.7	21	< 0.10	19	12
E-7 Top	$0 - 25$	9.9	313	0.67	13	14
E-7 Mid-1	$25 - 50$	9.3	32	< 0.10	15	16
E-7 Mid-2	50-75	9.5	36	< 0.10	15	16
E-7 Bot	75-100	9.7	29	0.10	16	16
$E-9-1$	$0 - 15$	10	838	0.49	11	11
$E-9-2$	15-30	8.2	313	0.57	14	9
$E-9-3$	$30 - 45$	8.4	140	0.55	16	$\overline{8}$
$E-9-4$	$45 - 60$	9.1	49	0.33	18	11
$E-9-5$	60-75	6.6	30	0.13	17	14
$E-9-6$	75-90	4.1	10	< 0.10	38	$\overline{3}$

TABLE 4.1.1 RESULTS OF TANNERY BAY EXTERIOR CORE SAMPLES

Station	Arsenic	Chromium	Mercury	% Solids	TOC	
	(mg/kg)	(mg/kg)	(mg/kg)		$\%$	
$I-1$	7.5	212	0.28	13	17	
$I-2$	8.8	259	0.29	14	15	
$I-3$	8.4	934	0.47	14	13	
$I-4$	9.0	1890	0.78	14	14	
$I-5$	174	4100	3.76	17	17	
$I-6$	10	2650	1.04	15	12	
$I-7$	8.3	2560	0.87	13	12	
$I-8$	8.6	515	0.39	15	21	
$E-1P$	6.1	23	0.17	17	16	
$E-2P$	8.1	64	0.21	15	16	
$E-3P$	9.2	43	0.22	16	13	
$E-4P$	8.4	344	0.30	14	14	
$E-5P$	8.6	492	0.39	12	13	
$E-6P$	9.5	771	0.68	11	12	
$E-7P$	8.6	541	0.63	12	13	
$E-9P$	9.1	369	0.28	11	13	

TABLE 4.1.2 RESULTS OF PONAR SAMPLES FROM TANNERY BAY EXTERIOR AND INTERIOR STATIONS

in the exterior station cores is shown in Figure 4.1.1. All stations have elevated chromium levels in the top sections of the cores except for the control location, E-1. These results show that significant deposition of anthropogenic chromium has occurred in the top 20-30 inches of sediment in eastern White Lake. The E-1 station is located upstream of the Tannery and situated in an area where significant anthropogenic inputs are not expected. This station can be used to illustrate background conditions. At the exterior sites with the exception of station E-9, chromium concentrations fall by almost an order of magnitude in the middle sections and continue at similar levels to the bottom of the core. Sediments below 30 inches do not show significant enrichment with chromium. Station E-9 does not follow this pattern as concentrations in excess of 100 mg/kg persist down to 60 inches. The highest level of chromium found at the exterior stations was detected in the 0-15 inch region of E-9 (838 mg/kg). This station is located in a deep region (53 ft) and may serve as a long-term deposition area for eastern White Lake. The presence of animal hair in the Ponar sample for benthic invertebrates at E-9 (Table 4.4.1) supports this theory. Lung (1975) examined the circulation patterns in White Lake and identified a gyer in the vicinity of station E-9. A gyer in this area would likely increase the amount of sedimentation at E-9 and also move suspended particulates from western locations in White Lake.

FIGURE 4.1.1 CHROMIUM RESULTS FOR CORE SAMPLES FROM TANNERY BAY EXTERIOR STATIONS, OCTOBER 1996.

Concentrations of arsenic and mercury in the exterior station cores are shown in Figures 4.1.2 and 4.1.3 respectively. Concentrations of arsenic show limited variation with depth, which suggests that levels ranging from 7 mg/kg to 10 mg/kg represent background concentrations.

The lower levels of arsenic detected in the mid and bottom sections of the core from the control location were from sediments with higher solids content ($>40\%$) than the other sediments. The high solids were due to the inclusion of coarse grained sands, which probably have limited amounts of native arsenic. The mercury data in Figure 4.1.3 is interesting in that the element is detected at most stations in the top section only. This pattern suggests that the introduction of mercury into White Lake is a recent event and that natural levels are below the detection limit $\left($ <0.10 mg/kg). Station E-9 exhibits a different profile as mercury is detected in all sections down to the 60-75 inch strata. Since mercury concentrations are in the same range as the top section of the other exterior station cores, the data supports the observation that this station is subject to a higher level of sediment deposition than the other areas investigated in this project.

The results of the exterior station Ponar samples are shown in Figure 4.1.4. Arsenic and mercury results are similar to top sections of the core samples. Chromium results reflect some variability that indicates a degree of heterogeneity in the sediments. It is interesting to note that the level of chromium in the Ponar sample from E-9 is considerably less than the top section of the core (369 mg/kg vs. 838 mg/kg). The lower value of chromium detected with the Ponar may indicate that sediment with less contamination was deposited in the area during recent times.

The interior station Ponar samples provide a description of the recent deposition pattern in Tannery Bay. The results of the Ponar samples are given in Figure 4.1.5. The highest concentrations of chromium (4100 mg/kg), arsenic (174 mg/kg), and mercury (3.76 mg/kg) were found at station I-5M which is located near the discharge point of the lagoons in the northwest corner of the Bay. This location also had the highest top section concentrations of these metals in the EPA/MDEQ (Bolattino and Fox, 1995) core samples. All interior stations had elevated chromium concentrations. A comparison of the top section data from the EPA/MDEQ core samples and the interior station Ponar samples is provided in Table 4.1.3 and displayed graphically in Figures 4.1.6 and 4.1.7. Average chromium levels are lower by a factor of two in the Ponar samples than the top section of the cores. Mercury follows a similar trend. The arsenic results are similar in both sets of data. Data for TOC and Percent Solids reflect a greater degree of organic matter deposition in the Ponar sample. These patterns suggest that sediments with lower levels of mercury and chromium have been recently deposited in Tannery Bay. This observation is consistent with the diversion of the process effluent from Tannery Bay to the City of Whitehall Wastewater Treatment Plant. With the direct discharge of Tannery wastes removed, the chromium, mercury, and arsenic levels in the Ponar samples reflect contamination from sediment resuspension, surface runoff, and possibly groundwater advection (Section 4.2).

FIGURE 4.1.2 ARSENIC RESULTS FOR CORE SAMPLES FROM TANNERY BAY EXTERIOR STATIONS, OCTOBER 1996.

FIGURE 4.1.3 MERCURY RESULTS FOR CORE SAMPLES FROM TANNERY BAY EXTERIOR STATIONS, OCTOBER 1996.

FIGURE 4.1.4 CONCENTRATIONS OF ARSENIC, CHROMIUM, AND MERCURY IN PONAR SAMPLES FROM TANNERY **BAY EXTERIOR STATIONS, OCTOBER 1996.**

FIGURE 4.1.5 CONCENTRATIONS OF ARSENIC, CHROMIUM, AND MERCURY IN PONAR SAMPLES FROM TANNERY **BAY INTERIOR STATIONS, OCTOBER 1996.**

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TABLE 4.1.3 COMPARISON OF CHEMISTRY DATA FROM PONAR SAMPLES (1996) AND THE TOP SECTIONS OF THE EPA 1994 CORE SAMPLES (BOLATTINO AND FOX 1995).

FIGURE 4.1.6 COMPARISON OF THE 1994 TOP CORE SECTIONS (BOLATTINO AND FOX 1995) AND 1996 PONAR SAMPLES FROM TANNERY BAY

FIGURE 4.1.7 COMPARISON OF THE CHROMIUM RESULTS FROM THE 1994 TOP CORE SECTIONS (BOLATTINO AND FOX 1995) AND 1996 PONAR SAMPLES FROM TANNERY BAY

The core samples taken by the U.S.EPA/MDEQ (Bolattino and Fox 1995) can be used to compare the subsurface sediment conditions in Tannery Bay with the exterior locations. Selected data from theses core samples are displayed in Figures 4.1.8, 4.1.9, and 4.1.10, for the top, middle, and bottom sections respectively. High levels of chromium, mercury, and arsenic were found throughout Tannery Bay. Contaminant levels were lower in the bottom sections of the cores taken in the area where Tannery Bay opens into White Lake.

Chromium levels are over an order of magnitude higher in the top sections of the interior cores compared to the exterior stations. Arsenic levels are high near the northwestern corner of Tannery Bay (125 mg/kg). The cores taken near the interface with White Lake have twice the level of arsenic as the exterior stations (20 mg/kg vs. 10 mg/kg). Mercury levels are higher within Tannery Bay and decrease by over 50% at the exterior locations. The highest top section concentration of arsenic (125 mg/kg) and mercury (5.93 mg/kg) was measured in the station near the northwest shoreline.

The middle and bottom sections of the Tannery Bay cores show considerable enrichment of arsenic, chromium, and mercury when compared to the exterior locations. The highest level of chromium (14,300 mg/kg) was found in the middle section (15-23 inches) of the core taken near the southwest corner of Tannery Bay. The highest level of arsenic (569 mg/kg) was also detected in the bottom section (23-40 inches) at this location. Mercury concentrations followed a similar pattern with the highest levels detected in the southwestern region of Tannery Bay (16.7 mg/kg and 6.72 mg/kg).

The results of the Ponar samples for the exterior and interior stations are displayed in Figures 4. 1.11, 4.1.12, and 4.1.13. Since the Ponar collects near surface zone sediments, the results of these samples characterized the recent sedimentation record. The arsenic results from Figure 4.1.11 show that station I-5M is the only location with an elevated concentration of the metal. It is apparent that the high arsenic concentrations found in Tannery Bay are localized in the deeper strata and at the surface at I-5M. There is no evidence of a flux of arsenic from Tannery Bay into White Lake. Since arsenic is known to form covalent bonds with sulfhydryl groups, the organic by-products of the Tannery operations may be responsible for limiting its mobility.

FIGURE 4.1.8 CHROMIUM RESULTS FOR CORE SAMPLES FROM THE 1994 EPA TANNERY BAY STATIONS, (BOLATTINO AND **FOX 1995).**

FIGURE 4.1.9 MERCURY RESULTS FOR CORE SAMPLES FROM THE 1994 EPA TANNERY BAY STATIONS, (BOLATTINO AND **FOX 1995).**

FIGURE 4.1.10 ARSENIC RESULTS FOR CORE SAMPLES FROM THE 1994 EPA TANNERY BAY STATIONS, (BOLATTINO AND **FOX 1995).**

FIGURE 4.1.11 COMPARISON OF ARSENIC CONCENTRATIONS FROM PONAR SAMPLES AT THE EXTERIOR AND INTERIOR STATIONS (1996)

FIGURE 4.1.12 COMPARISON OF MERCURY CONCENTRATIONS FROM PONAR SAMPLES AT THE EXTERIOR AND INTERIOR STATIONS (1996)

FIGURE 4.1.13 COMPARISON OF CHROMIUM CONCENTRATIONS FROM PONAR SAMPLES AT THE EXTERIOR AND INTERIOR STATIONS (1996)

Mercury concentrations as shown in Figure 4.1.12 show a different pattern. Levels of Mercury are elevated in the main section of Tannery Bay (I-4, I-5, I-6, and I-7) and in the down gradient exterior stations (E-5P, E-6P, and E-7P). Although mercury has greater affinity for sulfhydryl groups than arsenic, the data suggests some degree of mobility in the system. Mercury methylation may play a role in causing the movement of the element to the surface from the deeper sediments that carry a greater contaminant load.

