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PROJECT SUMMARY
OCONOMOWOC ELECTROPLATING COMPANY, INCORPORATED SITE
ASHIPPUN, WISCONSIN

The Oconomowoc Electroplating Company, Incorporated (OECI) Site is a former electroplating facility situated in the Town of Ashippun, Dodge County, Wisconsin. The study area is a portion of the Davy Creek riparian wetland adjacent to and downstream of the OECI facility. It is bounded ~~to~~ by agricultural fields, lowland and upland forests, and low density residential/commercial developments. Davy Creek flows in a westerly direction and forms the core of a wetland hydrosystem that drains into the Rock River, approximately 1.2 miles downstream of the site. When operational, the OECI facility discharged electroplating and other wastes to Davy Creek and various site contaminants have been detected as far downstream as the Rock River. The contaminants of concern at this site are cadmium, chromium, copper, nickel, zinc, and cyanide. The historic focus of this investigation is on the development of site specific ecologically derived clean up goals that are protective of the wetland community.

The U.S. Environmental Protection Agency (EPA) Region V Technical Assistance Team (TAT) conducted a study in 1987, in which they established a 500 foot by 450 foot grid, and collected surface and subsurface sediment samples from random grid nodes. That same year, the US EPA Environmental Response Team (ERT) in conjunction with the Response Engineering Analytical Contract (REAC) conducted elutriate toxicity tests on sediment samples collected systematically from 10 locations within the grid. Total metal concentrations (total metal refers to the sum of the cadmium, chromium, copper, nickel, and zinc values) from the TAT study ranged from 200 milligrams per kilogram (mg/kg) to 89,000 mg/kg. Results of toxicity tests conducted with elutriate prepared from sediment samples collected near the outfall indicated an LC50 (concentration resulting in 50% mortality of the test organism) to fathead minnows (*Pimephales promelas*) of approximately 6 percent. Elutriate concentrations estimated to be protective of the environment were determined; however, the toxicity data could not be statistically correlated with the sediment metal data for use in delineating the extent of contaminated sediment targeted for remediation or removal.

In 1990, the US EPA/ERT and REAC conducted an assessment of the site, with the objectives of (1) developing a conceptual model of metal contamination, (2) determining statistical variability associated with sediment sampling, and (3) determining whether toxicity assessment techniques could quantify the effects of metal and cyanide contamination on marsh biota. The ERT/REAC team reestablished the sample grid and collected sediment for metal and cyanide analyses and for an evaluation of toxicity. The effects of metal contamination on the photosynthetic function of wetland vegetation was measured using in-situ fluorometry. Finally, and the bioavailability and toxicity of whole sediment was assessed using single species acute toxicity evaluations employing *Hyalella azteca*.

During the course of three field investigations undertaken in July, August and December of 1990, the grid was reestablished and expanded to 500 by 500 feet. Sediment samples were collected from each 50 foot node, and analyzed in the field for cadmium, chromium, copper, nickel and zinc using X-ray fluorescence (XRF). Thirty of the sediment samples were also analyzed by atomic absorption (AA) spectroscopy as a second measure of contamination, and to establish a calibration model for XRF analysis. A portion of the samples collected were also analyzed for cyanide and Target Analyte List (TAL) metals.

Correlation analysis showed the metals to be highly collocated within a plume of contamination extending from the OECI outfall at the northern edge of the marsh, and southward into Davy Creek. Replicate analyses using XRF and AA yielded fairly similar results for cadmium and zinc, with less correspondence for nickel and copper. Analysis for chromium consistently revealed large differences between the two methods. Statistical comparison of duplicate readings indicated a high degree of variability within the data set, underscoring the fact that XRF is a preliminary screening method.

Contour plots based on XRF results showed that the extent of contamination was greater than previously measured. The boundary of contamination extended further south and west than measured in the 1987 TAT investigation. Cadmium was found to be present in the sediment in quantities as high as 4800 mg/kg, chromium and nickel to 23,000 mg/kg, copper to 22,000 mg/kg, and zinc to 47000 mg/kg. Cyanide analysis revealed no consistent trends, but showed contamination levels as high as 520 mg/kg near the outfall, with lower concentrations at locations further downstream.

Twenty sediment samples analyzed for TAL metals did not reveal concentrations of any other metals above background, with the exception of slightly elevated values for lead at three locations within the contamination plume. Several TAL metals however, exceeded US EPA water quality criteria in surface water samples collected from locations in Davy Creek adjacent to and downstream of the former OECI facility.

Analysis of the photosynthetic data was inconclusive and suggested that the vegetation evaluated is either resistant to metal contamination, or the methodologies employed lack the sensitivity necessary to detect metal stress under conditions encountered at this site. A rangefinding whole sediment toxicity evaluation of four samples indicated that the sediment total metal burden is acutely toxic to *H. azteca*. Further, mortality appears to be directly related to the total metal concentration. The results of the sediment toxicity evaluation indicate that an LC50 total metal burden lies between 158 mg/kg and 7,500 mg/kg. The greatest toxicity was observed when animals were exposed to sediment collected from locations closest to the outfall with decreased toxicity in sediment collected from locations progressively distant.

Results of the investigations summarized above were used to develop a sampling plan for definitive field and laboratory activities conducted in June of 1991, which integrated metal contamination levels with toxicity. This information was used to define boundaries of contaminated sediment required for remedial action. The sample grid and extent of contamination generated in previous investigation provided the spatial framework for this latter phase of the investigation.

A total of 28 sediment samples were collected and analyzed using XRF in the field for cadmium, chromium, copper, nickel and zinc. Of these, eleven were selected for a whole sediment toxicity evaluation using *H. azteca*. As measured by XRF in the field, the total metal concentration ranged from 193 mg/kg to 7817 mg/kg; the total metal burden as measured by AA ranged from 85 mg/kg to 15130 mg/kg. The corresponding toxicity to *H. azteca* ranged from 2 percent mortality to 100 percent mortality. In general, mortality in excess of 80 percent was associated with total metal concentrations greater than 200 mg/kg. However, there was not a clear distinction in mortality associated with total metal concentrations ranging from 220 mg/kg and 650 mg/kg. This may have been due to the variable concentrations of individual metals and cyanide.

Statistical analysis of the toxicity and contaminant data indicated that a weak correlation exists between mortality and the metals of concern. The lack of strong statistical significance was due to broad overlap of individual and total metal concentrations in the samples that exhibited low mortality and the lack of intermediate mortality values in moderately contaminated samples. Additionally, the variable concentration of specific metals and cyanide may have exerted individual effects in specific samples. For example, mortality ranged from 2 percent to 10 percent in three samples with a total metal burden range of 220 mg/kg to 628 mg/kg. In contrast, mortality ranged from 84 percent to 100 percent in eight samples with a total metal burden range of 221 mg/kg to 1260 mg/kg.

Clean-up goals were derived by comparing mortality data to concentrations of cyanide and individual metals of concern. A approach was taken that focused only on the data generated in the definitive investigation as well as one that considered both the definitive and the rangefinding data. The former approach was less conservative, as the population of *H. azteca* employed appeared to be slightly more tolerant than the population used in the latter study. Clean-up goals were derived from both the rangefinding and the definitive data set are the most conservative and are summarized as follows:

Cyanide	Background reference concentration of nondetectable at detection limit of 1.0 mg/kg

Cadmium	Background reference concentration of nondetectable at detection limit of 2.5 mg/kg
Chromium	35 mg/kg
Copper	Background reference concentration of nondetectable at detection limit of 5.0 mg/kg
Nickel	23 mg/kg
Zinc	Background reference concentration of 29 mg/kg

Clean-up goals derived solely from the site specific data set and are summarized as follows:

Cyanide	4 mg/kg
Cadmium	9 mg/kg
Chromium	140 mg/kg
Copper	22 mg/kg
Nickel	54 mg/kg
Zinc	140 mg/kg

These goals were site specific for the area remediated across from the OECI plant area and based on a no observed adverse effect level (NOAEL).

As part of the site remediation, the OECI facility was demolished and sediment removal activities occurred the wetland adjacent to and immediately downstream of the facility. The focus of the current phase of the investigation is on Davy Creek and an associated riparian wetland area downstream of the former OECI facility and adjacent to Fireman Park. A preliminary investigation was conducted in October of 1994 to locate the channel of Davy Creek and collect sediment samples for analysis of TAL metals, acid volatile sulfides (AVS), simultaneously extracted metals (SEM), and total organic carbon (TOC). The highest concentrations of cadmium, chromium, copper, nickel, and zinc were detected in sediment collected adjacent to the north bank of Davy Creek, with concentrations of 3200, 15000, 12000, 18000, and 18000 mg/kg, respectively. In contrast, lower levels were detected in a corresponding sample collected from the south bank where cadmium, chromium, copper, nickel, and zinc concentrations were 110, 330, 310, 280, 980 mg/kg, respectively. Further downstream, the copper, cadmium, chromium, nickel, and zinc concentrations ranged to 5500, 580, 7200, 6000, and 6300 mg/kg in three samples collected from a transect perpendicular to the axis of Davy Creek. Although no clear pattern of metal deposition was discernable, it appears that the higher metal concentrations are associated with the outer flood plain of Davy Creek rather than the stream banks or inner flood plain.

Results of the preliminary investigation summarized above as well as the historic database was used to develop a sampling plan for definitive field and laboratory activities conducted in August of 1995. As in 1991, the bioavailability and toxicity of whole sediment was assessed using a single species whole sediment toxicity evaluation. Unlike the 1991 investigation when the surrogate was *H. azteca*, larvae of the midge *Chironomus tentans*

(Diptera: Chironomidae) was used. This investigation continued to make use of XRF to identify samples within a predetermined metal concentration gradient. A total of 34 sediment samples were collected and analyzed using XRF in the field for cadmium, chromium, copper, nickel and zinc.

Consistent with previous investigation, the five metals of concern and cyanide continue to be collocated within a plume of contamination extending from the former OECI facility westward to Davy Creek and associated riparian wetlands. As measured by XRF, the total metal burden in samples selected for the toxicity evaluation ranged from 92 mg/kg to 20235 mg/kg; the total metal burden as measured by AA ranged from 81 mg/kg to 21300 mg/kg. Unlike the previous investigation, the mortality of *C. tentans* associated with the sediment metal gradient was not significantly different from the OECI field reference or the laboratory control and ranged from 7 to 40 percent. Similarly, the growth of *C. tentans* was not significantly reduced by exposure to site sediment. The total SEM burden to AVS ratios were greater than one ($\bar{x} = 2.68$) for most locations and suggests that considerable toxicity of benthic organisms would be observed. That was not the case and the results of this evaluation indicate that AVS is not a good predictor of sediment metal bioavailability and toxicity at this site.

