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Illinois State Water Survey

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ABSTRACT

The concentrations and potential toxicity of several heavy metals (cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)) and ammonia in sediments and pore waters of Peoria Lake to 30 cm depth have been characterized. There was little previous information on Peoria Lake pore water chemistry prior to our study. Pore water measurements also included dissolved organic carbon and pH. Complementary sediment solid analyses included Acid-Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM) concentrations. Sediment cores were collected in both April and October of 2000 to permit a first-order assessment of seasonal differences.

Pore water ammonia concentrations were high, ranging from about 0.5-36.0 mg/L (as N), while overlying water concentrations in samples collected at the same time near the sediment-water interface (≤ 15 cm) were much lower (≤ 0.2 mg/L). Ammonia pore water concentrations generally increased with depth, and were higher in October than April. Pore water pH values ranged from about 7.5 to 6.8 and generally decreased with depth. These pH values were lower than those of the overlying water column (7.8-8.5). All sediment samples contained detectable AVS, indicating Peoria Lake sediments are strongly reducing, even in the top 6 cm. The AVS values ranged from 10-40 μmol/g and no significant seasonal changes were observed. The sum of HCl-extractable Cd, Cu, Ni, Pb, and Zn (SEM) concentrations were less than corresponding AVS values in all sediment samples. Dissolved concentrations of Cd, Cu, Ni, Pb, and Zn were low in pore waters (<15 μg/L), and these concentrations were generally lower than those of the overlying water column. The formation of sparingly soluble metal sulfides is at least partially responsible for the low pore water concentrations of these metals.

Previous work indicates that for sediment solids with SEM<AVS the metals are not toxic to certain benthic organisms. Therefore, dissolved ammonia is potentially more toxic to sensitive indigenous species than dissolved Cd, Cd, Ni, Pb or Zn in Peoria Lake. However, total concentrations of Cd and Ni often exceed "Probable Effect Concentration" levels (MacDonald et al, 2000) at and below 15 cm sediment depth, indicating possible toxic effects on indigenous biota from these metals. In addition, hydrogen sulfide concentrations, as estimated with the aid of chemical equilibrium modeling, could also be high enough to be toxic.

INTRODUCTION

Excessive sediment deposition and contamination pose environmental problems in many regions of the world, including areas within the Illinois River basin. Peoria Lake, an impoundment on the Illinois River, has undergone severe sedimentation for the past century and had lost 68% of its 1903 capacity by 1985 (Illinois State Water Survey, 1994). Elevated concentrations of certain metals and organic pollutants in sediment contributed to portions of the Illinois River (including Peoria Lake) being designated as an area of probable concern for sediment contamination (U.S. EPA, 1997; 2001a).

Several previous studies dating to the early 1970s have investigated the chemistry of Peoria Lake sediments. Mathis and Cummings (1971; 1973) determined the distribution of various metals in the sediments, water and certain biota at five stations along the Illinois River, including two stations within Peoria Lake. Concentrations of potentially toxic heavy metals (Cu, Ni, Pb, Cr, Zn, Co, and Cd) were generally 2 to 4 times greater at the stations within Peoria Lake than those further downstream. Collinson and Shimp (1972) studied the chemical and mineralogical composition of sediments at eight stations within Upper Peoria Lake. They noted that the concentrations of many trace elements increased southward within Upper Peoria Lake, and that this increase was directly related to organic carbon content. Cahill and Steele (1986) collected and analyzed 27 sediment cores from 18 backwater lakes along the Illinois River, including Peoria Lake. These analyses included up to 40 inorganic constituents, organic carbon and grain-size analyses, as well as sedimentation rates at several locations. Sedimentation rates within Upper Peoria Lake ranged from 0.7 to 2.0 cm/yr. Cahill and Steele (1986) also included a comprehensive review of earlier sediment chemistry studies in their report.