The data for chromium in Figure 4.1.13 show that considerable contaminant flux has occurred in the recent sediment record. Stations close to the Tannery (I-5, I-6, and I-7) have concentrations of chromium in excess of 2000 mg/kg. In the stations near the open water of White Lake (I-3, I-4, and I-8), the concentrations still exceed 500 mg/kg. These levels are similar to the chromium concentrations found at E-6 and E-7, which are located down gradient from Tannery Bay. Contaminant transport mechanisms probably include surface runoff and the resuspension and export of contaminated sediments outside Tannery Bay by wind induced water currents and the natural westerly flow pattern found in White Lake. The stratigraphy and radiochemistry data present in Section 4.2 provide additional information to elucidate the sedimentation and transport dynamics in Tannery Bay.

Since trivalent chromium is highly insoluble above pH 4.5 (Palmer and Puls, 1994), it is likely that any soluble forms of chromium in the Tannery discharge would be rapidly precipitated out in Tannery Bay. The high levels of chromium found in the cores taken near

the discharge area are indicative of the rapid precipitation of the metal occurring upon contact with the waters of White Lake. In consideration of the insolubility of trivalent chromium, the wide spread contamination observed in eastern White Lake is probably due to the historical and continued export of Tannery Bay sediments by lake currents. The comparison of core and Ponar results for stations E-5, E-6, and E-7 also illustrate this observation. The core and Ponar results for these stations are summarized below:

The presence of significantly higher chromium levels in the Ponar samples indicate that the greatest degree of enrichment occurs in the near surface zone sediments. These data plus the information related to sediment resuspension in section 4.2 demonstrates that there is strong evidence of the continued resuspension and export of Tannery Bay sediments into eastern White Lake.

There is no single set of guidelines established for evaluating sediment quality. A summary of recently proposed sediment quality guidelines is provided in Table 4.1.4. These guidelines

TABLE 4.1.4. SUMMARY OF RECENT SEDIMENT QUALITY GUIDELINES

*=Not Calculated

are derived by combining the results the results of laboratory and field studies that include a variety of methodological approaches (background levels, equilibrium-partitioning, spiked sediment bioassays, field surveys, screening level concentrations, apparent effects thresholds, and bioeffects/contamination co-occurrence analyses) for both freshwater and marine sediments. These data are used to estimate the range of no effect, possible effect, and probable effect concentrations of contaminants in sediments. Threshold effect levels estimate the breakpoint between no effect and possible effect concentrations. The Effects Range Low (Long and Morgan 1990 and Ingersoll et al. 1996), Lower Effect Level (Persaud et al. 1992), and the Threshold Effect Level (Smith et al. 1996 and Ingersoll et al. 1996) are all estimates of contaminant concentrations where ecological effects are not anticipated if the

level is below the proposed guideline. The Effects Range Median (Long and Morgan 1990 and Ingersoll et al. 1996), Severe Effect Level (Persaud et al. 1992), and the Probable Effect Level (Smith et al. 1996 and Ingersoll et al. 1996) are all estimates of contaminant concentrations where ecological effects are anticipated if the level is above the proposed guideline. While these guidelines do not address all site specific conditions that may affect the availability of heavy metals, they are useful benchmarks for determining sediment quality (USEPA 1992).

A summary of the analytical results for Ponar samples from Tannery Bay and Eastern White Lake is provided in Table 4.1.5. All locations in Tannery Bay and 5 of the six

TABLE 4.1.5. COMPARISON OF PONAR SAMPLE RESULTS FROM TANNERY BAY AND EASTERN WHITE WITH SEDIMENT QUALITY GUIDELINES.

Tanne ry B ay Pon ar S a m p les

W hite Lake Ponar Samples

* Result exceeds all Probable Effect Concentrations

** Result below all Threshold Effect Concentrations

downgradient locations exceed probable effect levels for chromium. Most of the Tannery Bay stations exceed these guidelines by an order of magnitude. Only the background station E-1P had a chromium concentration below all the Threshold Effect Levels. Based on current sediment quality guidelines, adverse ecological effects would be anticipated from the high levels of chromium detected in Tannery Bay. Adverse effects would also be expected in many of the stations in Eastern White Lake that were located downgradient from Tannery Bay.

In conclusion, the chemistry data indicate that the sediments in Tannery Bay are highly contaminated with arsenic and chromium and are, to a lesser extent, contaminated with mercury. The entire study area in eastern White Lake exhibits chromium enrichment in the recent sediment record. Based on current sediment quality guidelines, adverse ecological effects would be anticipated from the high levels of chromium detected in Tannery Bay. Adverse effects would also be expected in many of the stations in eastern White Lake that were located downgradient from Tannery Bay. Even though the direct discharge from the Tannery ceased in 1976, export mechanisms have remained active in causing a flux of chromium from Tannery Bay into White Lake. Surface runoff from waste piles on the Tannery site and the resuspension and transport of sediments from Tannery Bay are the most probable mechanisms for the export of contaminants into White Lake.

4.2 Radiochemistry And Detailed Stratigraphy

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4.2.1 Detailed Stratigraphy

The results of the stratigraphy analyses for total chromium are given in Tables 4.2.1 and 4.2.2 for I-5M and I-7M respectively. The I-5M core shows a relatively uniform region of

TABLE 4.2.1 RESULTS OF DETAILED STRATIGRAPHY ANALYSIS OF THE PISTON CORE SAMPLE FROM STATION I-5M.

chromium concentrations ranging from 2500 mg/kg to 3600 mg/kg between 0 cm and 26 cm. This region is followed by more concentrated strata that vary from approximately 5,000 mg/kg to 23,000 mg/kg in the interval from 26-84 cm. Chromium in the remainder of the core decreases after 84 cm. Because this station was located in the discharge area of the waste treatment lagoons, the variations in chromium concentrations observed reflect differences in effluent

composition over time. Sudden reductions in chromium levels also correspond to strata that contain hair and hide fragments.

TABLE 4.2.2 RESULTS OF DETAILED STRATIGRAPHY ANALYSIS OF THE PISTON CORE SAMPLE FROM STATION I-7M.

The original piston core collected on October 9,1996 was not used for analysis due to an internal water leak that developed during extrusion. The visual description for this core (Appendix A, Table A-7) showed the purple colored sediment layer to begin at 20 cm. During sectioning, some colored sediment was noticed at 12 cm. The water leak may however have caused the migration of the purple material into the upper strata. In contrast, the core sample collected for the April 1997 toxicity evaluations (Section 4.3) showed the colored sediment to be located at 30 cm. These results in addition to stratigraphy core demonstrate that the sediments in this area are heterogeneous with respect to the depth of the purple sediment layer. Since the Ponar samples obtained for I-5M were collected at the time of the October 9, 1996 piston core, we assume that the stratigraphy described in Table A-7 reflects the conditions for the location sampled. The presence of purple colored sediment in the I-5M Ponar samples suggests that the sampling device may have penetrated to a depth below 20 cm.

The I-7M core follows a different depositional pattern. Concentrations of chromium gradually increase from approximately 2000 mg/kg to 5000 mg/kg over the interval from 0-36 cm. Concentrations then rapidly rise and remain elevated in the region from 38-128 cm. Purple sediment was found beginning at 80 cm. Chromium concentrations began to decrease after 128 cm. Higher levels of chromium were found in the I-7M core than at I-5M. The highest level found at I-5M was 22,800 mg/kg while several 2 cm strata at I-7M ranged from 34,000 mg/kg to 61,100 mg/kg. The strata containing the sediment with 61,100 mg/kg of chromium (52-54 cm) was blue in color. As mentioned previously, the I-7M station is located near the solid waste disposal area. Soil borings from the disposal area (Horizon Environmental, 1996 and 1997) found wastes containing 61,000 mg/kg of chromium at a depth of 4 ft near I-7M.

Plots of chromium concentration versus depth are presented in Figure 4.2.1 (I-5M) and Figure 4.2.2 (I-7M). Both plots show similar trends with high levels of chromium detected in the middle sections. Variations in concentrations in these regions may be due to historical changes in the composition and amount of Tannery waste discharged to the bay. Mats of hair (e.g. I-7M, 110-112 cm) characterized a number of the strata containing lower chromium concentrations. The depositional pattern shown for these cores also provide information that is useful for the interpretation of the results of Ponar and VibraCore samples. The I-5M Ponar contained purple colored sediment, indicating penetration below the 20 cm strata. This station contained a large amount of leather fragments that have decomposed to produce highly unconsolidated, gelatinous, and flocculent organic sediment. Sediment of this type would have properties similar to an organic sludge and not confine the Ponar to its typical 0-15 cm range. The average chromium concentration in the 0-12 cm region of the stratigraphy core from I-7M (2,600 mg/kg) was very close to the concentration measured in the Ponar sample (2,560 mg/kg). These data show that the Ponar did not penetrate below its typical range at this station. Since the I-5M station was the only location that was heavily impacted by animal hide fragments, it is likely that all of the other Ponar samples were collected from the 0-15 cm zone in the sediments.

The U.S.EPA/MDEQ cores collected in 1994 used 45-60 cm depths to mark the top sections collected near I-5M and I-7M. At both of these locations, the sediment cores contained strata with chromium concentrations > 20,000 mg/kg. The inclusion of the more contaminated strata in the EPA's top core sections results in a higher composite chromium concentration measured over the depth profile than determined in the Ponar samples. For this reason, the Ponar samples are more representative of sediments in the near surface zone than the top core sections.

Chromium Concentration (mg/kg)

FIGURE 4.2.1 RESULTS OF DETAILED STRATIGRAPHY ANALYSIS OF THE PISTON CORE FROM STATION I-5M.

Chromium Concentration (mg/kg)

FIGURE 4.2.2 RESULTS OF DETAILED STRATIGRAPHY ANALYSIS OF THE PISTON CORE FROM STATION I-7M.