The lack of significant mortality or a reduction in growth in the *C. tentans* whole sediment toxicity assay implies that remediation of the current study area may not be required. However, previous investigation in the wetland adjacent to the former OECI facility using the *H. azteca* solid phase toxicity assay suggests otherwise. As discussed above, toxicity in the *H. azteca* assay in excess of 80 percent was associated with total metal concentrations greater than 200 mg/kg. It was recognized that interspecific variation, in addition to test design, diluent water chemistry, test duration, and endpoint selection, among other things, may be responsible for the observed disparity in the *Hyalella* and the *Chironomus* data sets.

As mentioned above, the results of the current phase of this investigation suggest that the contaminants present in the wetland sediment are not likely to result in deleterious ecological effects.

1.0 INTRODUCTION

1.1 Site Description

The Oconomowoc Electroplating Company, Incorporated (OECI) Site is situated in the Town of Ashippun, Dodge County, Wisconsin and is the location of a former electroplating facility (Figure 1). When operational, the OECI facility discharged electroplating and other wastes to Davy Creek resulting in the contamination of sediment with cadmium, detected in concentrations ranging to 4800 milligrams per kilogram (mg/kg), copper to 22000 mg/kg, chromium and nickel to 23000 mg/kg, zinc to 47000 mg/kg, and cyanide to 520 mg/kg (Weston, 1988, 1991a). Analytical results indicate that the metals are collocated within a plume of contamination that extends from the former OECI outfall at the northern edge of the wetland into the Davy Creek and Rock River hydrosystems. A removal action in the wetland area immediately adjacent to the facility was necessitated by the results of a whole sediment toxicity evaluation which indicated that contaminants are acutely toxic to *Hyalella azteca*.

Existing data indicate that elevated concentrations of Target Analyte List (TAL) metals are present in the Davy Creek wetland area adjacent to Fireman Park (Weston 1995) The highest concentrations of cadmium, chromium, copper, nickel, and zinc were detected in sediment collected adjacent to Davy Creek, where concentrations were 3200, 15000, 12000, 18000, and 18000 mg/kg, respectively. Approximately 50 feet downstream, the cadmium, chromium, copper, nickel, and zinc concentrations ranged to 580, 7200, 5500, 6000, and 6300 mg/kg in three samples collected from a transect perpendicular to the axis of Davy Creek. Cadmium, chromium, copper, nickel, and zinc continued to be detected in elevated concentrations as far downstream as the Rock River (REAC, 1992b).

1.2 Investigative History

The US Environmental Protection Agency (EPA) Region V Technical Assistance Team (TAT) conducted a study in 1987, in which they established a 500 foot by 450 foot grid, and collected surface and subsurface sediment samples from random grid nodes. That same year, the US EPA Environmental Response Team (ERT) in conjunction with the Response Engineering Analytical Contract (REAC) conducted elutriate toxicity tests on sediment samples collected systematically from 10 locations within the grid. Total metal concentrations (total metal refers to the sum of the cadmium, chromium, copper, nickel, and zinc values) from the TAT study ranged from 200 milligrams per kilogram (mg/kg) to 89,000 mg/kg. Results of toxicity tests conducted with elutriate prepared from sediment samples collected near the outfall indicated an LC50 (concentration resulting in 50% mortality of the test organism) to fathead minnows (*Pimephales promelas*) of approximately 6 percent. Elutriate concentrations estimated to be protective of the environment were determined; however, the toxicity data could not be statistically correlated with the sediment metal data for use in delineating the extent of contaminated sediment targeted for remediation or removal.

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Analysis of the photosynthetic data was inconclusive and suggested that the vegetation evaluated was unaffected or the methodologies employed lack the sensitivity necessary to detect metal stress under conditions encountered at this site. A rangefinding whole sediment toxicity evaluation of four samples indicated that the sediment total metal burden is acutely toxic to *H. azteca*. Further, mortality appears to be directly related to the total metal concentration. The results of the sediment toxicity evaluation indicate that an LC50 total metal burden lies between 158 mg/kg and 7,500 mg/kg. The greatest toxicity was observed when animals were exposed to sediment collected from locations closest to the outfall with decreased toxicity in sediment collected from locations progressively distant.

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Clean-up goals derived solely from the site specific data set and are summarized as follows:

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These goals are site for the area remediated across from the OECI plant area and based on a no observed adverse effect level.

As part of the site remediation, the OECI facility was demolished and sediment removal activities occurred the wetland adjacent to and immediately downstream of the facility. The focus of the current phase of the investigation is on Davy Creek and an associated riparian wetland area downstream of the former OECI facility and adjacent to Fireman Park. A preliminary investigation was conducted in October of 1994 to locate the channel of Davy Creek and collect sediment samples for analysis of TAL metals, acid volatile sulfides (AVS), simultaneously extracted metals (SEM), and total organic carbon (TOC). The highest concentrations of cadmium, chromium, copper, nickel, and zinc were detected in sediment collected adjacent to the north bank of Davy Creek, with concentrations of 3200, 15000, 12000, 18000, and 18000 mg/kg, respectively. In contrast, lower levels were detected in a corresponding sample collected from the south bank where cadmium, chromium, copper, nickel, and zinc concentrations were 110, 330, 310, 280, 980 mg/kg, respectively. Further downstream, the copper, cadmium, chromium, nickel, and zinc concentrations ranged to 5500, 580, 7200, 6000, and 6300 mg/kg in three samples collected from a transect perpendicular to the axis of Davy Creek. Although no clear pattern of metal deposition was discernable, it appears that the higher metal concentrations are associated with the outer flood plain of Davy Creek rather than the stream banks or inner flood plain.

1.3 Project Objective

The objective of the current phase of this investigation is to evaluate the toxicity of metal and cyanide contaminated sediment collected from the wetland downstream of the former OECI facility and adjacent to a recreational area known as Fireman Park. This area is approximately 1,000 feet downstream of the former OECI facility and is located in the area identified as the State of Wisconsin Project Area. This data is anticiapted to be utilized by the US EPA to support an ecological risk assessment.

2.0 METHODS

2.1 Field Activities and Investigative Team

On July 31 through August 3, 1995 the US EPA/ERT and REAC conducted a field investigation at the OECI Site, Ashippun Wisconsin. Present were David W. Charters, US EPA/ERT Work Assignment Manager, Nancy Finley, US Fish and Wildlife Service, and Mark Finley, Christopher Gussman, Richard Henry, Mark Huston, Philip Kim, and George Molnar, REAC. Christopher Gussman, Richard Henry, and Philip Kim arrived on July 31, 1995 to organize equipment and establish a work and staging area. Nancy Finley, Mark Finley, Mark Huston, and George Molnar arrived on August 1, 1995 and David W. Charters arrived on August 2, 1995. Throughout the field investigation, the equipment was stored in locked trucks within the secured confines of the former OECI facility. All sampling, sample management, logistical, and XRF activities also occurred within or were staged from this location. Activities completed during this investigation included the following:

- establishment of a work and staging area within the secured confines of the former OECI facility
- collection of sediment from the Davy Creek wetland area adjacent to Fireman Park for field screening using XRF
- analysis of select sediment samples for TAL metals, cyanide, TOC, AVS, SEM, grain size, and toxicity

2.2 Investigative Strategy

Existing data and results of the preliminary survey indicate that elevated concentrations of TAL metals are present in the Davy Creek wetland area adjacent to Fireman Park however, the spatial extent of contamination has not been established (Weston, 1995). As discussed previously, no clear pattern of metal deposition is discernable, and it appears that higher metal concentrations are associated with the outer flood plain of Davy Creek rather than the stream banks or inner flood plain and that metal concentrations decrease with increasing distance from the site.

Previous investigation in the OECI study area has indicated that a total metal concentration yielding survival of *H. azteca* not significantly different than the reference lies between background (approximately 200 mg/kg total metals) and approximately 650 mg/kg (Weston, 1991b; Weston, 1992a). Additionally, the literature suggests that an LC50 total metal burden for *C. tentans* lies between 1000 and 2000 mg/kg and that the no observed adverse effect level (NOAEL) will range well below this (Appendix A). The sampling effort was aimed at the collection of sediment within this metal concentration range. The species chosen for the toxicity test are species that are anticipated based on the phisical characteristics of the site and the water quality. *C. tentans* was chosen as the species that was approriate as dissolved oxygen in the surface water was less than 3% oxygen saturation.

Sampling locations in the current phase of the investigation were initially selected on the basis of preliminary analytical results and anticipated sediment deposition patterns. Subsequent locations were selected on the basis of field screening results, topographic characteristics, and distance from the Davy Creek channel. The areas sampled were broadly representative of the Davy Creek hydrosystem in terms of hydrologic, ecological, and physical characteristics. To ensure that the samples submitted for laboratory analyses bracket a toxicologically significant concentration range, sediment was screened in the field with XRF. The sampling effort was terminated when a total of 11 samples (10 contaminated samples and one reference sample) were collected along the target gradient.

2.3 Study Area

The study area is a 1-acre portion of the wetland downstream of the former OECI facility and adjacent to a recreational area known as Fireman Park (Figure 2). The area consists of wetlands surrounding Davy Creek and is bounded by agricultural fields, lowland and upland forests, and low density residential/commercial developments. Davy Creek flows in a westerly direction and forms the core of the wetland hydrosystem that drains into the Rock River, approximately 1.2-miles downstream of the site. Davy Creek is a low gradient, third order stream that meanders through the wetland, often flowing beneath encroaching vegetation which has formed a floating mat indistinguishable from the surrounding landscape. Where exposed, the surface water is typically covered with a thick mat of duckweed (*Lemna minor*). Although the stream is less than 4 feet wide, it is at least 5 feet deep in places. The study area is dominated by reed canary grass (*Phalaris arundinacea*), which forms an almost pure monoculture in the wetland areas adjacent to Davy Creek. The open portions of the wetland are dotted with the large trunks of dead or dying ash (*Fraxinus pennsylvanica*). Areas further to the north and south are slightly higher in elevation as perceived by plant species, such as bluejoint grass (*Calamagrostis canadensis*), and goldenrods

(*Solidago* sp.), which are adapted for less saturated conditions than the reed canary grass. The borders of the wetland are forested with large stands of ash along with several species of willow (*Salix nigra, S. amygdaloides, S. exigua, and S. bebbiana*) and red maple (*Acer rubrum*).