In 1996, the State of Illinois Lieutenant Governor's office coordinated the development of an Integrated Management Plan for the Illinois River Watershed, and a report outlining 34 key recommendations for this Management Plan was published in 1997 (State of Illinois, 1997). This Plan formed the basis of an ongoing State of Illinois-U.S. Army Corps of Engineers partnership to identify appropriate restoration activities within the watershed. Further information concerning this partnership is available at http://www.mvr.usace.army.mil/ILRiverEco/default.htm. Sediment chemistry impacts several of the recommendations contained in the Integrated Management Plan, including promoting the beneficial use of dredged materials and the development of appropriate sediment management strategies. Prudent implementation of these recommendations requires that the chemical composition of the sediment be thoroughly characterized, especially with respect to potentially toxic chemical constituents. To collect such background chemical information before potential dredging within Peoria Lake, Cahill (2001) collected and analyzed ten sediment cores for a variety of chemical constituents including metals, nutrients and organic compounds on a total sediment basis. Of the metals determined, Cd and Ni most often exceeded various sediment quality guidelines. In addition, the concentrations of some polyaromatic hydrocarbon (PAH) compounds also exceeded some sediment quality guidelines. A key recommendation was for more research to understand the source, distribution and fate of PAH compounds in Peoria Lake sediments.

Dredging of sediment requires consideration of two important factors. First, the resuspension of sediments during dredging operations can lead to the release of potentially toxic species such as ammonia (NH_3) and hydrogen sulfide (H_2S), as well as other toxic inorganic or organic chemical species. These effects are usually short term. Second, the disposal or beneficial reuse of dredged sediments for island building, soil amendments or other uses can lead to longer-term release of sediment contaminants (Forstner and Calmano, 1998).

The short-term effects of sediment resuspension have been studied in the laboratory. Simpson et al. (1998) mixed contaminated anoxic estuarine sediments with oxygenated water for periods up to 8 hours. They observed that FeS and MnS were rapidly oxidized, but that CdS, CuS, PbS, and ZnS were oxidized more slowly. They suggested that the much more abundant FeS and MnS phases buffered the oxidation of the trace metal sulfides. Di Toro et. al. (1996a; 1996b) oxidized synthetic FeS and sediments containing Acid Volatile Sulfides (AVS, metal sulfides that are soluble in cold 1M HCl) in a series of laboratory experiments, and developed a particle oxidation model to rationalize the results. They observed that the oxidation rates of the synthetic FeS and sediments were essentially equal at the same pH, which demonstrated that FeS was the dominant and most rapidly oxidized AVS phase present. They also observed that 10 to 20% of the total sediment AVS fraction resisted oxidation on the time scale of hours. Bordas and Bourg (2001) suspended oxic river sediments at various solid/liquid ratios ranging from 0.1 to 50 g/L and observed that the fractions of Cu, Pb, Zn and Cd released into solution increased strongly as the solid/liquid ratio decreased. They ascribed this to an increase in the effective solid/liquid interfacial area as the solid/liquid ratio decreased.

Van den Berg et al. (2001) investigated the mobilization of trace metals (Zn, Cu, Cd, and Pb) resulting from dredging at a site in the Netherlands. Trace metal concentrations in suspended particulate matter increased during dredging, but dissolved trace metal concentrations did not. They speculated that this was due to trace metal binding mechanisms remaining unchanged during resuspension, or to a fast redistribution among sorptive phases in response to oxidation. An example of the latter possibility would be the oxidation of FeS, followed by the rapid formation of ferric oxide phases, and the subsequent sorption of dissolved trace metals.

A related concern is the longer-term behavior of sediment contaminants in response to beneficial reuse or disposal of dredged sediments. Singh et al. (2000) utilized a dilute acid leach (HNO_3) at pH 4 to assess potential metal leachability from several sediments that had been dredged and disposed of on land from 1 to 12 years earlier. Metal leachability decreased in the order As>Cu>Cr>Ni>Zn>Cd>Co>Pb. Also, metal leachability in dredged sediments one year after disposal was not significantly different from sediments that had been disposed of 12 years earlier. This suggests that any potential effects resulting from sediment oxidation occur rather quickly. Stephens et al. (2001) conducted shorter term leaching tests of trace metals from dredged canal sediments from the United Kingdom. The sediments were allowed to air-dry and then they were leached with water over a 12-week period. Metal leachability increased over the first five weeks and then decreased between weeks 5 and 12. Both Singh et al. (2000) and Stephens et al. (2001) caution that their results are only applicable for the specific leaching methods utilized and sediments studied. However, a general conclusion from these studies is that significant trace metal leaching that might occur during land disposal of dredged sediments is primarily a short-term (weeks to months) phenomenon.