4.2.2 Radiochemistry

The radiochemistry data is summarized in Tables 4.2.3 and 4.2.4. The profiles of ^{210}Pb activity for Station I-5M (Figs. 4.2.3 and 4.2.4) and Station I-7M (Figs. 4.2.5 and 4.2.6) provide other information about historical sedimentation at the White Lake sites. First, ^{210}Pb activity generally decreases with depth. Second, several stratigraphic layers can be identified based on ^{210}Pb activity. Four layers are present in core I-5M: 0-15 cm, 15-30 cm, 30-50 cm, and 50-65 cm; and four layers can also be identified in I-7M: 0-20 cm, 20-35 cm, 35-45 cm, and 45-70 cm. The total ²¹⁰Pb activity in the top layer in both cores was similar, ranging from 10-12 dpm/g, and the activity in the lowest layer was also similar in both cores. Supported ^{210}Pb is by far the largest fraction in the lowest layer. Finally, because excess ²¹⁰Pb is generally not measurable in sediments with ages older than five or six half lives, we can conclude that the ages in sediments above the bottom layer with measurable levels of excess ²¹⁰Pb activity are probably not older than 110 to 130 year.

	Total			Excess				Mass	
	$Pb-210$	$Ra-226$	$Cs - 137$	$Pb-210$		Age		Sedimentation	MSR
Depth	Activity	Activity	Activity	Activity	Age	Error	Date	Rate	Error
(cm)	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)	(years)	(1s)		(mg/cm2/yr)	(1s)
5	11.951	1.735	1.565	10.358	3.965	.222	1992.7	167.23	8.36
10 ¹	11.552	1.592	1.437	10.103	10.534	1.339	1986.2	145.68	7.68
15	10.7	1.73	1.614	9.1	17.992	1.490	1978.7	130.06	8.22
20 ¹	8.55	1.276	1.449	7.38	29.222	1.848	1967.5	120.21	7.18
25	8.81	1.015	1.598	7.911	46.450	2.604	1950.2	72.50	5.86
30 ¹	7.455	1.423	2.414	6.123	68.841	4.523	1927.9	50.96	5.95
35	4.931	2.967	3.769	1.996	81.028	5.603	1915.7	89.93	22.61
40	2.641	1.753	3.142	0.904	90.010	5.747	1906.7	142.50	61.92
45	2.696	1.398	2.468	1.32	104.612	6.991	1892.1	67.94	22.25
50	2.889	1.224	1.139	1.689	149.286	21.588	1847.4	22.63	9.26
55	1.243	0.703	0.437	0.549					
60	0.44	0.757	0.024	-0.322					

TABLE 4.2.3 RADIOCHEMISTRY RESULTS FOR I-5M.

TABLE 4.2.4 RADIOCHEMISTRY RESULTS FOR I-7M.

	Total			Excess				Mass	
	$Pb-210$	Ra-226	$Cs - 137$	$Pb-210$		$A\,g\,e$		Sedimentation	MSR
Depth	Activity	Activity	Activity	Activity	Age	Error	Date	Rate	Error
(cm)	(dpm/g)	(dpm/g)	(dpm/g)	(dpm/g)	(years)	(1s)		(mg/cm2/yr)	(1s)
5	12.512	1.555	1.281	11.109	2.414	1.710	1994.3	225.77	14.85
10	12.697	1.986	1.442	10.864	5.460	1.790	1991.2	212.07	16.31
15	11.085	2.028	1.347	9.187	11.621	1.938	1985.1	217.52	19.10
20	12.147	1.733	1.534	10.565	21.897	2.375	1974.8	146.84	9.77
25	8.768	1.738	1.421	7.135	31.666	2.865	1965.0	159.07	16.91
30	8.322	1.836	1.663	6.583	44.497	3.744	1952.2	121.58	15.67
35	7.978	1.799	1.637	6.273	65.115	6.126	1931.6	76.58	12.89
40	6.995	2.354	1.946	4.712	101.819	16.452	1894.9	43.32	13.97
45	5.777	3.379	2.817	2.435					
50	2.439	3.637	1.218	-1.215					
55	2.298	3.361	0.85	-1.079					

FIGURE 4.2.3 ACTIVITY VERSUS DEPTH OF TOTAL ²¹⁰PB AND ²²⁶RA AT STATION I-5M.

FIGURE 4.2.4 ACTIVITY VERSUS DEPTH OF EXCESS²¹⁰PB AND ¹³⁷CS AT STATION I-5M.

FIGURE 4.2.5 ACTIVITY VERSUS DEPTH OF TOTAL ²¹⁰PB AND ²²⁶RA AT STATION I-7M.

FIGURE 4.2.6 ACTIVITY VERSUS DEPTH OF EXCESS²¹⁰PB AND ¹³⁷CS AT STATION I-7M.
Combined plots of chromium stratigraphy and radiochemistry data are shown in Figure 4.2.7 for I-5M and in Figure 4.2.8 for I-7M. The four regions in each core described earlier suggest distinct layers. Sediments that are well mixed would have relatively uniform $210Pb$ activity as illustrated from the surface to the 10-20 cm zone. These results are significant as the ^{210}Pb profile demonstrates a mixed zone near the surface that is isolated from the sediments below approximately 20 cm. Levels of chromium in excess of 20,000 mg/kg begin at 40 cm at I-7M and at 30 cm at I-5M. Based on the 210 Pb profile, a region of unmixed sediment lies between the heavily contaminated strata and the mixed sediment zone. The zones of greatest chromium contamination therefore appear to be isolated from the surface sediments that are subject to mixing. Sedimentation rate data for both stations suggest that I-7M has a greater rate (225 mg/cm^2 /yr) than I-5M (167 mg/cm²/yr). This observation is supported by the chromium profile discussed above.

The isolation of the heavily contaminated sediments and the mixing of the top 15-20 cm region does not explain the relatively uniform concentration of chromium encountered near the surface. In the top 20 cm sediment zone, chromium concentrations are relatively uniform at I-5M and exhibit a two fold increase with depth at I-7M. The lack of sediments containing lower levels of chromium near the surface suggests that another source is contributing the metal to the surface region. Surface runoff may be a factor in mobilization of contaminated soils and wastes into the sediment of Tannery Bay. Another possibility is that present concentrations within the surface mixed layer are not in equilibrium with the recently deposited sediments.

The peak input of fallout $137Cs$ in the late 1950s and early 1960s has been used to provide a timedependent horizon in cores. This approach was used to verify CRS dates in Lake Erie cores (Schelske and Hodell 1995). Neither a sharp peak nor a large peak in ^{137}Cs activity was found in the White Lake cores. Therefore, this measurement was not useful in establishing the ^{137}Cs horizon. The low inventory of 137 Cs activity in both cores is in sharp contrast to the high inventory of ²¹⁰Pb activity. These results indicate that ¹³⁷Cs was deposited and not retained at these sites for the following reasons:

- sediment resuspension focused the $137Cs$ to other locations
- the $137Cs$ was diluted by the introduction of large quantities of tannery wastes
- ionic $137Cs$ was advected with pore waters from the core site

The latter mechanism is prevalent at locations where groundwater is moving through deposited sediments. It seems unlikely that resuspension or dilution was a primary mechanism because of the large inventories of 210 Pb activity at both sites. The most plausible explanation for the absence of the ¹³⁷Cs horizon is, therefore, groundwater advection. Horizon (1997) identified Tannery bay as a discharge zone for local groundwater.

The influence of groundwater advection on chromium may also be a factor in its fate and transport. As discussed previously, the absence of the 137Cs horizon suggested that the movement of local groundwater through the sediments was responsible for advective losses. Since the local groundwater is known to discharge in the near shore area of Tannery Bay,

FIGURE 4.2.7 CHROMIUM CONCENTRATIONS AND EXCESS ²¹⁰PB VERSUS DEPTH AT STATION I-5M.

FIGURE 4.2.8 CHROMIUM CONCENTRATIONS AND EXCESS ²¹⁰PB VERSUS DEPTH AT STATION I-7M.

chromium may also be mobilized from the deeper layers and transported to the surface. While the solubility of trivalent chromium is generally limited due to the precipitation of insoluble hydroxides, the formation of organic complexes has been shown to increase its solubility. Kaczynski and Kleber (1994), James and Bartlett (1983), and Hassan and Garrison (1996) noticed that the solubility of trivalent chromium was increased in the presence of organic complexing agents. The latter authors noticed an increase in solubility in the presence of cysteine under low Eh conditions. The low Eh environment present in the sediments of Tannery Bay, in addition to the organosulfur compounds produced during the decomposition of animal hides and hair, may produce conditions that promote chromium solubility. It was also noted that a large amount of humic material was released from the Tannery Bay sediments during alkaline digestion. These materials may also serve as complexing agents to increase chromium solubility. The presence of a soluble chromium fraction in the sediment pore water and its potential role in the advection of chromium needs to be evaluated as long as groundwater continues to enter Tannery Bay.

Since the direct discharge of tannery effluent to Tannery Bay ceased in 1976, evidence of the deposition of sediments with less chromium contamination should be evident. The lack of a decreasing gradient of chromium concentrations in the surficial sediments (0-20 cm) may be explained by several mechanisms:

- continued surface runoff
- groundwater advection
- continual sediment mixing and resuspension in the 0-20 cm zone

Since the levels of excess ^{210}Pb in the surfacial sediments are normal and do not reflect excessive dilution with terrestria soil, surface runoff would only be significant if small amounts of highly contaminated material were continuously eroding into Tannery Bay. As discussed previously, groundwater advection may be responsible for some migration of chromium from deeper sediment layers to the surface. It is, however, doubtful that this mechanism would be responsible for chromium levels in excess of 2,000 mg/kg. The most likely process that would produce the observed chromium levels is that of sediment mixing and resuspension. The flocculent, finegrained sediments in Tannery Bay may be mixed to a degree that prohibits the formation of concentration gradients. The continued mixing of flocculent materials would result in an unstable, resuspended sediment that could be exported readily into White Lake by currents and wave action. The prevalence of the high levels of chromium in the White Lake Ponar samples collected down gradient from Tannery Bay would support the continued export of resuspended sediments.

Total and excess 210 Pb activity decreased with depth (Figs. 4.2.3 and 4.2.4), but not exponentially which would be expected if the sedimentation rate was relatively constant. Therefore, the CRS model (Appleby and Oldfield 1983) was selected to calculate ages. Ages calculated from the model placed 1892 at 45 cm and 1847 at 50 cm for core I-5M, and 1895 at 40 cm for core I-7M. These ages, however, were much younger than expected based on other information available for the core. For example, the chromium concentration exceeded 10,000 mg/kg from 62-82 cm in I-5M, or in sediments older than 1847 according to the calculated ²¹⁰Pb ages (Fig. 4.2.5). The

chromium concentration exceeded 10,000 mg/kg at depths as deep as 84 cm and higher than background to a depth of 126 cm in I-7M. By contrast only the upper 40 cm of this core contained sufficient levels of excess ²¹⁰Pb for dating. This lack of conformity shows that the calculated ages are not credible. Results from the CRS ²¹⁰Pb age model that are not credible can be a product of the point transformations that are used in the CRS model (Robbins and Herche 1993). Independent assessment of dating is therefore required for the CRS model. For the White Lake cores, data for chromium and tannery waste by-products provide independent time markers that are at variance with the calculated ^{210}Pb ages. Since high levels of chromium and tannery waste byproducts (hair and dye coloration) persist well below the calculated 1847 date, the dating chronology must be rejected. Large inputs of waste materials could confound the chronological record not only by diluting the natural sediments, but also by altering the physical-chemical environment.