2.4 Wetland Sediment Sampling

Locations sampled during the preliminary investigation were identified by referencing existing landmarks and wooden stakes driven into the sediment. Candidate locations for the current investigation were selected on the basis of existing data, XRF results, surface water drainage patterns, topography, and vegetation patterns. Each location was marked with a 6-foot wooden stake that was spray-painted orange, labeled with the appropriate identification number, and securely driven into the sediment. Due to the relatively high concentration of metals observed at most of the initial sampling locations, it was necessary to range slightly farther downstream and north of Davy Creek than originally anticipated.

Sediment for all analyses with the exception of AVS/SEM was collected as per ERT/REAC Standard Operating Procedure (SOP) # 2016, Sediment Sampling. A four-inch hand auger was used to sample sediment from the 0 to 6 inch depth. The sediment is located beneath a layer of recently deposited (i.e. last seasons growth) and matted organic material which was pushed aside prior to sampling. Several collocated borings were generally required to collect a volume of sediment sufficient to fulfill the analytical requirements. Individual grabs of sediment were extracted from the auger, composited into a 2.5-gallon plastic bucket, and homogenized with a plastic trowel until approximately 1 gallon of sediment was collected. The buckets were labelled with the location identification number and transported to the staging area where a 4-ounce aliquot was removed for determination of metals by XRF. The sample buckets were sealed and archived on ice and secured in the staging area pending the results of the field screening. When a sufficient number of samples with the specified physical/chemical characteristics were collected, aliquots for laboratory analyses were dispensed into appropriate sample containers and placed on wet ice at 4 degrees centigrade (°C). Residual material from samples that were selected for analytical determinations, as well as samples not selected, were returned to the site. Two additional samples were collected from the wetland area adjacent to the Fireman's Park in the area previously remediated. These samples were designated FILLA and FILLB and were collected for XRF screening only.

A sample for analysis of AVS/SEM was collected from each location selected for laboratory analyses. Each sample consisted of a 12-inch sediment core, and AVS/SEM determinations were made from an aliquot removed from the 1 to 2-inch depth. Samples were collected using an acetate lined core sampler as per ERT/REAC SOP #2016, Sediment Sampling. To minimize the disturbance of sediment, the device was used without the standard eggshell check valve. The matted organic layer was cleared from the sampling area and the coring device was pushed completely into the sediment. Upon recovery, the core sampler was disassembled and the acetate sleeve carefully removed and sealed at both ends with a plastic cap; head space was not present in any of the cores collected. The caps were taped securely with duct tape and the location identification number and the orientation of the sediment was indicated on the acetate sleeve using a waterproof marker and appropriate arrows. The acetate sleeve was placed in individual resealable plastic bags and wrapped with duct tape. The bag and enclosed sample were placed in a cooler in an upright orientation (i.e., the sediment surface up) and kept on wet ice at 4°C. Existing data and the literature suggest that there can be high AVS/SEM variability within relatively small areas. To quantify the degree of variation, three additional cores were collected from a 1-square meter area at each of three locations. Areas of low, moderate, and high contamination (location numbers REF, 8, and 3 respectively) were selected for additional sampling. As above, the AVS/SEM determinations were made from an aliquot removed from the surface to 1 inch depth in these sleeves.

A correlation analysis was performed using AA results to determine if the contaminants were uniformly distributed. Total organic carbon, cyanide, and toxicity values were included in this analysis as well. This analysis was performed using SAS statistical software (SAS, 1988).

Sediment samples were relinquished to the REAC laboratory, Edison NJ for analysis of TAL metals and grain size; to Southwest Research, San Antonio, TX for analysis of cyanide and TOC; and to Michigan State University, East Lansing, MI for analysis of toxicity. Specific analytical methods are discussed in Appendix B and D.

2.5 X-ray Fluorescence

The concentration of cadmium, chromium, copper, nickel, and zinc in all samples were determined on-site using a field portable Sepctrace 9000 XRF. The Spectrace 9000 XRF is a multi-element analyzer that permits the simultaneous determination of up to 25 metals, ranging from atomic numbers 16 (sulfur) to 92 (uranium). This technique is relatively inexpensive and less time consuming than AA techniques. Further, the procedure provided real-time results which allowed the field team to fine tune decisions concerning the number and location of samples.

The Spectrace unit was operated and calibrated as per the operating manual supplied by the manufacturer, ERT/REAC SOP #1713, Spectrace 9000 Field Portable X-Ray Fluorescence Operating Procedures, and ERT/REAC SOP #1710, General Considerations for Using X-Ray Fluorescence. The specific procedures and instrument settings used in this field investigation are discussed in Appendix C. An instrument logbook was used to document XRF field calibration, energy and resolution checks, and other field analytical data. Data disks of raw and processed XRF results were generated and archived for future project documentation or reanalysis if sample anomalies occurred. The Spectrace 9000 unit was regularly calibrated by taking measurements on a set of standards. Approximately 94 percent of the samples were systematically selected for duplicate XRF readings and approximately 20 percent of the samples were analyzed in replicate. The XRF values discussed throughout this report are the mean of duplicate and/or replicate observations made at a particular location.

Although *in-situ* determinations are possible, the high moisture content of the sediment necessitated that all samples were collected for *ex-situ* analysis at the staging area. A 4-ounce aliquot of homogenized sediment was removed from the sample bucket, placed in an aluminum weight boat, and dried in an oven. The dried sediment was disaggregated and passed through a decontaminated number 10-mesh (2 millimeter (mm)) stainless steel sieve to remove pebbles, organic matter, and other extraneous material. A 31-mm polyethylene X-ray sample cup was labeled, filled with approximately five grams of sediment, and sealed with polypropylene X-ray film. The sample cup was placed directly on the XRF probe aperture window and the instrument initialized for analysis. The sample number and the XRF analytical results were stored in the Spectrace internal datalogger memory and manually recorded in an XRF laboratory notebook.

The cadmium, chromium, copper, nickel, and zinc results of a sand blank and a set of three National Institute of Standards and Technology Standard Reference Materials (NIST-SRMs) were used to determine the minimum detection limit (MDL), the minimum quantitation limit (MQL), and the accuracy/precision for each analyte. A statistical approach was used to derive the MDL and MQL. Multiple analyses of the NIST-SRMs were run throughout the analytical episode, and a mean and standard deviation of a population (n) with n-1 were calculated. The MDL was set at three times the standard deviation of the mean and the MQL was set at ten times the standard deviation of the mean. X-ray fluorescence results below the MDL were qualified with a "U", signifying the instrument response was indistinguishable from signal noise and below the detection limit. X-ray fluorescence results above the MDL but below the MQL were qualified with a "J", signifying the instrument response was distinguishable from signal noise but below a predetermined and statistically reliable quantification limit. The J value is considered an estimated concentration associated with a degree of statistical uncertainty.

As mentioned above, the XRF data set was used in the field to fine-tune the sampling effort and select sediment for additional analytical determinations and the toxicity evaluation. The uncertainty associated with the field data was estimated by evaluating the qualifiers applied to the XRF results. The proportion of values that were qualified with either a U or J were calculated for each metal of concern. The proportion of values falling below the MDL and between the MDL and the MQL is an estimate of the confidence in each data set. The XRF data was also compared to the TAL metal results to determine the accuracy associated with the field screening data and degree of correspondence between these two methods. The relative percent difference (RPD) between the two data sets was determined, which assesses the validity of the XRF calibration and the data. The RPD between the XRF and AA data sets was calculated as follows:

$$\text{RPD} = \frac{(|\text{AA DATA SET} - \text{XRF DATA SET}|)}{0.5 \times (\text{AA DATA SET} + \text{XRF DATA SET})} \times 100$$

2.6 Sediment Toxicity Evaluation

A 10-day whole sediment toxicity assay was employed to evaluate the bioavailability and toxicity of contaminants in the sediment. Larvae of the midge *C. tentans* served as a surrogate for the wetland community. In this assay, the surrogate was exposed to site contaminants in a sediment and diluent water microcosm. As discussed previously, contaminant exposure pathways and mechanisms are a function of the life history characteristics of a biological receptor. Larval *C. tentans* are bottom dwelling, burrowing organisms that maintain a strong physical contact with the substrate and feed on detrital matter and vegetative debris incorporated into the sediment. Likely exposure routes include ingestion of contaminated items and direct physical contact (especially respiratory surfaces) with contaminated sediment and pore water.

Toxicity test procedures were similar to those described in Giesy et al. 1989; Mosher 1982; Mosher and Adams 1982; and Mosher et al. 1982 wherein *C. tentans* larvae are exposed to sediment in a static system. Specific methods, procedures and Quality Assurance/Quality Control (QA/QC) criteria are described in Appendix D. The endpoints were mortality and growth, and were noted at the conclusion of the exposure period. Mortality in the site sediment was compared to the OECI field reference and laboratory control sediment. Similarly, growth in the site sediment was compared to the biomass (dry weight) of organisms grown the OECI field reference area and laboratory control sediment. Behavioral abnormalities (i.e., avoidance of sediment) were noted throughout the duration of the exposure, but such observations are not completely reliable due to the burrowing habits and sessile nature of *C. tentans* larva.

The test organisms were selected from the Michigan State University, Aquatic Toxicology Laboratory culture and were of uniform age (second instar) and size at the start of the assay. This culture has been continuously maintained for nine years with periodic additions of egg masses from EPA Duluth and National Biological Service cultures to maintain genetic diversity.

A laboratory control sediment was collected by the Michigan Stat University from Carp Lake, a field location of known environmental quality. Sediment collected from Carp Lake has been used by the University for laboratory toxicity test controls and other aquatic studies for several years, and an extensive database exists regarding environmental conditions and quality. The laboratory control test was performed in conjunction with the site sediment under identical conditions. To fulfill the QA/QC objectives, the pH, dissolved oxygen, and temperature was maintained within test protocol limits throughout the duration of the test. Additionally, mortality was not to exceed 20 percent in the control (Appendix D).