4.2.3 Sediment Fate And Transport

Given the insolubility of trivalent chromium in the natural water (Palmer and Puls 1994), the predominant mechanism driving the flux of this metal in White Lake is sediment export. The hydrodynamics of White Lake support the progressive transport of sediments in a westerly direction following the natural water currents. Prevailing winds function to mix the near shore sediments and move the resuspended material out into the main lake. The 0-20 cm zone of sediment mixing determined by the 210 Pb data reflects the action of the prevailing winds and the wave induced resuspension. The well mixed nature of the top 20 cm zone also suggests that these sediments are unstable and easily exported. In addition, the differences in stratigraphy between I-5M and I-7M are consistent with wind induced wave action. Station I-5M has a greater exposure to the westerly wind and has a lower calculated sedimentation rate $(167.23 \text{ mg/cm}^2/\text{yr})$ and a shallower interval of sediment above the highly contaminated zone. In contrast, station I-7M is more protected from wave action and exhibits a greater calculated sedimentation rate (225.77 mg/cm²/yr) and a stratigraphy profile reflecting a greater depth of less contaminated material.

The discharge of tannery waste was located near the shore of Tannery Bay in the northeast corner. The EPA/MDEQ core samples indicate heavy sediment contamination with chromium in the near shore and middle areas of Tannery Bay. Stations near the confluence with White Lake have considerably less chromium in the sediments. This pattern reflects a discharge of insoluble chromium that was rapidly incorporated into the sediments. Based on this information, the historical and current mechanism for chromium transport in White Lake is sediment export from Tannery Bay by the prevailing circulation pattern and wave action. Chromium export from Tannery Bay into White Lake proper will continue as long as the contaminated sediments are influenced by hydrodynamic circulation patterns.

4.3 Sediment Toxicity Results

The physical description of the sediment samples used for the toxicity evaluations is provided in Table 4.3.1. The standard Ponar samples collected during October 1996 consisted of fine particulate organic sediments. Animal hair and hides were found in samples from I-4 and I-5M. In addition, the sample from I-5M was purple in color, indicating that it contained sediments from below the 12-20 cm zone (Table A-7).

The sediments collected from the April 3, 1997 collection are described in Table 4.3.2. The core samples were sectioned at 0-30 cm and 30-70 cm to evaluate the toxicity of the sediment near the surface. Since the stratigraphy and radiochemistry showed that stable sediment with an order of magnitude higher level of chromium is present below 30 cm, it is important to evaluate the toxicity of these strata separately. The 30 cm zone in the core sample represented the transition from black flocculent material to a purple gelatinous sediment.

Sampling Location	Comments			
$E-1P$	Dark brown/black color, very fine particles, found two burrowing mayflies (Hexagenia)			
$I-1$	Dark brown/black color, very fine particles			
$I-2$	Dark brown/black color, very fine particles			
$I-3$	Dark brown/black color, very fine particles			
$I-4$	Pieces of animal hide, black hair, wood pieces (2-3mm)			
$I-5M$	Purple (cordovan brown) color, pieces of animal hide, black hair			
$I-6$	Grassy, leafy (detritus)			
$I-7M$	Dark brown/black color, very fine particles			
$I-8$	Dark brown/black color, very fine particles, wood pieces (2- 3mm)			

TABLE 4.3.1 PHYSICAL APPEARANCE OF SEDIMENTS COLLECTED IN OCTOBER 1996

<u> 1989 - Johann Stoff, deutscher Stoff, der S</u>

i.

4.3.1 November 1996 Tests

The first set of toxicity evaluations of the White Lake sediments was initiated on November 1, 1996 and completed on November 11, 1996. Composite sediment samples collected on the same day from nine different sites were employed in exposing both *Hyalella azteca* and *Chironomus tentans* over this period. The chemical measurements for the sediment toxicity experiments are summarized in Appendix B.

Temperature and dissolved oxygen measurements were taken and recorded twice daily throughout the duration of the tests (Appendix B: Tables B-1, B-3). The test beakers were maintained in a climate controlled room, and little variation in temperature was observed. The dissolved oxygen remained above 40% saturation in both the *Hyalella azteca* and *Chironomus tentans* test beakers. Conductivity, hardness, alkalinity, ammonia, and pH were determined at the beginning and on the tenth day of each test, and these data are shown in Appendix B: Tables B-2, B-4. With the exception of ammonia, these parameters remained relatively constant, with a variation of less than 50%, from initial to final measurements for both test species.

Ammonia levels in all 9 of the *Hyalella azteca* sediments and in 6 of the *Chironomus tentans* sediments (E-1P, 1-4, 1-5M, I-6, I-7M and I-8) decreased by more than 50% over the 10 day test period.

4.3.2 *Hyalella azteca*

The evaluation of White Lake's sediment began on November 1, 1996, and the resulting survival data are presented in Table 4.3.1. The survival in the control treatment exceeded the required 80%. The 10 day exposures resulted in 100% lethality for 7 of the 8 exposures with Station I-2 sediment and 5 of the 8 exposures with Station I-5M. Low survival was also noted in exposures with sediment from Station I-7M and I-8.

Statistical analyses were performed on the toxicity data and the results are summarized in Table 4.3.2. The un-transformed survival data required square root (y) transformation in order to pass normality employing Kolmogorov's Test at alpha = 0.01 and Bartlett's Test for homogeneity at $p = 0.01$. Dunnett's Test showed a statistically significant (alpha = 0.05) difference on the transformed survival data, in six out of eight sediments when each was compared to the control (E-1P) (Table 4.2.3). Based on amphipod mortality, the six sediments listed in order of increasing toxicity are I-6, I-4, I-7M, I-8, I-3, I-5M/I-1 (tie), and I-2.

TABLE 4.3.3 SUMMARY OF *HYALELLA AZTECA* **SURVIVAL DATA OBTAINED DURING THE 10 DAY TOXICITY TEST WITH WHITE LAKE SEDIMENTS**

TABLE 4.3.4 STATISTICAL ANALYSIS OF *HYALELLA AZTECA* **SURVIVAL DATA**

DUNNETT'S TEST - Ho:Control<Treatment

Dunnett critical value = 2.4400 (1 Tailed, alpha = 0.05, df [used] = 8,60) $(Actual df = 8,63)$

4.3.3 *Chironomus tentans*

The midge survival data are presented in Table 4.3.4. The survival in the control treatment exceeded the required 70%. Low survival $(\leq 50\%)$ was noted in five of the eight exposures using sediment from I-2 and two of the eight exposures with I-5M.

Statistical analyses were performed on the toxicity data, and the results are summarized in Table 4.3.5. Un-transformed survival data were evaluated for normality with Kolmogorov's Test at alpha = 0.01 and Bartlett's Test for homogeneity of variance at $p = 0.01$ and passed both. These data were then analyzed for effects on survival employing Dunnett's Test. A statistically significant (alpha = 0.05) difference from the control (E-1P) was observed in sediments I-2 and I-5M (Table 4.3.6). As observed with *Hyalella azteca*, I-2 was most toxic to the midge, whereas I-5M elicited over 41% midge mortality

TABLE 4.3.5 SUMMARY OF *CHIRONOMUS TENTANS* **SURVIVAL DATA OBTAINED DURING THE 10 DAY TOXICITY TEST WITH WHITE LAKE SEDIMENTS**

DUNNETT'S TEST - Ho:Control<Treatment

Dunnett critical value = 2.4400 (1 Tailed, alpha = 0.05, df [used] = 8,60) (Actual df = $8,63$)

4.3.4 April 1997 Core And Ponar Sample Tests With *Hyalella azteca*

Additional sampling of White Lake sediments occurred in April 1997 from three locations that were evaluated in the October 1996. From Stations I-5M and I-7M sediments were collected from two depths using a piston core sampler. Samples designated as I-5M-Top and I-7M-Top were taken from the 0-30 cm interval while I-5M-Mid and I-7M-Mid consisted of sediments secured from the 30-70 cm interval. The toxicity evaluation of these sediments was initiated on April 17, 1997 and completed on April 27, 1997 with *Hyalella azteca*. A sample from I-2 was taken with a petite Ponar. The petite Ponar would not penetrate as far in the sediments as the standard Ponar due to its smaller size and weight. The sample collected at I-2 was collected to confirm the high toxicity obtained in the assays of the October 1996 sediments. Shredded paper toweling was used as the control. Chemical measurements for the sediment toxicity tests are summarized in Appendix B.

As before, temperature and dissolved oxygen measurements were taken and recorded twice daily throughout the duration of the tests (Appendix B: Table B-5 and B-6). The test beakers were maintained in a climate controlled room, and little variation in temperature was observed. The dissolved oxygen remained above 40% saturation in the overlying water. Conductivity, hardness, alkalinity, ammonia, and pH were measured and recorded at the beginning and on the tenth day in each sediment test (Appendix B: B -6). With the exception of ammonia, these parameters remained relatively constant from the initial to the final measurements and varied less than the recommended 50%.

Ammonia concentrations in all of the sediments tested decreased by more than 50% over the ten day test period. As in the fall period, the overlying water was renewed once before the organisms were introduced to the test beakers, thus avoiding the initial high levels of ammonia. In the shredded paper towel control the ammonia level also decreased by 50%,

however the initial level was very low (0.02 mg/l), making this decrease somewhat misleading.

The resulting data for these tests are presented in Table 4.3.6.The survival in the control sediment exceeded the required 80%. The sediments from sites I-2, I-5M-Mid, and I-7M-Mid elicited 100% mortality over the ten day test period, while the sediments from I-5M-Top and I-7M-Top had mean amphipod survivals of 2.4 and 3.0 organisms per replicate. The untransformed data were analyzed with the nonparametric Steel's Many One Rank Test. A statistically significant (alpha $= 0.05$) difference in survival from the control was observed for all the sediments evaluated.

TABLE 4.3.7 SUMMARY OF *HYALELLA AZTECA* **SURVIVAL DATA OBTAINED DURING THE 10 DAY TOXICITY TEST WITH WHITE LAKE SEDIMENTS, APRIL 1997 SAMPLES**

A summary of the statistical analyses is presented in Table 4.3.7. The un-transformed data were analyzed with the nonparametric Steel's Many One Rank Test. A statistically significant (alpha $= 0.05$) difference in survival from the control was observed for all the sediments examined. These data were also evaluated using Kruskal - Wallis' Test for multiple comparison. This analysis performed a pair-wise comparison on the survival means for the individual sampling sites. The results showed no statistically significant (alpha $=$ 0.05) difference between the survival means for I-5M-Top and I-7M-Top. There was, however, a statistically significant difference (alpha $= 0.05$) for the sites with 100% mortality (I-2, I-5M-Mid, and I-7M-Mid) when compared to I-5M-Top and I-7M-Top that had some survival. These results indicate that surface sediment layer found from 0-30 cm is less toxic to *Hyalella azteca* than the deeper strata.

GROUP	IDENTIFICATION	MEAN IN ORIGINAL	RANK SUM	CRIT. VALUE	DF	SIG 0.05
		UNITS				
	Control	8.8750				
2	$I-2$	0.0000	36.00	46.00	8.00	\ast
3	$I-5M$	0.0000	36.00	46.00	8.00	\ast
$\overline{4}$	$I-5T$	2.3750	36.00	46.00	8.00	\ast
5	$I-7M$	0.0000	36.00	46.00	8.00	\ast
n	$I-7T$	3.0000	36.00	46.00	8.00	\ast

TABLE 4.3.8 STATISTICAL ANALYSIS OF *HYALELLA AZTECA* **SURVIVAL DATA, APRIL 1997.**

Critical values are 1 tailed ($k = 5$)

4.3.5 Reference Toxicity Tests

The results of the reference toxicity tests with sodium chloride are summarized in Appendix D.

4.3.6 Summary

Statistically significant (alpha $= 0.05$) acute toxicity effects were observed in the sediments from the October Stations I-1, I-2, I-3, I-5M, I-7M, and I-8 on the amphipod *Hyalella azteca*. In addition, statistically significant (alpha $= 0.05$) mortality was seen on the midge, *Chironomus tentans* in sediments from sites I-2 and I-5M. In the second set of samples evaluated, all sediments (I-2, I-5M-Mid, I-7M-Mid, I-5M-Top, and I-7M-Top) demonstrated a difference in survival that was statistically significant (alpha $= 0.05$) from the control. Furthermore, a statistically significant (alpha $= 0.05$) difference in amphipod survival was observed between shallow and deeper layered sediments (I-5M-Top and I-7M-Top versus 5M-Mid and I-7M-Mid). These results would indicate that more contaminated sediments (I-5M-Mid and I-7M-Mid) have been covered by the deposition of less toxic material. The lower levels of chromium observed in the detailed stratigraphy analyses support these data. These toxicity tests do not prove or disprove that chromium is the toxic agent in the sediments. The sediment from I-2 exhibited the greatest toxicity to amphipods and had a total chromium concentration of 259 mg/kg. In contrast, the sediment at station I-6 had a total chromium concentration of 2,650 mg/kg and exhibited no significant toxicity. Sediment toxicity may be a function of a combination of the heavy metals and other chemicals (e.g., ammonia, etc.) or related to the form that the toxicant exists in. The analyses conducted for this project were for total metals. Since the toxicity of metals in sediments can be a function particle size, acid-volatile sulfide concentration, mineral type, and their association with organic compounds, it is possible that toxicity is related to a complex interaction between the toxicants and the substrate. In consideration of this complexity, it would be very difficult to determine the causative agent/agents.

The results also suggest that *Hyalella azteca* is more sensitive to the pollutants in the sediments than *Chironomus tentans*. The amphipod showed statistically significant mortality α (alpha = 0.05) when compared to the control in six of the eight sediments. The dipteran had statistically significant (alpha $= 0.05$) mortality in only two out of eight sediments. It is interesting to note that a ranking of sediments based on percentage of survival was nearly identical for both species; however, *Hyalella azteca* was more sensitive to the contaminants. In addition, survival variability among the replicates was much greater for the amphipod than that for the midge. This is reflected by the high coefficient of variation (C.V.%) for *Hyalella azteca* as compared to *Chironomus tentans*. These differences in tolerance and variability are attributed to physiological and behavioral differences between these two species.

Stations I-1 and I-2 are located in an area that may be influenced by potential sources located upgradient in White Lake. The presence of elevated chromium levels, animal hide fragments, and hair in the sediments at these stations indicates, however, that the tannery was the predominant source of anthropogenic activity. In Tannery Bay proper, the morphology of the surrounding land around Tannery Bay would prevent other sources from significantly influencing the sediment chemistry. The peninsula located on the northeastern edge of Tannery Bay provides hydrodynamic isolation from any upstream sources. In addition, the westerly flow pattern of White Lake would result in water currents moving past Tannery Bay. These factors would prevent downgradient and upgradient sources from significantly influencing the Bay.

Since the toxic response was observed from both the 0-30 cm and 30-70 cm regions of the sediment cores, it is evident that the agent/agents responsible for the observed toxicity were deposited over an extended period of time. Even though this investigation was unable to determine the chemical/chemicals responsible for the observed toxicity, it is important to consider the following factors in evaluating the source of toxic response:

- the secluded nature of Tannery Bay from the rest of White Lake
- the proximity of the Tannery's discharge and waste disposal areas to the sampling stations
- the depth of sediments that were toxic to amphipods
- the temporal consistency of results with respect to horizontal and vertical extent

These factors preclude the consideration of sources other than the tannery from being causative of the toxic response.

4.4 Benthic Macroinvertebrates

A description of the contents of the elutriated sediment samples is given in Table 4.4.1. Elutriation removes the fine particulate sediments from the samples and provides a better medium to describe the nature of the detrital fraction. Animal hair and/or hide fragments were found in all Tannery Bay locations except for I-8. Animal hair was also noted in exterior station samples from E-7 and E-9. The presence of animal hair at E-9 is interesting since it is approximately one mile down gradient from Tannery Bay and on the opposite side of the lake. This station has a depth of 53 ft and may function as a long term deposition area for contaminants from the Tannery. This observation is consistent with the elevated levels of chromium detected at the site.

The results of the benthic macroinvertebrate enumeration and identification for the October collections are given in Tables 4.4.2. and 4.4.3 The pollution intolerant organisms *Hexagenia* sp. and *Sialis* sp. were found at the control station E-1. These organisms were not detected at the other exterior stations or the Tannery Bay interior locations. The benthic macroinvertebrate assemblages found at the control location reflect a moderate number of organisms representing a diverse group of taxa. The remaining exterior locations are characterized by greater numbers of chironomids and Oligochaetes. Similarly, the Tannery Bay interior stations also have benthic macroinvertebrate populations that are dominated by chironomids and Oligochaetes. The interior stations, however, support dense populations of amphipods (*Hyallella* sp.) and zebra mussels (*Dreissena polymorpha*). *Hyallella* sp. was associated with the dense growth of macrophytes growing above the sediment while *Dreissena polymorpha* was found attached to the surface mats of animal hide fragments. The data for the second sediment collection in April 1997 are shown in Table 4.4.4. The results for the Tannery Bay stations were similar to the October 1996 samples. Chironomid numbers were higher and more taxa were present in the spring. This difference is probably related to the life cycle and body size of these organisms. More early instar individuals may have been present in the fall than the spring; these smaller individuals would be more likely to pass through the screen during elutriation.

The benthic macroinvertebrate data were analyzed by ANOVA methods to determine if significant differences existed between the populations in three regions of the study area. For the October 1996 data, Region 1 included stations within Tannery Bay most impacted by contamination (Stations I-5 and I-6), Region 2 included stations within the Tannery Bay area but less subject to contamination (I-1, I-2, I-3, I-4, I-7, and I-8), and Region 3 included control stations or stations least influenced by contamination (E-1, E-2, E-3, E-4, E-5, E-6, E-7, and E-9). The results of the ANOVA are shown in Tables 4.4.5 and 4.4.6. There was no significant difference between the three regions with respect to the abundance of chironomids and oligochaetes. The abundance of zebra mussels, isopods, gastropods, turbellarians, and amphipods was significantly different with higher numbers found in the Tannery Bay stations. These groups occur at the sediment surface and/or are associated with aquatic macrophytes. Higher abundances in Region 1 reflect the greater number of aquatic plants in this region.

TABLE 4.4.1 DESCRIPTION OF SUBSTRATE MATERIAL LEFT IN THE SAMPLE AFTER ELUTRIATION THROUGH A NITEX SLEEVE WITH OPENINGS OF 0.5-MM.

TABLE 4.4.2 MEAN(± SE) DENSITY PER SQUARE METER OF TAXA COLLECTED AT THE **EXTERIOR STATIONS IN WHITE LAKE IN OCTOBER 1996.**

TABLE 4.4.3 MEAN(± SE) DENSITY PER SQUARE METER OF TAXA COLLECTED AT THE **INTERIOR STATIONS IN WHITE LAKE IN OCTOBER 1996.**

TABLE 4.4.4 MEAN(± SE) DENSITY PER SQUARE METER OF TAXA COLLECTED AT THE **INTERIOR AND CONTROL STATIONS IN WHITE LAKE IN APRIL 1997.**

TABLE 4.4.5 MEAN (+ SE) DENSITY (PER SQUARE METER) OF MOST ABUNDANT BENTHIC MACROINVERTEBRATE TAXA IN THREE REGIONS IN WHITE LAKE, OCTOBER 1996.

Region 1 includes stations within Tannery Bay most impacted by contamination (Stations I-5 and I-6), Region 2 includes stations within the Tannery Bay area but less subject to contamination (I-1, I-2, I-3, I-4, I-7, and I-8), and Region 3 includes control stations or stations least influenced by contamination (E-1, E-2, E-3, E-4, E-5, E-6, E-7, and E-9). Differences between the three regions were tested using ANOVA on $log(x+1)$ transformed values. Values given are the P-levels. Region 1: n=7; Region 2: n=18; Region 3: n=24.

While the analysis of chironomid abundance at the family level show no significant difference between populations in Tannery Bay and the exterior stations, the data for taxa at the genus level produced a different result. A t- Test analysis of the October 1996 abundance of *Chironomus* sp. between the interior and exterior stations yielded a P value of 0.026. *Chironomus* sp. were significantly less abundant in the Tannery Bay stations. Organisms in the genus *Chironomus* commonly feed on detrital material in the sediments. The chironomid populations in Tannery Bay were characterized by more predatory genera/species such as *Cryptochironomus* sp., *Chryptochironomus digitatus-gr*., *Clinotanypus* sp., and *Coelotanypus* sp. These organisms commonly feed on oligochaetes and mircocrustacians (Usinger 1974). Since the grain size and organic carbon content of the exterior and interior stations were similar, both regions should have comparable chironomid populations. These results suggest that the quality of the detrital food source or sediment toxicity maybe responsible for the depression of the *Chironomus* sp. population. The presence of detrital material from the aquatic macrophytes would tend to reduce the probability that food source quality is a significant factor. Sediment toxicity would not affect predatory species to a large extent if the prey populations were abundant.