The diluent water used was of known quality from a source familiar to the testing laboratory. The total hardness and alkalinity were determined at the start and conclusion of the exposure period and the pH, dissolved oxygen, and temperature were measured on a daily basis. Dissolved oxygen was maintained above 60 percent saturation by gently aerating the test chambers with Pasteur pipets that extend 2 to 4 mm below the water surface in a fashion that did not cause turbulence or disturb the sediment surface. The test temperature was maintained at 23 +/- 2°C. Lighting was maintained at 50 to 100 foot candles with a 16-hour light and 8-hour dark photoperiod and a 30-minute phase-in/phase-out period. The diluent water lost to evaporation was replaced on daily basis with distilled water in a way that minimized turbulence and disturbance of the sediment. The test organisms were fed 0.1 milliliter (ml) of a 0.06 gram per millimeter (g/ml) Tetramin suspension on a daily basis. Preparation of food and feeding rates are described in detail in Nebeker *et al.* (1984).

Whole sediment used 15 replicate plastic 50 ml centrifuge tubes for each test and control sediment. Each chamber contained approximately 7.5 g (wet weight) of sediment and 47 ml of dilution water. Prior to initiating the test, the sediment was homogenized in the shipping container and sieved through a 1 mm mesh to remove large particles and potential predators. The diluent water and sediment was added to the test chamber and allowed to settle for 24 hours prior to the introduction of the test organisms. One individual test organism was placed in each of the 15 replicate chambers in a random fashion.

At the conclusion of the test period, surviving organisms were recovered by transferring the sediment to glass culture dishes and separating the organisms from debris. This was facilitated by sieving the sediment. Organisms not recovered were presumed to have died during the assay. Surviving organisms were rinsed with distilled water, transferred to individual tared aluminum weighing boats, and baked at 80°C until dry. When dry, the boats were transferred to a desiccator, allowed to cool, and weighed to determine dry weight.

A reference toxicant test of the organisms was conducted to determine the appropriateness of the test population. As described in Nebeker *et al.* (1986), a reference toxicant test of the organisms was conducted to determine the sensitivity of the test population. Cadmium chloride ($CdCl_2$) spiked Florissant soil was tested under conditions identical to those described above.

Statistical interpretation of the toxicity test results was performed using analysis of variance (ANOVA). If the ANOVA identified a difference between treatment means, multiple comparisons were performed to statistically identify treatment means that were significantly different. The data were analyzed using Dunnet's T test to identify mean dry weights that were significantly different from the control means. Tukey's test was used to identify significant differences among means. The hypothes that mortality and growth in the control is equal to mortality and growth in each site sediment was tested with Fisher's Exact Test. These analyses was performed using SAS statistical software (SAS, 1988).

2.7 *In-Situ* Water Quality

In-situ water quality of Davy Creek was determined with a Hydrolab Surveyor field monitoring instrument. The instrument was calibrated prior to use, and was operated as per Hydrolab Corporation Surveyor Operating Manual and ERT/REAC SOP #2139, Operation of the Hydrolab Surveyor Water Quality Management System. A post-use calibration was also performed to ensure that the data collected was not adversely affected by sensor fouling or instrument drift. Parameters measured included dissolved oxygen, conductivity, pH, oxidation-reduction potential (ORP), temperature, and depth. Three locations in Davy Creek in the general vicinity of the sediment sampling activities were evaluated (Figure 2).

2.8 Standard Operating Procedures

Where possible, dedicated field equipment was utilized, otherwise, equipment was thoroughly decontaminated both prior to and following all sampling activities as per ERT/REAC SOP #2006, Sampling and Equipment Decontamination. The procedure used was as follows:

- detergent and potable water wash;
- nitric acid wash;
- distilled water rinse;
- acetone wash;
- distilled water rinse (2X);
- air dry;
- aluminum foil wrap.

The selected environmental matrices were sampled utilizing the methodologies specified above. Field sampling, documentation, chain of custody, and sample handling procedures not detailed above followed ERT/REAC SOPs #2001, General Field Sampling Guidelines; #2002, Sample Documentation; #2004, Sample Packaging and Shipment; and #2005, QA/QC Samples; and any other procedure applicable for the media sampled. Field data, site characteristics, and observations were recorded in field logbooks, on field data sheets, and were photodocumented. Each field team member was responsible for documenting all activities and observations as appropriate. The appropriate health and safety precautions were followed as per

ERT/REAC policy and guidelines (ERT/REAC SOP series 3000) and the Site Health and Safety Plan.

Once collected, the samples were preserved and placed in containers suitable for the matrices and designated analyses as specified in REAC SOP # 2003, Sample Storage, Preservation, and Handling by Parameter or Group of Parameters. Because surrogate species for toxicity evaluations are exposed to varying concentrations of contaminated sample material, no chemical preservatives were used for samples thus designated. The preservative and storage protocol was, therefore, limited to holding the samples on ice at four degrees centigrade for the holding time specified by parameter or group of parameters in ERT/REAC SOP #2003. Prior to shipping (ERT/REAC SOP #2004), the laboratory performing the specified analyses were notified of any potential hazards that may be associated with the samples. Sample material remaining following analysis and data validation was disposed of in accordance with the appropriate regulations and protocol.

3.0 RESULTS

3.1 Results of Wetland Sediment Analyses

A total of 34 sediment samples were collected and screened in the field for cadmium, chromium, copper, nickel, and zinc using XRF. Results were typically available to the sampling team within 12 hours of sampling and are summarized in Table 1. These values were used to fine-tune the sampling effort and select samples within the range of metal concentrations targeted for additional analytical determinations and the toxicity evaluation. The total XRF metal burden (the total metal burden is the sum of the cadmium, chromium, copper, nickel, and zinc values) ranged from 84 mg/kg at location 33 to 26000 mg/kg at location 3. Although not detected at a number of locations in the wetland, the largest percent of the total metal burden was typically the result of chromium, which ranged in concentration to 8500 mg/kg at location 3. Nickel also was also a dominant component of the total burden and ranged to 8300 mg/kg at location 3. Zinc and copper were intermediate in concentration and ranged to 4200 and 3900 mg/kg, respectively. Cadmium was rarely detected in concentrations above the detection limit.

The total metal burden in FILLA and FILLB was 1375 and 1370 mg/kg, respectively. Chromium, copper, nickel, and zinc were detected by XRF in concentrations similar to those detected in the locations 7, 10, 13, 16, 19, 24, 28, and 30.

The quality of the XRF data generated in the field was assessed using a statistical approach, and collectively, a high percentage of the observations used to make field decisions were qualified (Table 2). Of the 390 XRF observation, 228 were qualified as below the MDL or MQL. A total of 112 XRF observations were below the MDL implying the instrument response was statistically indistinguishable from random variation in the fluorescence signal, and the analyte is reported as not detected at the indicated concentration. Of these, the largest proportion were associated with cadmium (83 percent) with fewer associated with chromium, copper, and nickel, and none associated with zinc. Similarly, a total of 116 XRF observations fell between the MDL and the MQL. A value within this range implies that the instrument response is distinguishable from random variation in the fluorescence signal, but is estimated and still associated with a degree of statistical uncertainty. In particular, 45 and 46 percent of the chromium and nickel values, respectively were between the MDL and the MQL; 23, 21, 13 percent of the copper, zinc, and cadmium values, respectively were between the MDL and the MQL.

The sediment samples submitted for the analytical determinations and the toxicity evaluation were selected on the basis of the unqualified XRF total metal concentration gradient (Table 3). The total metal gradient ranged from 97 mg/kg at location 33 to 20235 mg/kg at location 3, and the total metal burden at the reference location was 92 mg/kg. Zinc was the only metal detected by XRF above the MDL at all the selected locations and ranged to 3600 mg/kg, whereas cadmium, chromium, copper, and nickel were not detected at a number of locations. Cadmium was detected by XRF above the MDL at only three of the locations submitted for laboratory analyses and ranged to 850 mg/kg. Chromium, copper, and nickel were detected at 7, 6, and 8 locations, and ranged to 6550, 2085, and 7150 mg/kg, respectively. When detected, the individual metals increased roughly in proportion to the total metal gradient, however the concentrations were not monotonically increasing as specified by the probit and trimmed Spearman-Karber methods of determining an LC50 (Finney 1971; Hamilton et al; 1977).

Results of the analysis of sediment for TAL metals using AA spectroscopy are summarized in Tables 4 and 5. As suggested by the XRF results, the highest concentrations of the metals of concern were detected at location 3. In addition, concentrations of several other TAL metals were highest at this location including aluminum, barium, beryllium, cobalt, lead, mercury, potassium, selenium, sodium, vanadium, and silver. In contrast to the XRF results, the dominant metal of concern is chromium, but only at the locations where the highest total metal burdens were detected. These include locations 16, 26, 8, 32, and 3 where the total metal burden ranged from 1036 to 21300 mg/kg and the concentration of chromium ranged from 290 to 7300 mg/kg. At other locations, the total metal burden ranged from 81 to 902 mg/kg and zinc was the dominant metal of concern. Chromium was also detected at these locations, but in lower concentrations. A correlation analysis was performed using the results of the AA analysis to determine if cadmium, chromium, copper, nickel, and zinc were collocated. The analytical results were not normally distributed and were log normalized prior to analysis using the Pearson correlation coefficient. The analysis indicates that the metals are significantly ($p<0.05$) collocated (Appendix E).

The highest concentration of a number of TAL metals were detected at locations 28 and 3 where the total TAL metal burden was 108908 mg/kg and 101404 mg/kg, respectively (Table 5). At location 28, calcium and magnesium represented the largest proportion of the burden and were detected at 57,000 and 35,000 mg/kg, respectively (Table 4). These concentrations were substantially higher than those observed at most other locations in the study area. In contrast, the total burden at location 3 was distributed among several metals including aluminum, cadmium, chromium, copper, iron, nickel, potassium, and zinc. The total TAL metal burden at the other locations ranged from 44991 mg/kg at location 29 to 84,920 mg/kg at location 23 and the total TAL metal burden was 61553 mg/kg at the reference. The difference between the lower and higher burdens at these locations was largely due to aluminum, calcium, iron, and magnesium. For example, the total TAL burden at locations 29 and 23 is 44791 mg/kg and 84698 mg/kg, respectively. The elevated burden at the latter location is largely due to calcium where the concentration was 42000 mg/kg. In contrast, the calcium concentration at location 29 was 7300 mg/kg and the total metal burden was 200 mg/kg and 222 mg/kg at locations 29 and 23, respectively.