An ANOVA was also performed on the April 1997 data. The same regions in Tannery Bay were used for analysis. The third region consisted of the control location E-1. The other exterior stations were not sampled during this collection. The results of the ANOVA are shown in Table 4.4.4. As with the previous data set, similar trends with respect to the abundance were noted. There was no significant difference between the three regions with

respect to the abundance of chironomids and oligochaetes. The abundance of zebra mussels, isopods, gastropods, turbellarians, and amphipods were significantly different with higher numbers found in the Tannery Bay stations. As in October, groups most closely associated with aquatic plants or the sediment surface were more abundant in Region 1. The exception were Oligochaetes, which were infaunal forms.

TABLE 4.4.6 MEAN (+ SE) DENSITY PER SQUARE METER OF MOST ABUNDANT BENTHIC MACROINVERTEBRATE GROUPS IN THREE REGIONS IN WHITE LAKE, APRIL 1997.

Region 1 includes stations within Tannery Bay most impacted by contamination (Stations I-5 and I-6), Region 2 includes stations within the Tannery Bay area but less subject to contamination (I-1, I-2, I-3, I-4, and I-7), and Region 3 is basically a control station (E-1). Differences between the three regions were tested using ANOVA on $log(x+1)$ transformed values. Values given are the P-levels. Region 1: n=6; Region 2: n=15; Region 3: n=3.

4.4.1 Comparison Of Benthic Macroinvertebrate And Sediment Toxicity Data

Populations of *Hyalella* sp. and *Chironomus* sp. were present at I-2 and I5M. Sediments from these stations exhibited toxic effects to the same organisms under laboratory conditions. This discrepancy can be explained by sampling bias and environmental factors. As discussed in Section 4.2, typically the Ponar samples sediments from 0-15 cm in depth. However, most of the benthic macroinvertebrate community only occupies the top 2 cm of the sediment. Given the differences in the stratigraphy of chromium, a Ponar sample taken at I-5M would expose organisms to higher contaminant levels in the toxicity test than in the actual environment. The chromium concentration in the Ponar sample from I-5M was 4100 mg/kg while the 0-2 cm stratigraphy layer contained 2740 mg/kg. The difference in toxicity noted between the 0-30 cm core sample and the 30-70 cm region also supports this observation.

The large population of *Hyalella sp.* present at these stations was associated with the macrophytic plants. Under these conditions, the organisms would spend most of their time in the water and not in the sediment. In the laboratory toxicity test, macrophytes are not present, and the organisms burrow into the sediment. While the laboratory toxicity tests show that sediments from these locations are toxic to amphipods, the benthic populations of these

organisms exhibit no evidence of perturbation. The laboratory tests, therefore, reflect toxic chemicals that are deposited in the near surface zone sediments and not the sediment/water interface, which is inhabited by the amphipods. In contrast, populations of *Chironomus* sp. were significantly lower at the interior stations suggesting the presence of an inhibitory agent in the sediments. Predatory chironomids that do not ingest detritus as their primary food source were more abundant than *Chironomus* sp.in Tannery Bay.

4.5 Mercury Bioaccumulation

The bioaccumulation of mercury was investigated under laboratory conditions with *Lumbriculus variegatus* and *in-situ* with mesocosms. The laboratory bioaccumulation evaluation with *Lumbriculus variegatus* also included a four day toxicity screening test.

4.5.1 *Lumbriculus variegatus* Bioaccumulation Test

4.5.1.1 Preliminary Toxicity Screening Test

The preliminary toxicity screening of the White Lake sediments was initiated on October 19, 1996 and completed on October 23, 1996. Composite sediment samples collected on the same day from three different sites were employed in exposing *L. variegatus* over this period. Temperature and dissolved oxygen measurements were taken and recorded twice daily throughout the duration of the test (Appendix C: Table C-1). Temperature varied little, which was expected since the test beakers were kept in a temperature controlled room. The dissolved oxygen never dropped below 40% saturation; consequently, no aeration was required. Conductivity, hardness, alkalinity, ammonia, and pH were determined at the beginning and on the fourth day of the test, and these data are shown in Appendix C: Table C-2. With the exception of ammonia and alkalinity in sample I-7M, these parameters remained relatively constant, with a variation of less than 50%, from initial to final measurements.

The results of the four day toxicity test are provided in Table 4.5.1. The results suggest that these sediments were not acutely toxic to *L. variegatus* over the four day exposure period. Furthermore, any contaminants in the sediment did not seem to inhibit the oligochaetes from burrowing into the sediment. In light of these findings, it may be stated that the variation in the ammonia content and alkalinity in sample I-7M were not important factors in this preliminary screening.

TABLE 4.5.1 SUMMARY OF OLIGACHAETE SURVIVAL DATA OBTAINED WHEN EXPOSED TO WHITE LAKE SEDIMENTS FOR FOUR DAYS

4.5.1.2 Bioaccumulation Test

The bioaccumulation test of the White Lake sediments was initiated on October 25, 1996 and completed on November 21, 1996. The same sediment samples used in the toxicity screening were used to expose *L. variegatus* for the 28 day test period.

As in the toxicity screening, temperature and dissolved oxygen measurements were taken and recorded twice daily throughout the duration of the test (Appendix C: Table C-3). Again, temperature varied little. However, in this test it was noted that the dissolved oxygen was not being maintained at the recommended 40% saturation level, as a result, aeration of the exposure chambers was initiated on day 5 of the test. Conductivity, hardness, alkalinity, ammonia, and pH were determined at the beginning and on the $7th$, $14th$, and final day of the test. These data are shown in Appendix C: Table C-4. Conductivity and pH remained relatively constant from initial to final measurements. Ammonia decreased by more than 80% in all three sediments, alkalinity dropped more than 60% in I-5M and I-7M, and hardness fell more than 50% in only the sediment from I-5M.

The results of the mercury analyses are summarized in Table 4.5.3. The mercury levels in the test organisms exposed to Tannery Bay sediments exhibited similar body burdens as the organisms exposed to the control sediment (E-1P). No significant mercury bioaccumulation was observed under laboratory conditions.

4.5.1.3 Reference Toxicity Test Results

The results of the reference toxicity test for *L. variegatus* are summarized in Appendix E.

TABLE 4.5.2 RESULTS OF MERCURY BIOACCUMULATION EXPERIMENTS WITH

LUMBRICULUS VARIEGATUS

4.5.2 Mesocosms

The mesocosms were deployed near I-7M and E-1P. These points were located closer to the shoreline in both areas due to the depth limitation of the enclosures (3 m). Good recovery was obtained with the catfish from all replicates. Recovery of the fathead minnows however was poor. Low recoveries of the minnows may be a function of predation by the catfish, the recovery technique itself, or losses during the experiment. One of the mesocosms at the I-7M location changed dramatically after the first 10 days of exposure. The water turned black and exhibited a strong sulfur odor. All of the minnows and catfish died during this event. An analysis of the water found an ammonia concentration of 3.8 mg/l, which may have directly caused the toxic response. The loss of this mesocosm appears to be the result of a localized disturbance of the sediments. Gas production from the sediments (methane) may have caused the resuspension of fine particulates and the subsequent release of ammonia. Ammonia release from the sediments was observed during the toxicity experiments (Section 4.3).

The results of mercury analyses on the catfish are presented in Table 4.5.3. Initial mercury levels were similar to the concentrations observed the mesocosms located at Station E-1 and the Tannery Bay location. No evidence of mercury bioaccumulation was noted. These results were similar to the laboratory tests with *Lumbriculus variegatus.* Although elevated mercury concentrations are present in the Tannery Bay sediments, bioaccumulation does not appear to be significant during 30 day laboratory or *in-situ* mesocosm exposures.

TABLE 4.5.3 RESULTS OF MERCURY ANALYSES CONDUCTED ON *ICTALURUS PUNCTATUS* **FROM THE MESOCOSMS**

4.6 Organic Analysis Of Selected Sediment Cores

The results of semivolatiles analyses conducted on the core samples for exterior stations E-7 and E-9 are displayed in Figure 4.6.1. As discussed earlier, Station E-9 was selected to determine if organic chemicals related to the historic discharge from the Hooker Chemical and Plastics facility were still present in White Lake. This facility began operations in 1954 and closed in 1982. The sampling station is located in the deep region near the historical effluent discharge. With the exception of trace amounts of 1,4-dichlorobenzene, none of the target analytes were present in the 0-15 inch region of the core. Detectable levels of dichlorobenzenes (2.4 mg/kg), hexachlorobenzene (2.1 mg/kg), and hexachlorobutadiene (0.66 mg/kg) were found in the 15-30 inch section. In addition, the GC/MS scan also identified PCBs and residues of mirex. The PCBs were confirmed by GC-ECD analysis, and the results are reported in Figure 4.6.1. Lower levels of the same chemicals were found in the 30-45 inch core section. The sections representing the 45-60 inch and the 60-90 inch regions contained no detectable target compounds. Using historical information concerning the Hooker Chemical discharge, the core region below 45 inches probably predates the mid 1950s. The region of 15-45 inches reflects the discharge of process effluent and contaminated groundwater into White Lake from 1954 to 1982. Because none of the chlorinated organic compounds were detected in the top 15 inches, these sediments probably represent material that was deposited after the mid 1980s.

The presence of high levels of PCBs in the 15-30 inch region is interesting in that this material has not previously been associated with the Hooker Chemical discharge. While the PCBs appear to be covered by 15 inches of stable sediment, the extent and source of contamination need to be investigated. Since the E-9 location appears to be a long term deposition zone for sediments from eastern White Lake, it is possible that the PCBs may have originated from a different location.

The deposition of the chlorinated organics at this location also provides information that is useful in the interpretation of the chromium data. The high chromium concentrations found in the top 15 inches of sediment (838 mg/kg) probably represent material deposited prior to 1980 since there are no chlorinated organics associated with the Hooker Chemical discharge detected. It is also interesting to note that the chromium levels are low (49 mg/kg) in the sediments that predate the 1950s. These data suggest that the deposition of chromium at Station E-9 has been increasing since the 1950s. The greatest flux of chromium to this location has occurred after 1980. This pattern is consistent with a mass of contaminated sediment that is moving out of Tannery Bay into eastern White Lake.

The core sample from E-7 contained no detectable semivolatiles. There was no evidence of the deposition of target organic compounds related to the Koch Chemical NPL Site in this area of White Lake.

FIGURE 4.6.1 RESULTS OF SEMIVOLATILES ANALYSIS ON CORE SAMPLES FROM STATIONS E-7 AND E-9.