The XRF values were compared with AA values for all samples where data for both was available (Table 6). As measured by the mean RPD, there was only moderate agreement between the chromium and nickel analyses (52 and 61 RPD, respectively), with greater agreement for cadmium, copper, and zinc (24, 21 and 45 RPD, respectively). The greater agreement in the analyses of the latter metals is a reflection of their higher concentration relative to the respective detection and quantitative limits. Overall the RPD between the XRF and the AA data for individual metals ranged from 3 percent to 105 percent. The RPD for the total metal burden ranged from 2 to 76 percent (Table 7). With the exception of locations 9 and 26, there was good agreement between the two data sets and the XRF values predicted the AA gradient fairly well.

Results of the cyanide analysis indicate that the concentration ranges from 1.8 mg/kg at location 29 to 54 mg/kg at location 3 (Table 4); cyanide was not detected in sediment collected from 4 of the locations sampled including the reference, 33, 9, and 16. A correlation analysis indicates that the individual metals and cyanide are significantly ($p < 0.1$) collocated (Appendix E) and it is interesting to note that the highest cyanide concentrations were detected at the same locations as the highest concentrations of the metals of concern.

Results of TOC analyses indicate that the sediment is highly organic with carbon concentrations ranging from 3.9 percent at locations 33 and 23 to 22 percent at location 3 (Table 4). Correlation analysis indicates that the distribution of TOC is not significantly ($p<0.05$) related to the distribution of metals or cyanide (Appendix E).

The concentration of individual SEMs as well as the total SEM burden reflected the trends observed in the XRF and TAL metal datasets (Table 8). The highest concentration of simultaneously extracted cadmium, copper, lead, nickel, and zinc were detected at location 3 where 14000, 29000, 620, 70000, and 64000 nanomoles per gram (nMol/g) were observed, respectively. As mentioned above, the highest concentration of most TAL metals were also detected at this location. Similarly, the lowest concentrations of individual SEM and TAL metals were detected at the reference and locations 33, 29, 23, and 9. The trend of increasing TAL metal concentrations at locations 28, 16, 26, 8, and 32 was closely paralleled by the SEMs.

The TAL metal results represent the total extractable metal concentration in a sample whereas the SEMs represent the potentially "reactive" metals. To qualitatively compare the TAL metal concentrations with the SEM concentrations, the former were converted from mg/kg to nMol/g by dividing the TAL metal concentration by the respective atomic mass (Table 9). As expected, the converted TAL metal concentrations corresponded fairly well with the SEM metal concentrations (Table10). The SEM to TAL metal ratios ranged from 0.503 for nickel at location 28 to 2.24 for cadmium at location 23. Although no distinct trends were obvious, the lowest ratios were observed for copper and nickel ($\bar{x}$ = 0.75 and 0.89, respectively) with higher ratios for cadmium, lead, and zinc ($\bar{x}$ = 1.05, 0.99, and 0.94, respectively). A correlation analysis indicates that the individual simultaneously extracted metals are significantly ($p < 0.1$) collocated (Appendix E).

Acid volatile sulfides were detected in all the samples and ranged from 480 nMol/g at location 33 to 120000 nMol/g at location 28 (Table 8). Although no distinct trends were evident, it is interesting to note that the AVS concentration was relatively high at the most contaminated locations. The ratios of individual and total SEMs to AVS are summarized in Table 11. The ratios were lowest for cadmium ($\bar{x}$ = 0.0.14) and lead ($\bar{x}$ = 0.04) and ranged from 0.003 to 0.48 and 0.0005 to 0.13, respectively. The greatest ratios were for nickel ($\bar{x}$ = 0.98) and zinc ($\bar{x}$ = 0.98) ranged from 0.03 to 3.50 and 0.03 to 3.14, respectively. The SEM to AVS ratios for the total SEM burden ($\bar{x}$ = 2.68) were greater than one for most locations and ranged from 0.06 to 8.94.

The spatial variability AVS was estimated in areas of low (reference location), moderate (location 8), and high (location 3) contamination. The analytical data suggests that there is relatively high variability in AVS within the wetland as well as within small parcels of the wetland (Table 12). For example, across the study area, AVS concentrations ranged from 360 nMol/g at the reference location to 170000 nMol/g at location 3. The AVS concentration within a sampling location displayed a range that was reflective of the variability observed within the entire study area. For example the AVS concentration at the reference ranged from 360 nMol/g to 81000 nMol/g. Statistical analysis using Bartletts test for homogeneity of variance indicates that the range of SEM values was significantly ($p<0.1$) different between locations.

The variability in the SEM within the study area reflected the trends observed in the metal analysis by XRF and AA. The highest concentrations continued to be detected at location 3 with intermediate concentrations at location 8 and low concentrations at the reference. The variability within each of these locations was not as large as displayed by AVS and was and was greater for the location with the highest metal concentration. Statistical analysis using Bartletts test for homogeneity of variance indicates that the range of SEM values was significantly ($p<0.1$) different between locations.

The results of grain size analyses indicate the sediment is predominantly silt and clay (Table 13). The mean particle size ranged from 7.4 microns at location 29 to 48 microns at location 3. The fine texture observed within the study area is typical of a depositional environment and is generally more chemically reactive than coarser material. With the exception of location 26, all sediment collected was very poorly sorted indicating that there is a relatively wide distribution in particle sizes within each sample. The sorting value observed at location 26 indicated that the sediment was extremely poorly sorted.

3.3 In-Situ Water Quality

The water quality of Davy Creek was determined with a Hydrolab at three locations with open water. The temperature was uniform through the study area was 20.8 degrees centigrade (°C) at all locations (Table 14). Similarly, pH and conductivity were relatively uniform and ranged from 6.9 to 6.8 units and 1.09 to 0.984 units, respectively. The dissolved oxygen was uniformly depressed at all locations and ranged from 0.07 to 0.19 mg/L. The oxidation-reduction potential ranged from -.0208 to -0.185 and were reflective of strongly reducing environment.

3.2 Results of Sediment Toxicity Assay

The mortality of *C. tentans* exposed to sediment ranged from 7 percent at location 23 to 40 percent at location 16 (Table 15). Mortality was also observed in *C. tentans* exposed to the OECI field reference and the laboratory control (Carp Lake) sediment where mortality was 20 and 13 percent, respectively. Statistical analysis indicated that mortality of *C. tentans* exposed to sediment collected from the site was not significantly ($p < 0.05$) different than mortality observed in the OECI field reference sediment or in laboratory control sediment (Appendix E).

Growth, measured in terms of dry weight at the conclusion of the exposure period, was assessed for surviving individuals (Table 15). Inclusive of dead individuals (included as 0 grams in the analysis), the mean dry weight of *C. tentans* exposed to site sediment ranged from 1.01 mg at location 16 to 2.42 mg at location 8; the mean dry weight in OECI field reference and laboratory control sediment was 1.28 and 1.93 mg, respectively. Exclusive of dead individuals, the mean dry weight of *C. tentans* exposed to site sediment ranged from 1.56 mg at location 32 to 3.03 mg at location 8; the mean dry weight in the OECI field reference and laboratory control sediment was 1.60 and 2.23 mg, respectively. The Wilkes-Shapiro test was utilized to verify the normality of the dry weight data with the probability level set to 0.10. Results indicate that the growth data was not normally distributed (p-value > 0.10 in all cases) and the values were log-transferred prior to additional statistical analyses. Tukey's Multiple Comparison of the means with a probability level of 0.10 was used to compare the results at each location with all other locations. Inclusive and exclusive of the dead individuals, no significant difference (p<0.1) was found between laboratory control sediment dry weight results and results for the site sediment. Inclusive of dead individuals (again included as 0 gram in the analysis), location 8 was found to have significantly (p>0.1) greater growth than the OECI field reference sediment. Similarly, inclusive of dead individuals, locations 8 and 9 were found to have significantly (p>0.1) greater growth than the OECI field reference sediment (Appendix E).

The mortality of *C. tentans* exposed to the OECI field reference and laboratory control sediment was 20 and 13 percent, respectively (Table 15) and met the QA/QC criteria. Further, the water quality criteria and physical conditions were in conformity with the test protocol throughout the duration of the assay (Appendix D). The low mortality observed in the OECI field reference and the laboratory control sediment indicate that the test populations were healthy and any mortality observed can be attributed to contaminants and not handling stress, disease, or substrate incompatibility. The 10 day cadmium chloride reference toxicant test resulted in a EC50 (growth) value of 24.0 mg/kg and a LC50 value of 28.45 mg/kg (Appendix D). These values correspond to sediment pore water concentrations of 19.9 ug/L and 23.65 ug/L for the EC50 and LC50, respectively. These values are somewhat lower than that observed by Nebeker et al. (1986) who reported a 96 hour LC50 cadmium chloride LC50 of 8.0 ug/l, suggesting that the test population used in this study was slightly less sensitive than those used in the former study.

4.0 DISCUSSION

The XRF results were used in the field to approximate a gradient for selecting samples for the laboratory analysis and toxicity evaluation. As suggested by the QA/QC results for the TAL metal analysis, the AA data is more definitive in nature than the XRF data and is thus a more reliable estimator of the absolute metal value. For example, the percent recoveries for the QC analysis ranged from 96 to 110 percent, indicating relatively good instrument performance and calibration (Appendix B). The quality of the field data can therefore be evaluated by an analysis of the RPD between the XRF and AA data. There was moderate agreement between the XRF and AA data for cadmium and copper, with less correspondence for chromium, nickel, and zinc. This suggests that there may have been some errors due to line interferences and/or matrix effects. A second measure of data reliability are the percentage of values which are qualified with respect to the MDL and the MQL. A relatively high proportion of the XRF data was qualified for all metals indicating their presence, however, the ability of XRF to quantify the amount was poor. These results emphasize the intrinsic uncertainty in XRF data as a result of the heterogenous nature of sediment and the relatively coarse particle size (on the scale of x-ray penetration). The uncertainty observed in this study was also a reflection of the relatively low concentration range targeted by the sampling effort, highlighting the fact that this technique has been developed as a real-time screening instrument to assess gross metal concentrations. Despite the limitations, the resulting gradient chosen met the requirements of the study at a significant cost savings.

Previous investigations have shown that the metals in the wetland adjacent to the former OECI facility were highly collocated within a plume of contamination extending from the OECI outfall at the northern edge of the marsh, southward into Davy Creek and as far downstream as the Rock River. A correlation analysis performed using the results of the current study indicate that cadmium, chromium, copper, nickel, and zinc as well as cyanide continue to be strongly collocated within the Davy Creek wetland adjacent to Fireman Park. The magnitude of contamination in wetland adjacent to the former OECI facility was greater than in the current study area. Adjacent to the former OECI facility, cadmium was found to be present in the sediment in quantities as high as 4800 mg/kg, chromium and nickel to 23,000 mg/kg, copper to 22,000 mg/kg, zinc to 47,000 mg/kg, and cyanide to 520 mg/kg. In contrast, concentrations of cadmium to 1300 mg/kg, chromium to 7300 mg/kg, copper to 3400 mg/kg, nickel to 5500 mg/kg, zinc 3800 mg/kg, and cyanide to 54 mg/kg were detected in the current study area.

Classical toxicity evaluations expose a surrogate species to a measured dose of a chemical through oral, cutaneous, or inhalation pathways. Environmental toxicity evaluations differ from classical toxicology in several ways. First, the chemical or chemicals are a characteristic of the site history and the mixtures may impact the surrogate in a variety of ways, or may interact within the matrix to form more or less toxic compounds Second, the concentration of chemicals is a function of the sample location, migration pathways, and chemical fate. Third, the exposure (i.e. dose) is a function of the matrix and surrogate life history and ecological characteristics, and not necessarily directly related to the analytical concentration. The toxicity evaluation used in this investigation and the surrogate organism selected, were fashioned to minimize some of the uncertainties discussed above.

Toxicity evaluations involve subjecting surrogate species to a range of samples to determine a matrix concentration necessary to elicit a predetermined response (i.e. mortality or growth). Acute assays typically employ a mortality endpoint and chronic tests typically use sublethal, long-term (relative to the life cycle of the surrogate) endpoints that evaluations growth, reproductive success, or other rate processes. This investigation focused on both mortality and growth of *C. tentans* following a 10-day exposure to sediment.

The objective of this investigation was to evaluate the toxicity of contaminated wetland sediment and to use this data for a risk assessment. Following remediation, the concentration of residual contamination should represent in an acceptable degree of ecological risk. For example, remediation with an LC50 value as a clean-up goal will clearly not result in an acceptable reduction of ecological risk. In the current investigation, the toxicity to *C. tentans* ranged from 7 to 40 percent, but was not significantly different than the OECI field reference or the laboratory control ($P < 0.1$) . And, in general, mortality of *C. tentans* exposed to site sediment was not correlated with the total metal burden or individual metals. Growth, measured in terms of dry weight, was assessed for surviving individuals. Although significant effects were noted at location 8 and 9, the growth at these locations was greater than the OECI field reference and the laboratory control in spite of the elevated metal concentrations detected. A narrow evaluation of this data would lead to the conclusion that contaminants present in the sediment (including those at the most contaminated locations) represent an acceptable degree of ecological risk at ambient concentrations.

This investigation incorporated several assumptions concerning the response of organisms to toxicants in the environment. The toxicity evaluation involved exposing organisms to sediment contaminated with a range of concentrations expected to elicit a range of responses. Each sample would represent a discrete finding (i.e., a measured concentration, observed mortality and growth) and predictions regarding clean up goals would be made on the assumption that mortality or changes in growth are directly related to the contaminant concentration. Review of the data indicates that this relationship is not necessarily true, or not evident in the small data set generated in this investigation. Undoubtedly, other factors are involved (i.e. exposure, bioavailability, interspecific and intraspecific variation, etc.), and the relationship between contamination concentration and mortality/growth is not direct or simple. This underscores the complexity of the matrix and the biological response.

Acid volatile sulfide is an operationally defined term used to estimate the amount of reactive sulfur and amorphous iron monosulfide present. Since severe heated acid treatments release sulfide from pyrite or other non-reactive sulfur compounds, AVS is extracted from samples using an unheated mild acid (Allen et al. 1991). Acid volatile sulfide is an important partitioning phase for divalent transitional metals (i.e. cadmium, copper, lead, mercury, nickel, and zinc) in marine and freshwater sediments under reducing anoxic conditions (Di Toro, 1990; Ankley *et al.*, 1993). After reacting with AVS, these divalent metals form insoluble metal sulfides which are not bioavailable (Allen *et al.*, 1993). Cadmium, copper, lead, mercury, nickel, and zinc simultaneously extracted during the procedure mentioned above are used to quantify the reactive metals present in the sediment sample.

It has been suggested that acid volatile sulfide concentrations can explain the toxicity results of acute toxicity tests for metals in marine and freshwater sediments for a number of different test species (Allen *et al.*, 1993; Casas and Crecelius, 1994; Di Toro *et al.*, 1990; Di Toro *et al.*, 1992). When the molar SEM to AVS ratio for these metals is below 1, the metals are not expected to be present in the pore water and acute toxicity is not expected. If the molar ratio exceeds 1, the metals should be detected in the sediment pore water and there is a potential for acute toxicity.

Acid volatile sulfides alone may not always predict bioavailability of all divalent metals and it has been suggested that oxides of iron and manganese, humic acids, ion exchange sites on clay minerals, and organic compounds may also be relevant in determining the toxicity of metals in sediments (US EPA, 1989). For example, Ankley *et al.* (1993) observed that in freshwater sediments, normalization of sediment copper concentrations to AVS accurately predicted that sediment would be nontoxic when the molar concentration of copper to AVS were less than 1; however, toxicity was frequently not observed in samples with molar copper to AVS ratios significantly greater than 1. Ankley *et al.* (1993) concluded that pore water concentrations provided an accurate prediction of copper toxicity, and AVS alone did not explain the copper partitioning.

In situations such as the OECI site where multiple divalent transitional metals occur in the sediment, molar concentrations of total SEM metals to AVS are expected to be an important factor in predicting acute toxicity (Di Toro *et al.*, 1990). Any divalent metal that has a lower sulfide solubility parameter than amorphous iron monosulfide (Table 16) would be expected to form an insoluble metal sulfide, as long as AVS was still available. The expected additivity of the metals does not come from the nature of the mechanism that causes toxicity but rather from the ability for any of these divalent metals to bind with and utilize the available sulfide (Di Toro *et al.*, 1990). When the molar concentration of total SEM metals to AVS exceeds 1, it is expected that the more insoluble transitional metals (i.e., mercury and copper) would form metals sulfides while the least insoluble metals (i.e., nickel and zinc) would be present in the pore water in ionic form.

As alluded to above, the toxicity data may be interpreted in light of the AVS and SEM ratios. The ratios were lowest for lead ($\bar{x}$ = 0.04), cadmium ($\bar{x}$ = 0.14), and copper ($\bar{x}$ = 0.54) , with greatest ratios for nickel ($\bar{x}$ = 0.98) and zinc ($\bar{x}$ = 0.98). When viewed in light of individual simultaneously extracted metals, the ratios predict that the sediment would not be toxic to *C. tentans*. However, since it is more appropriate to view the SEM data in light of the total SEM burden. The total SEM to AVS ratios were greater than one ($\bar{x}$ = 2.68) for most locations. A AVS/SEM ratio above one is not predictive but requires that site specific toxicity tests be conducted to determine toxicity. The results of this evaluation indicate that for this AVS is not a good predictor of sediment metal bioavailability and toxicity at AVS/SEM ratios greater than one.

5.0 CONCLUSIONS

The objective of the current phase of this investigation was to evaluate the toxicity of metal and cyanide contaminated sediment collected from the wetland downstream of the former OECI facility and adjacent to Fireman Park in Ashippun, WI. The toxicological data was evaluated in light of the sediment contaminant burden, acid volatile sulfides, and historic dataset to suggest clean-up goals that would be protective of the species employed as a surrogate of the wetland community. Conclusions reached from these results are listed below.

1) Consistent with previous investigations, the five metals of concern and cyanide continue to be collocated within a plume of contamination extending from the former OECI facility and westward to Davy Creek and associated riparian wetlands.

2) Metal results generated by XRF and AA corresponded best for copper and cadmium, followed by zinc, chromium, and nickel as measured by relative percent difference. Differences between the two methods may be a result of interferences, or most likely the inability of XRF to efficiently analyze low concentrations of contaminants.

3) There was a broad range in the total metal burden that was associated with the whole sediment toxicity assay. The total metal gradient measured by AA ranged from 107.5 mg/kg at location 33 to 21300 mg/kg at location 3, and the total metal burden at the reference location was 81 mg/kg.

4) The total SEM burden to AVS ratios were greater than one ($\bar{x}$ = 2.68, range 0.06 to 8.94) for most locations and none of the locations showed toxicty. The results of this evaluation indicate that AVS is not a good predictor of toxicity at this site.

5) The mortality of *Chironomus tentans* associated with sediment collected from the site was not significantly different from the OECI field reference or the laboratory control. Similarly, the growth of *C. tentans* was not significantly reduced by exposure to site sediment.

6.0 RECOMMENDATIONS

1) In that the toxicity tests conducted on the wetland adjacent to Fireman's Park in Ashippun WI. showed not adverse impacts significantly different from the laboratory control and the OECI site specific reference, a no action alternative be selected based on ecological risk.

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Table 1. Results of XRF Field Screening of Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

DRAFT

Concentrations reported in mg/kg (dry weight)

Sample Location	Cadmium	Chromium	Copper	Nickel	Zinc	Total Metals
01	120 U	480 J	160 J	360 J	210	1210
01 DUP	120 U	1300	420	1000	470	3190
02	170 J	950	730	1100	900	3850
03	1100	8500	3900	8300	4200	26000
03 DUP	600	4600	2700	6000	3000	16900
04	120 U	590 J	400	1100	620	2710
04 DUP	160 U	490 J	180	880	510	2060
04 REP	150 J	630 J	380	1100	690	2950
05	120 U	700 J	350	630	590	2270
05 DUP	120 U	1300	490	1200	800	3790
05 REP	120 U	1100	490	1200	690	3480
06	120 U	820	480	740	950	2990
07	120 U	1100	270	700	540	2610
07 DUP	120 U	620 J	84 J	470 J	280	1454
08	120 U	1200	320	890	470	2880
08 DUP	130 J	1100	280	830	520	2860
08 REP	120 U	1200	270	870	470	2810
09	120 U	300 J	51 U	200 J	190	690
09 DUP	120 U	230 U	51 U	180 J	210	390
10	120 U	430 J	200	320 J	340	1290
10 DUP	120 U	280 J	51 U	160 J	220	660
11	120 U	580 J	88 J	390 J	360	1418
11 DUP	120 U	780	260	620	630	2290
12	120 U	230U	51 U	220 J	150 J	370
12 DUP	120 U	240 J	51 U	180 J	230	650
13	120 U	430 J	64 J	490 J	490	1474
13 DUP	120 U	230 U	64 J	250 J	220	534
14	170 J	2400	1200	2200	1400	7370
14 DUP	260 J	2400	1200	2000	1600	7460
15	120 U	840	360	650	570	2420
15 DUP	120 U	890	370	500	610	2370
16	120 U	370 J	130 J	330 J	310	1140
16 DUP	120 U	500 J	87 J	340 J	310	1237
16 REP	120 U	230 U	83 J	270 J	290	643
17	120 U	920	380	720	630	2650
17 DUP	120 U	1300	980	1400	1100	4780
18	120 U	420 J	51 U	200 J	160 J	780
18 DUP	120 U	400 J	59 U	290 J	160 J	850
19	120 U	520 J	88 J	600	240	1448
19 DUP	120 U	550 J	110 J	390 J	200	1250
20	120 U	300 J	69 J	150 U	210	579
20 DUP	120 U	280 J	51 U	170 J	170 J	620
21	120 U	230 U	51 U	240 J	180 J	420
21 DUP	120 U	430 J	51 U	230 J	200	860
22	150 J	1500	870	1500	1400	5420