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5.0 Summary

By using a combination of chemistry, toxicological evaluation, ecological analysis, and radiodating, this investigation has defined the ecological effects and the nature and extent of sediment contamination in the Tannery Bay area of eastern White Lake. The sediments in Tannery Bay represent a source of chromium transport for most of the eastern basin of White Lake. The recent deposition of chromium contaminated sediments exceeding 500 mg/kg in down gradient locations shows that export processes are responsible for the movement of this material from Tannery Bay. Arsenic and mercury appear to be less mobile and are retained in the sediments of Tannery Bay. Chromium export from Tannery Bay into White Lake proper will continue as long as the contaminated sediments are influenced by hydrodynamic circulation patterns and wave action.

Chromium stratigraphy in the Tannery Bay region indicates that the top 15-20 cm of sediment are less contaminated (2,000-4,000 mg/kg) than sediment located at >30 cm $(0.5,000 \text{ mg/kg})$. Radionuclide results suggest that this surface sediment layer is well mixed, however, distinct from the deeper more highly contaminated sediments. Presently this near surface sediment layer (15-20 cm) does not physically mix with the deeper, more contaminated sediment. The 0-20 cm layer is followed by a region (30-80 cm) that contains chromium levels in excess of 20,000 mg/kg. Since the direct discharge of tannery effluent to this area ceased in 1976, evidence of the deposition of sediment with less chromium contamination should be apparent. The lack of a decreasing gradient of chromium concentration in the near surface zone sediments (0-20 cm) suggests that the processes of mixing and resuspension continue to be active in Tannery Bay. In addition, chromium transport to the 0-20 cm sediment zone may also be occuring by other mechanisms including surface runoff of contaminated soils and groundwater advection. The lack of a significant $137Cs$ horizon in the sediments indicates that groundwater is discharging in this region; however, the linkage with chromium mobility requires further investigation.

The laboratory toxicity evaluation of the Tannery Bay sediments (Ponar samples) found six of eight locations to be toxic to amphipods and two of eight locations to be toxic to midges. The amphipod toxicity was found to be dependent on the depth the sediment. Sediments evaluated below 30 cm exhibited extreme toxicity to amphipods while some survival was observed in the region of 0-30 cm. We were unable to identify the chemical/chemicals responsible for the toxicity observed in the sediments. Amphipod populations did not reflect the laboratory sediment toxicity as *Hyalella* sp. was found at the same locations that were toxic to the test organisms. This apparent paradox can be explained by examining the natural habitat of these organisms. The native amphipod populations were primarily associated with macrophytic plants and other submerged materials. They did not appear to be associated with the sediments. Similar abundances of chironomids were found at the interior and exterior stations; however, populations of *Chironomus* sp. were significantly lower in the interior stations. The lower abundances of this genera may reflect a response to toxic chemicals in the sediment since they feed on detrital material. Even though chironomids were found in the Tannery Bay area, a majority of the genera were predators which do not ingest detritus as their primary food source. Finally, mercury bioaccumulation was not observed under laboratory or field conditions.

Chromium concentrations in all locations of Tannery Bay and in five of the six downgradient locations in eastern White Lake exceeded current sediment quality guidelines for probable adverse ecological effects. Most of the Tannery Bay stations exceeded these guidelines by an order of magnitude. Only the background station E-1P had a chromium concentration below the sediment quality guideline that would indicate no adverse effects.

APPENDIX A

Summary Of The Physical And Chemical Data For White Lake Sediments

Table A-1. GPS and Loran Coordinates for Tannery Bay Interior and Exterior Stations.

April 3, 1997 were collected with a Differential GPS

Table A-2. Sampling Station Information and Visual Descriptions for the Tannery Bay Interior and Exterior Core Samples.

Table A-3. Sampling Station Information and Visual Descriptions for the Tannery Bay Interior and Exterior Ponar Samples.

Table A-4. Grain Size Distributions for Tannery Bay Exterior Core Samples.

Table A-5. Grain Size Distributions for Tannery Bay Exterior and Interior Station Ponar Samples.

Table A-6. Metals, TOC, and % Solids Results for the Tannery Bay Interior and Exterior Stations.

Table A-7. Visual Description of Stratigraphy Core Collected at I-5M on October 9, 1996*.

*A water leak developed during extrusion. Core sample was not analyzed.

Table A-8. Visual Description of Stratigraphy Core Collected at I-5M on October 29, 1996.

	Depth (cm) Cr (mg/kg)	Visual Description		Depth (cm) Cr (mg/kg)	Visual Description	
$0 - 2$	2060	Loose black floc	72-74	12900	Grey organic silts	
$2 - 4$	2440	Loose black floc	74-76	10900	Grey organic silts	
$4 - 6$	2280	Loose black floc	76-78	14700	Grey organic silts	
$6 - 8$	2650	Loose black floc	78-80	14800	Grey organic silts	
$8 - 10$	2800	Loose black floc	80-82	41600	Purple organic silts, hair mats	
$10 - 12$	3580	Loose black floc	82-84	14000	Purple organic silts, hair mats	
$12 - 14$	3770	Loose black floc	84-86	6980	Purple organic silts, hair mats	
$14 - 16$	3800	Loose black floc	86-88	6330	Purple organic silts, hair mats	
$16 - 18$	4070	Loose black floc	88-90	7300	Purple organic silts, hair mats	
18-20	4410	Black organic silts	90-92	5690	Purple/red organic silts, hair mats	
$20 - 22$	4070	Black organic silts, hair	92-94	6460	Purple/red organic silts, hair mats	
$22 - 24$	4290	Black organic silts, hair	94-96	11500	Purple/red organic silts, hair mats	
$24 - 26$	4200	Black organic silts, hair	96-98	14100	Purple/red organic silts, hair mats	
26-28	4370	Black organic silts, hair	98-100	7850	Purple/red organic silts, hair mats	
28-30	4500	Black organic silts, hair mats	100-102	14500	Purple organic silts, hair	
30-32	4260	Black organic silts, hair mats	102-104	14000	Purple organic silts, hair	
32-34	4640	Black organic silts	104-106	16400	Purple organic silts, hair	
34-36	5310	Black organic silts	106-108	15100	Purple organic silts, hair	
36-38	5700	Black organic silts	108-110	11500	Purple organic silts, hair	
38-40	18300	Black organic silts	110-112	1670	Purple organic silts, hair	
40-42	20900	Black organic silts	112-114	10300	Purple organic silts, hair	
42-44	20100	Black organic silts	114-116	10100	Purple organic silts, hair	
44-46	23500	Black organic silts	116-118	13100	Purple organic silts, hair	
46-48	34200	Black organic silts	118-120	9850	Purple organic silts, hair	
48-50	37400	Black organic silts	120-122	9270	Purple organic silts, hair	
50-52	43300	Black organic silts	122-124	12100	Purple organic silts, hair	
52-54	61100	Blue silts	124-126	8180	Purple organic silts, hair	
54-56	25400	Black organic silts	126-128	8690	Purple organic silts, hair	
56-58	25800	Black organic silts	128-130	2020	Purple organic silts, hair	
58-60	10500	Black organic silts	130-132	1420	Purple organic silts, hair mats	
60-62	6700	Grey organic silts	132-134	1600	Purple organic silts, hair mats	
$62 - 64$	6640	Grey organic silts	134-136	1430	Purple organic silts, hair mats	
64-66	6910	Grey organic silts	136-138	410	Purple organic silts, hair mats	
68-70	9090	Grey organic silts	138-140	280	Purple organic silts, hair mats	
70-72	9250	Grey organic silts	140-142	4220	Purple organic silts, hair mats	

Table A-9. Visual Description of Stratigraphy Core Collected at I-7M on October 9, 1996.

Table A-10. Spiked Sample Results for Total Chromium in Sediment Samples.

Table A-11. Laboratory Duplicate Sample Results for Total Chromium in Sediment Samples.

Table A-12. Spiked Sample Results for Total Arsenic and Total Mercury in Sediment .

Table A-13. Laboratory Duplicate Sample Results for Total Arsenic, Total Mercury, and TOC in Sediment Samples. Table A-14. Semivolatile Organics Results for Tannery Bay Exterior Stations E-7 and E-9.

Table A-15. Semivolatile Organics Matrix Spike and Matrix Spike Duplicate Results.

* %RPD based on ug spiked

Table A-16. PCB results for Exterior Station E-9.

APPENDIX B

Summary Of Chemical Measurements For The Toxicity Test With Sediments From White Lake

Test No: CH-961101 CH-961101 Toxicant: White Lake Sediment Test Start: 11/1/96 1500

Organism: Hyalella azteca Christianus Christianus Test Stop: 11/11/96 1500 Organism: **Hyalella azteca**

Table B-1. Summary of Initial and Final Chemical Measurements for the *Hyalella azteca* **Sediment Toxicity Tests**

Test No: CM-961101 Analyst: kcb, jh, kg + Toxicant: <u>White Lake Sediment</u> North Test Start: 11/1/96 1500 Organism: **Chironomus tentans** Test Stop: 11/11/96 1500

Table B-4. Summary of Chemical Measurements for the *Chironomus tentans* **Sediment Toxicity Tests.**

Test No: CH-970401 CH-970401 Toxicant: White Lake Sediment Test Start: 4/17/97 1500

Organism: *Hyalella azteca* Test Stop: 4/27/97 1500

Table B-5. Summary of Initial and Final Chemical Measurements for the *Hyalella azteca* **April 1997 Sediment Toxicity Tests.**

APPENDIX C

Summary Of Data For The *Lumbriculus variegatus* **Toxicity Screening And Mercury Bioaccumulation Tests With Sediments From White Lake**

	Test No: AL-961001	Analyst: kcb	
Toxicant:	White Lake	Test Start - 10/19/96	
	Sediment	Date/Time: 1500	
Organism:	Lumbriculus	Test Stop -	10/23/96
	variegatus	Date/Time:	1500

Table C-1. Summary of Daily Temperature and Dissolved Oxygen Measurements for the *Lumbriculus variegatus* **Screening Test.**

Table C-2. Summary of Initial and Final Chemical Measurements the *Lumbriculus variegatus* **Screening Test**

Analyst: kcb, jh, kg Test Start - Date $/T$ ime: 10/25/96 1500 Organism: Lumbriculus variegatus and the state of the Control of Test Stop - Date /Time: 11/21/96 1500

Table C-3. Summary of Daily Temperature and Dissolved Oxygen Measurements for the *Lumbriculus variegatus* **Bioaccumulation Test.**

*started areation

Table C-4. Summary of Initial and Final Chemical Measurements for the *Lumbriculus variegatus* **Bioaccumulation Test.**

APPENDIX D

Summary Reference Test Data For Solid Phase Toxicity Evaluation Of White Lake Sediments

1.0 INTRODUCTION

This report contains the reference toxicity methods and data interpretation for the 96 hour acute tests for *Hyalella azteca* and *Chironomus tentans* when exposed to various concentrations of sodium chloride (NaCl).

2.0 PROCEDURES AND METHODS

Two 96 hour acute static renewal survival tests were performed with both *Hyalella azteca* and *Chironomus tentans*. Methods as outlined in EPA-600/R-94/002 were followed. The *H. azteca* tests were performed from April 14-18, 1997 and the *C. tentans* tests were run from June 13-17, 1997.