Table 1. Results of XRF Field Screening of Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in mg/kg (dry weight)

Sample Location	Cadmium	Chromium	Copper	Nickel	Zinc	Total Metals
22 DUP	120 U	1700	880	1600	1500	5680
23	120 U	230 U	51 U	150 U	160 J	160
23 DUP	120 U	230 U	51 U	150 U	150 J	150
24	120 U	230 U	71 J	150 U	200	271
24 DUP	120 U	470 J	160 J	300 J	330	1260
24 REP	120 U	450 J	230	290 J	350	1320
24 GRN	120 U	230 U	51 U	150 U	58 J	58
25	120 U	450 J	220	380 J	520	1570
25 DUP	120 U	430 J	190	260 J	320	1200
26	120 U	1200	400	840	640	3080
26 DUP	120 U	1200	250	680	520	2650
27	210 J	1700	1400	1100	1800	6210
27 DUP	190 J	1300	1100	1100	1600	5290
27 REP	130 J	1500	1100	1100	1500	5330
28	120 U	280 J	170 J	290 J	430	1170
28 DUP	120 U	430 J	96 J	400 J	450	1376
29	120 U	230 U	51 U	170 J	140 J	310
29 DUP	120 U	230 U	51 U	160 J	96 J	256
30	120 U	330 J	180	410 J	280	1200
30 DUP	120 U	250 J	160 J	290 J	270	970
30 REP	120 U	400 J	160 J	490 J	330	1380
31	120 U	230 U	51 U	170 J	130 J	300
31 DUP	120 U	320 J	51 U	150 U	73 J	393
32	410	2700	2100	3900	1500	10610
32 DUP	340 J	2000	1600	2900	1200	8040
33	120 U	230 U	51 U	150 U	84 J	84
33 DUP	120 U	230 U	51 U	150 U	110 J	110
FILL A	120 U	310 J	200	380 J	590	1480
FILL A DUP	120 U	450 J	110 J	340 J	370	1270
FILL B	120 U	330 J	150 J	350 J	390	1220
FILL B DUP	120 U	470 J	180	460 J	410	1520
REF	120 U	230 U	51 U	150 U	98 J	98
REF DUP	120 U	230 U	51 U	150 U	87 J	87
MDL	120	230	51	150	54	
MQL	380	760	170	490	180	

XRF	X-Ray Fluorescence	U	Not detected at MDL
MDL	Minimum Detection Limit	J	Approximated value above MDL but below MQL
MQL	Minimum Quantification Limit		

Total metal is the sum of cadmium, chromium, copper, nickel, and zinc values

Table 2. Data Qualifiers for XRF Observations of Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

DRAFT

Metal	Number and Percent of Data Qualified					
	U		J		Total	
	No.	Percent	No.	Percent	No.	Percent
Cadmium	65	83	10	13	75	96
Chromium	16	21	35	45	51	65
Copper	21	27	19	24	40	51
Nickel	10	13	36	46	46	59
Zinc	0	-	16	21	16	21
Total	112	28	116	30	228	58

XRF	X-Ray Fluorescence
MDL	Minimum Detection Limit
MQL	Minimum Quantification Limit
U	Observation below MDL
J	Observation above MDL and below MQL

Total number of XRF observations per metal was 78

Total number of XRF observations was 390

Table 3. XRF Metal Gradient in Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in mg/kg (dry weight)*

Location	Cadmium	Chromium	Copper	Nickel	Zinc	Total Metals
Reference	U	U	U	U	92 J	92
33	U	U	U	U	97 J	97
23	U	U	U	U	155 J	155
29	U	U	U	165 J	118 J	283
9	U	265 J	U	190 J	200	655
16	U	366 J	100 J	313 J	303	1082
28	U	355 J	133 J	345 J	440	1273
26	U	1200	325	760	580	2865
8	123 J	1167	290	863	487	2930
32	375	2350	1850	3400	1350	9325
3	850	6550	2085	7150	3600	20235
MDL	120	230	51	150	54	
MQL	380	760	170	490	180	

*	Values are the mean of duplicate or replicate observations
XRF	X-Ray Fluorescence
MDL	Minimum Detection Limit
MQL	Minimum Quantification Limit
U	Observation below MDL
J	Observation above MDL and below MQL

Total number of observations was 78

Table 4. Target Analyte List Metals, Cyanide, and Total Organic Carbon Detected in Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in mg/kg (dry weight)

Analyte	Sample Location										
	Ref.	33	29	23	9	28	16	26	8	32	3
Aluminum	8300	10000	9000	4800	9400	3200	11000	2700	10000	5800	17000
Arsenic	2.1	3.4	2.4	7.7	3.4	19	3.0	5.5	3.9	3.3	6.6
Barium	100	110	170	57	200	36	150	46	130	130	380
Beryllium	0.47	0.51	0.53	0.30	0.57	0.21	0.58	0.25 U	0.54	0.28	0.68
Cadmium	0.40 U	3.5	10	10	15	52	66	100	150	420	1300
Calcium	24000	4500	7300	42000	13000	57000	19000	41000	20000	17000	23000
Chromium	13	27	35	60	61	180	290	390	1200	1700	7300
Cobalt	5.9	6.3	8.2	5.2	12	7.1	10	7.8	14	13	62
Copper	13	14	34	32	43	140	150	240	320	1300	3400
Iron	15000	30000	25000	12000	48000	12000	25000	9600	18000	12000	29000
Lead	12	7.6	8.9	7.9	14	15	23	13	27	33	130
Magnesium	13000	2600	2600	25000	4300	35000	8600	21000	9500	8200	8600
Manganese	310	260	130	230	960	200	480	140	210	180	460
Mercury	0.07	0.05	0.13	0.04 U	0.08	0.04 U	0.08	0.04	0.07	0.06	0.20
Nickel	11	22	57	47	64	210	270	300	780	1800	5500
Potassium	640	290	450	450	480	390	690	250 U	910	430	1200
Selenium	0.55 U	0.46 U	0.82	0.45	1.1	0.66	0.80	0.57	1.3	1.1	3.4
Silver	0.67 U	0.41 U	0.68 U	0.35	0.91	0.71	0.89	0.98	2.5	2.0	17
Sodium	77	77	95	120	130	120	100	100	180	100	200
Vanadium	23	30	24	19	25	17	28	9.1	29	17	41
Zinc	44	41	64	73	110	320	260	310	430	990	3800
Cyanide	0.97 U	0.7 U	1.8	2.9	1.0 U	2.8	1.1 U	8.6	2.8	30	54
TOC (%)	15	3.9	6.5	3.9	17	2.8	17	7.2	22	8.6	22

U Not detected at indicated concentration

Table 5. Summary of TAL Contaminants of Concern, Cyanide, and Metal Burdens Detected in Sediment Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in mg/kg (dry weight)

Parameter	Sample Location										
	Reference	33	29	23	9	28	16	26	8	32	3
Cadmium	0.40 U	3.5	10	10	15	52	66	100	150	420	1300
Chromium	13	27	35	60	61	180	290	390	1200	1700	7300
Copper	13	14	34	32	43	140	150	240	320	1300	3400
Nickel	11	22	57	47	64	210	270	300	780	1800	5500
Zinc	44	41	64	73	110	320	260	310	430	990	3800
Cyanide	0.97 U	0.7 U	1.8	2.9	1.0 U	2.8	1.1 U	8.6	2.8	30	54
Total Metal Burden	81	107.5	200	222	293	902	1036	1340	2880	6210	21300
Total TCL Metal Burden	61553	47993	44991	84920	76820	108908	66123	76213	61888	50120	101404

Table 6. Comparison of XRF and AA Results for Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippum, WI
July 31 - August 3, 1995

Concentrations reported in mg/kg (dry weight)

Location	Cadmium			Chromium			Copper			Nickel			Zinc		
	AA	XRF	RPD	AA	XRF	RPD	AA	XRF	RPD	AA	XRF	RPD	AA	XRF	RPD
Ref	0.40U	120U	-	13	230U	-	13	51U	-	11	150U	-	44	92J	71
33	3.5	120U	-	27	230U	-	14	51U	-	22	150U	-	41	97J	81
29	10	120U	-	35	230U	-	34	51U	-	57	165J	97	64	118J	59
23	10	120U	-	60	230U	-	32	51U	-	47	150U	105	73	155J	72
9	15	120U	-	61	265J	125	43	51U	-	64	190J	99	110	200	58
28	52	120U	-	180	355J	65	140	133J	5	210	345J	49	320	440	32
16	66	120U	-	290	366J	23	150	100J	40	270	313J	15	260	303	15
26	100	120U	-	390	1200	102	240	325	30	300	760	87	310	580	61
8	150	123J	20	1200	1167	3	320	290	10	780	863	10	430	487	12
32	420	375	11	3	2350	32	1300	1850	35	1800	3400	62	990	1350	31
3	1300	850	42	7300	6550	11	3400	3300	3	5500	7150	26	3800	3600	5
Mean			24			52			21			61			45

(1)	XRF data includes both qualified and unqualified observations
AA	Atomic Absorption
XRF	X-Ray Fluorescence
RPD	Relative Percent Difference
MDL	Minimum Detection Limit
MQL	Minimum Quantification Limit
U	Observation below MDL
J	Observation above MDL and below MQL

Table 7. Comparison of Total XRF and AA Values for Sediment Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippum, WI
July 31 - August 3, 1995

Concentrations reported in mg/kg (dry weight)

Sample Location	Total Metal Concentration		RPD
	XRF	AA	
Reference	92	81	13
33	97	107.5	10
29	283	200	34
23	155	222	36
9	655	293	76
28	1273	902	34
16	1082	1036	4
26	2865	1340	72
8	2930	2880	2
32	9325	6210	40
3	20235	21300	5

(1)	XRF data includes both qualified and unqualified observations
AA	Atomic Absorption
XRF	X-Ray Fluorescence
RPD	Relative Percent Difference
MDL	Minimum Detection Limit
MQL	Minimum Quantification Limit
U	Observation below MDL
J	Observation above MDL and below MQL

Table 8. Simultaneously Extracted Metals and Acid Volatile Sulfides
Detected in Sediment Collected from the Davy Creek Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in nMol/g (dry weight)

Analyte	Sample Location										
	Ref.	33	29	23	9	28	16	26	8	32	3
Cadmium	43 U	32	110	200	130	310	670	820	1200	4400	14000
Copper	210	170	360	620	620	1500	2400	2900	5300	23000	29000
Lead	86	33	52	52	89	55	140	61	140	170	620
Nickel	180	290	1100	710	1000	1800	4900	3500	9400	26000	70000
Zinc	620	480	790	2000	1700	3400	4400	4600	6200	17000	64000
Total SEM	1096	1005	2412	3582	3539	7065	12510	11881	22240	70570	177620
AVS	5900	480	1100	18000	670	120000	1400	12000	5300	28000	59000

U Not detected at indicated concentration

Table 9. Converted Results of Select Target Analyte List Metals Detected in Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in uMol/g (dry weight)

Analyte	Sample Location										
	Ref.	33	29	23	9	23	16	26	8	32	3
Cadmium	U	31	89	89	133	463	587	890	1335	3737	11566
Copper	205	220	535	504	677	2203	2361	3777	5036	20460	53510
Lead	58	37	43	38	68	72	111	63	130	159	627
Nickel	187	375	971	801	1090	3578	4600	5111	13288	30664	93697
Zinc	673	627	979	1117	1682	4894	3977	4742	6577	15142	58122
Total	1123	1259	2528	2459	3517	10748	11048	13692	25031	66426	205956

U Not detected

Table 10. Ratio of Simultaneously Extracted Metals to Target Analyte List Metals Detected in Sediment
Collected from the Davy Creek Riparian Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Analyte	Sample Location											Mean
	Ref.	33	29	23	9	28	16	26	8	32	3	
Cadmium	U	1.03	1.24	2.25	0.97	0.67	1.14	0.92	0.9	1.18	1.21	1.05
Copper	1.03	0.77	0.67	1.23	0.92	0.68	1.02	0.77	1.05	1.12	1.54	0.89
Lead	1.48	0.9	1.21	1.36	1.32	0.76	1.26	0.97	1.07	1.07	0.99	0.99
Nickel	0.96	0.77	1.13	0.89	0.92	0.5	1.07	0.68	0.71	0.85	0.75	0.75
Zinc	0.92	0.77	0.81	1.79	1.01	0.69	1.11	0.97	0.94	1.12	1.10	0.94

U Not detected

DRAFT

Table 11. Ratio of Simultaneously Extracted Metals to Acid Volatile Sulfides
Detected in Sediment Collected from the Davy Creek Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Analyte	Sample Location											Mean
	Ref.	33	29	23	9	28	16	26	8	32	3	
Cadmium	U	0.07	0.10	0.01	0.19	0.003	0.48	0.07	0.23	0.16	0.24	0.14
Copper	0.04	0.35	0.33	0.03	0.93	0.01	1.71	0.24	1.0	0.82	0.49	0.54
Lead	0.01	0.07	0.05	0.003	0.13	0.0005	0.10	0.005	0.03	0.006	0.01	0.04
Nickel	0.03	0.60	1.0	0.04	1.49	0.02	3.50	0.29	1.77	0.93	1.19	0.98
Zinc	0.11	1.0	0.72	0.11	2.54	0.03	3.14	0.38	1.17	0.61	1.08	0.98
Total	0.19	2.09	2.19	0.20	5.28	0.06	8.94	0.98	4.20	2.52	3.01	2.68

Table 12. Simultaneously Extracted Metals and Acid Volatile Sulfides Detected in Collocated Sediment Samples Collected from the Davy Creek Wetland Area Adjacent to Fireman Park

OECI Site, Ashippun, WI
July 31 - August 3, 1995

Concentrations reported in nMol/g (dry weight)

Analyte	Sample Location											
	Reference				8				3			
	A	B	C	D	A	B	C	D	A	B	C	D
Cadmium	43 U	68 U	48 U	48 U	1200	1600	650	350	14000	3400	12000	5900
Copper	210	290	180	230	5300	5800	2400	1400	29000	24000	18000	34000
Lead	86	98	73	100	140	160	110	59	620	440	260	1200
Nickel	180	180	130	200	9400	9900	4200	1500	70000	13000	43000	25000
Zinc	620	910	550	710	6200	8800	3300	2000	64000	33000	29000	62000
AVS	5900	81000	14000	360	5300	9100	6600	4100	59000	8200	55000	170000

U Not detected at indicated concentration

DRAFT

Table 13. Physical Characteristics of Sediment Collected from the Davy Creek Wetland Adjacent to Fireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Metric	Sample Location										
	Reference	33	23	29	9	16	28	26	8	32	3
% Sand	13	34	30	26	22	25	29	37	30	36	45
% Silt	54	46	49	37	52	43	57	60	56	52	51
% Clay	33	20	21	37	26	32	14	3	14	12	4
Mean Particle Size (microns)	10.1	10.9	21.8	7.4	14.8	13.3	26.4	41.2	26.4	38.4	48
Mean Particle Size (phi)	6.7	6.6	5.6	7.1	6.1	6.3	5.3	4.6	5.3	4.7	4.4
Sorting Value (phi)	3.0	3.5	3.0	3.6	2.9	3.5	2.4	1.8	2.4	3.0	2.1

Table 14. *In-Situ* Water Quality of Davy Creek in Vicinity of the Wetland Area Adjacent to Fireman Park
OECI Site, Ashippun, Wisconsin
July 31- August 3, 1995

Parameter	Location		
	A	B	C
Time (hours)	1630	1657	1707
Temperature (°C)	20.8	20.8	20.8
pH (standard units)	6.9	6.8	6.8
Dissolved O_2 (mg/l)	0.07	0.04	0.19
Conductivity (mmhos/cm)	1.09	1.04	0.984
ORP (volts)	-0.208	-0.235	-0.185
Salinity (ppt)	0.0	0.0	0.0

Table 15. Summary of Toxicity Evaluation Results for *Chironomus tentans* Larva
Exposed to Sediment Collected from the Davy Creek Wetland Area Adjacent toFireman Park
OECI Site, Ashippun, WI
July 31 - August 3, 1995

Individual Dry Weights (mg)

Replicate	Sampling Location											
	Field Ref.	33	23	29	9	16	28	26	8	32	3	Carp Lake
1	1.97	3.46	2.86	DNR	3.11	DNR	1.76	2.06	DNR	DNR	2.16	2.19
2	0.45	3.04	3.02	2.64	0.89	DNR	2.66	1.87	4.53	DNR	1.67	2.24
3	2.31	2.57	3.22	3.01	3.28	DNR	1.34	DNR	4.93	DNR	0.22	1.67
4	1.45	2.69	2.77	1.73	3.58	0.21	DNR	0.75	2.22	0.88	DNR	0.35
5	1.16	1.19	2.49	DNR	2.49	1.04	2.71	DNR	3.19	0.31	DNR	DNR
6	DNR	1.18	1.21	1.92	DNR	1.43	1.21	1.82	DNR	2.23	2.56	DNR
7	DNR	2.42	2.33	1.73	3.46	2.94	DNR	2.51	DNR	1.56	1.91	2.76
8	2.68	1.47	0.93	DNR	1.65	DNR	1.49	2.67	2.98	DNR	DNR	3.04
9	0.27	0.67	2.14	2.15	DNR	1.98	0.99	2.78	1.18	0.94	2.13	0.87
10	DNR	3.21	1.92	DNR	2.16	DNR	DNR	1.96	3.17	1.82	0.91	1.41
11	0.33	DNR	2.97	0.84	DNR	2.44	DNR	2.46	2.23	DNR	0.97	2.94
12	2.52	2.81	2.56	DNR	2.72	DNR	2.13	3.77	2.45	1.69	1.98	2.56
13	1.01	DNR	DNR	2.86	3.19	2.19	2.16	3.14	3.76	2.28	2.36	3.46
14	2.15	1.97	2.17	0.19	2.53	1.18	2.44	2.11	4.07	2.16	0.83	2.95
15	2.95	1.74	2.12	0.89	1.21	1.67	3.67	3.46	1.61	1.76	1.74	2.49
Mean[1]	1.28	1.89	2.18	1.20	2.02	1.01	1.50	2.09	2.42	1.04	1.84	1.93
Std. Dev.[1]	1.08	1.12	0.88	1.15	1.31	1.05	1.15	1.12	1.62	0.93	2.21	1.15
Mean[2]	1.60	2.19	2.34	1.80	2.52	1.68	2.05	2.41	3.03	1.56	2.30	2.23
Std. Dev.[2]	0.96	0.88	0.66	0.93	0.89	0.82	0.80	0.79	1.15	0.65	2.25	0.91
Mortality[3]	3	2	1	5	3	6	4	2	3	5	3	2
Mortality[4]	20	13	7	33	20	10	27	13	20	33	20	13

DNR Dead - Not Recovered

[1] Dead organisms included in calculation at weight = 0

[2] Dead organisms not included in calculation

[3] Number dead at conclusion of test (n = 15)

[4] Percent mortality

Table 16. Solubility Products of Metal Sulfides
OECI Site, Ashippun, WI

Metal Sulfide	Log K[1,2]
MnS(solid)	-19.15 (Most Soluble)
FeS(amorphic)	-21.80
FeS(solid)	-22.39
NiS(solid)	-27.98
ZnS(solid)	-28.39
CdS(solid)	-32.85
PbS(solid)	-33.42
CuS(solid)	-40.94
HgS(solid)	-57.25 (Least Soluble)

[1] Di Toro *et al.* (1990)

[2] Solubility Product, the product of the concentrations of ions in a saturated solution.