2.1 Laboratory Water Supply

A moderately hard water is employed in our facility for *H. azteca* and *C. tentans* cultures. Preparation of the reconstituted laboratory water is outlined in EPA-600/4-91/002. This water is made up in volumes of 200 L on which water quality parameters are run to check for consistencies between batches. Moderately hard water was used to make up the various concentrations of sodium chloride for exposures of *H. azteca* and *C. tentans*.

2.2 Test Organisms

H. azteca and *C. tentans* used in these reference experiments were from the same stock as those organisms employed in the sediment toxicity tests. The *H. azteca* used were 7- 14 days old and *C. tentans* were third instar larvae and 12 to 14 days old.

2.3 Experimental Design

The purpose of this series of tests was to evaluate the "relative sensitivity" of both organisms to our reference toxicant, sodium chloride. *H. azteca* were exposed to five different concentrations of NaCl and one control with 10 replicates, one organism per replicate, for each treatment. The organisms were fed 0.1ml of YCS at the beginning of the test and after 48 hours. Renewal of the exposure solutions occurred after 48 hours. The *C. tentans* tests followed the same procedure as described above, except the concentrations of NaCl were different and the organisms were fed 0.25ml of Tetrafin[®] (4 g/L suspension) on day 0 and 2. Routine parameters were measured prior to the transfer of organisms to their respective exposure vessels and at the end of the test.

2.4 Statistical Analysis

Survival data for all tests were normally distributed according to Chi-square analysis, as a result, estimated EC_{50} values were calculated using the Probit model. Tukey's method of multiple comparisons was employed to determine if there was a significant difference between the EC₅₀ values for *H. azteca* and *C. tentans.*

3.0 RESULTS AND DISCUSSION

Reference toxicity evaluations with *H. azteca* began on April 14, 1997 and on June 13, 1997 for *C. tentans*. The results of the reference toxicity tests are given in Tables D-1–D-4. Statistical analyses are presented in Tables D-5–D-9. All tests satisfied the validity requirement of 90% survival in the control. The routine physical-chemical parameters varied little over the test periods, the data are presented in Tables D-1 and D-2. Fo H. azteca and Tables D-3 and D-4 for *C. tentans*. Dissolved oxygen for *H. azteca* increased over the test period. This is not usual, but in this case it can be attributed to fact that the membrane on the dissolved oxygen probe was changed subsequent to making the initial measurements because it was noted that the old membrane was defective. As expected, conductivity increased with increasing NaCl concentrations.

3.1 *Hyalella azteca*

Survival data for this organism are presented in test numbers Tables D-1 and D-2. The Probit model calculated a 96 hour EC_{50} values of 4.13g/L NaCl with a 95% confidence interval ranging from 3.87, 4.41g/L NaCl for the first test. An EC_{50} value of 4.04g/L with a 95% confidence interval of 3.76 to 4.34g/L NaCl was obtained for the second test. Statistical analyses are presented in Tables D-5 and D-6.

3.2 *Chironomus tentans*

Survival and chemistry results are presented in Tables D-3 and D-4 for this organism. The resulting 96 hour EC_{50} values and 95% confidence intervals were calculated using the Probit model and are 7.84g/L NaCl, [7.43, 8.28] for the first test and 8.07g/L NaCl, [7.59, 8.58] for the second test. Statistical analyses are presented in Tables D-7 and D-8.

3.3 Comparison of Toxicity Test Results

Tukey's method of multiple comparisons found a statistically significant

 $(p = 0.05)$ difference between the EC50 values of the two test organisms. These results are summarized in Table D-9. This indicates that *H. azteca* is more sensitive to the reference toxicant sodium chloride than *C. tentans*.

4.0 SUMMARY

Separate reference toxicity tests with *Hyalella azteca* and *Chironomus tentans* were carried out with sodium chloride. Both sets of tests proved valid since 90% or greater survival in the controls was achieved after the four day period. In addition, it was determined that the amphipod, *H. azteca* is more sensitive to sodium chloride than the dipteran, *C. tentans*.

Table D-1. Summary of Results of Reference Toxicity Test #1 for *Hyalella azteca.*

Date/Time: Test Start - 4/14/97 1300 Date/Time: 4/18/97 1300

0 hr

48 hr

Table D-2. Summary of Results of Reference Toxicity Test #2 for *Hyalella azteca.*

Test No. AH-970402R **AN-970402R** Analyst: PL Date/Time: Test Start - 4/14/97 1300 Date/Time: 4/18/97 1300

0 hr

48 hr

Table D-3. Summary of Results of Reference Toxicity Test #1 for *Chironomus tentans.*

Analyst: JH, KCB Date/Time: Test Start - 6/13/97 1300 Date/Time:

0 hr

48 hr

Table D-4. Summary of Results of Reference Toxicity Test #2 for *Chironomus tentans.*

Date/Time: Test Start - 6/13/97 1300 Date/Time:

0 hr

48 hr

Table D-5 AH-970401R SODIUM CHLORIDE REFERENCE TEST 96-Hour EC50 for *Hyalella azteca*

SUMMARY STATISTICS ON DATA -- Transform: NO TRANSFORMATION

PROBIT ANALYSIS - USING SMOOTHED PROPORTIONS -- Transform: LOG 10 DOSE

Est. Mu = 0.6161 Est. Sigma = 0.0440 $sd = 0.0143$ $sd = 0.0128$

Chi-Square lack of fit $= 0.1952$ Likelihood lack of fit $= 0.3085$ Table Chi-square = 11.3449 (alpha = 0.01, df = 3) Table Chi-square = 7.8147 (alpha = 0.05, df = 3)

PROBIT EC ESTIMATES -- WITHOUT CONTROL DATA

Table D-6 AH-970402R SODIUM CHLORIDE REFERENCE TEST 96-Hour EC50 for *Hyalella azteca*

SUMMARY STATISTICS ON DATA -- Transform: NO TRANSFORMATION

	NUMBER	NUMBER	OBSERVE	SMOOTHE	PREDICTE
DOSE (g/L)	SUBJECTS	OBSERVE	PROPORTI	PROPORTI	PROPORTI
			ON	ON	ON
2.00	10	10	1.0000	1.0000	1.0000
2.80	10	10	1.0000	1.0000	0.9987
3.60	10	8	0.8000	0.8000	0.8283
4.40	10		0.3000	0.3000	0.2441
5.20	10		0.0000	0.0000	0.0197
.	0.6000 m 0.01	0.0521			

PROBIT ANALYSIS - USING SMOOTHED PROPORTIONS -- Transform: LOG 10 DOSE

Est. Mu = 0.6066 Est. Sigma = 0.0531 $sd = 0.0158$ $sd = 0.0151$

Chi-Square lack of fit $= 0.4405$ Likelihood lack of fit $= 0.6414$ Table Chi-square = 11.3449 (alpha = 0.01, df = 3) Table Chi-square = 7.8147 (alpha = 0.05, df = 3)

PROBIT EC ESTIMATES -- WITHOUT CONTROL DATA

Table D-7 AM-970601R SODIUM CHLORIDE REFERENCE TEST 96-Hour EC50 for *Chironomus tentans*

SUMMARY STATISTICS ON DATA -- Transform: NO TRANSFORMATION

PROBIT ANALYSIS - USING SMOOTHED PROPORTIONS -- Transform: LOG 10 DOSE

Est. Mu = 0.8945 Est. Sigma = 0.0470 $sd = 0.0120$ $sd = 0.0113$

Chi-Square lack of fit $= 0.6354$ Likelihood lack of fit $= 0.8044$ Table Chi-square = 11.3449 (alpha = 0.01, df = 3) Table Chi-square = 7.8147 (alpha = 0.05, df = 3)

PROBIT EC ESTIMATES -- WITHOUT CONTROL DATA

Table D-8 AM-970602R SODIUM CHLORIDE REFERENCE TEST 96-Hour EC50 for *Chironomus tentans*

SUMMARY STATISTICS ON DATA -- Transform: NO TRANSFORMATION

	NUMBER	NUMBER	OBSERVE	SMOOTHE	PREDICTE
DOSE(g/L)	SUBJECTS	OBSERVE	PROPORTI	PROPORTI	PROPORTI
		D	ON	ON	ON
6.00	10	10	1.0000	1.0000	0.9868
7.00	10		0.9000	0.9000	0.8566
8.00	10		0.4000	0.4000	0.5259
9.00	10	\mathcal{D}_{\cdot}	0.2000	0.2000	0.2069
10.00	10		0.1000	0.1000	0.0541
Γ \sim Λ \sim	0.0000 \mathbf{E} at \mathbf{C} is the set of \mathbf{C}	0.0500			

PROBIT ANALYSIS - USING SMOOTHED PROPORTIONS -- Transform: LOG 10 DOSE

Est. Mu = 0.9069 Est. Sigma = 0.0580

 $sd = 0.0135$ $sd = 0.0135$

Chi-Square lack of fit $= 1.3379$ Likelihood lack of fit $= 1.4082$ Table Chi-square = 11.3449 (alpha = 0.01, df = 3) Table Chi-square = 7.8147 (alpha = 0.05, df = 3)

PROBIT EC ESTIMATES -- WITHOUT CONTROL DATA

Table D-9 Comparison of 96 Hour EC50 Values for the Reference Toxicant Sodium Chloride Between *Hyalella azteca* **and** *Chironomus tentans*

SUMMARY STATISTICS ON DATA -- Transform: NO TRANSFORMATION

CHI-SQUARE TEST FOR NORMALITY: Actual and Expected Frequencies

Calculated Chi-Square goodness of fit test statistic $= 4.2645$ Table Chi-Square value (alpha $= 0.01$) = 13.277

Data PASS normality test. Continue analysis.

SHAPIRO - WILK'S TEST FOR NORMALITY -- Transform: NO TRANSFORMATION

 $D = 0.029$ $W = 0.981$ Critical W (P = 0.05) (n = 4) = 0.748 Critical W (P = 0.01) (n = 4) = 0.687

Data PASS normality test at P=0.01 level. Continue analysis.

Table D-9 Comparison of 96 Hour EC50 Values for the Reference Toxicant Sodium Chloride Between *Hyalella azteca* **and** *Chironomus tentans* **(continued)**

ANOVA Table -- Transform: NO TRANSFORMATION

Critical F = 98.5025 (alpha = 0.01, df = 1,2)

18.5128 (alpha = 0.05, df = 1,2)

Since $F >$ Critical F REJECT Ho: All equal (alpha = 0.05)

TUKEY METHOD OF MULTIPLE COMPARISONS -- Transform: NO TRANSFORMATION

* = significant difference ($p=0.05$) \cdot = no significant difference Tukey value $(2,2) = 6.08$ s = 0.015