The U.S. EPA and Army Corps of Engineers have published a testing manual for the evaluation of dredged material proposed for discharge in water (U.S. EPA and U.S. Army Corps of Engineers, 1998). This manual contains technical guidance for assessing the potential of contaminant-related impacts of discharging of dredged material into open water disposal areas, and for impacts associated with dredged material runoff from confined disposal areas. Potential impacts are assessed using a four-tiered approach. The first tier uses readily available, existing information (including all previous testing). Tier II is concerned solely with sediment and water chemistry with respect to water column effects and bioaccumulation potential. Tier III is concerned with well defined and nationally accepted toxicity and bioaccumulation testing methods. Tier IV allows for case-specific laboratory and field testing, and is intended for use only in unusual circumstances. This tiered approach is intended to help guide and standardize the testing and evaluation of dredged material intended for open water or near shore disposal. Data from the present study could be used in Tier II assessments of dredging and disposal of Peoria Lake sediments.

A number of empirical and theoretical approaches for developing sediment quality guidelines (SQGs) for metals (including Cu, Pb, Cd, Zn, Ni and Ag), as well as various organic compounds (including various PAH compounds and their mixtures) have been proposed by the U.S. EPA and others. Many of these proposed SQGs have been summarized by McCauley et al. (2000). Empirically based SQGs are typically developed from correlating adverse biological effects (usually to benthic invertebrates) with chemical concentrations in sediments (usually expressed on a dry weight basis). Theoretically based SQGs are based primarily on an understanding of how chemicals partition between biologically available and unavailable forms in a particular sediment environment. Consensus-based approaches that combine facets of both empirical and theoretical SQGs have also been proposed (Swartz, 1999). MacDonald et al. (2000) recently developed consensus-based SQG's for 28 chemicals (8 metals, 10 PAHs, total PCBs, and 9 pesticides) in freshwater sediments. Two SQGs were developed for each chemical, a "threshold effects concentration" (TEC), below which the chemical is not likely to be toxic to benthic organisms, and a "probable effects concentration" (PEC), above which adverse effects on benthic organisms are likely. Both TEC and PEC values are expressed on dry weight basis.

Each approach to developing SQG's has various limitations and uncertainties since the bioavailability and toxicity of potentially toxic chemical species depends on a number of physical, chemical, and biological processes that interact on a site-specific basis and are not easily quantified (U.S. Army Corps of Engineers, 1998; Chapman and Mann, 1999; U.S. EPA, 2000; Ahlf and Förstner, 2001). A number of these factors are summarized in Table 1.

Consequently, SQGs are useful primarily as initial screening tools, as in for example dredged material assessments. The U.S. EPA prefers theoretically derived SQGs based on equilibrium partitioning (between sediment solids, pore water, and benthic organisms), since they feel that approach better accounts for varying biological availability in different sediment environments. In fact, draft guidelines utilizing the equilibrium partitioning approach are under review for metals (Cd, Cu, Pb, Ni, Ag, Zn, and their mixtures), nonionic organics, PAH mixtures, dieldrin, and endrin (U.S. EPA, 2001b-f).

Table 1. Important Factors that Influence the Bioavailability of Sediment-associated Chemicals (from U.S. EPA, 2000).

Physical Factors	**Chemical Factors**	**Biological Factors**
• Rate of mixing	• AVS concentrations for Cu, Cd, Pb, Ni, Zn	• Biotransformation
• Rate of sedimentation	• Redox conditions	• Bioturbation
• Diffusion	• pH	• Organism size/age
• Resuspension	• Interstitial water hardness	• Lipid content
	• Sediment organic carbon content	• Gender
	• Dissolved organic carbon content	• Organism behavior
	• Organic-water equilibration constants for organic compounds	• Diet, including sediment ingestion, feeding mechanism
	• Organic matter characteristics	• Organism response to physicochemical conditions
	• Equilibration time with sediment	

In anoxic sediments, AVS help control bioavailable concentrations of Cu, Pb, Cd, Zn, and Ni (DiToro et al., 1992; Ankley et al., 1996; Chapman et al., 1998; U.S. EPA, 2001g). Determination of sediment AVS concentrations, as well as the concentrations of simultaneously extracted Cu, Pb, Cd, Zn, and Ni, (collectively termed simultaneously extracted metals; SEM) is performed using a cold HCl extraction (typically 1N), followed by determination of sulfide and SEM concentrations in the extracts

(Allen et al., 1993). Several studies have demonstrated that sediments with SEM/AVS molar ratios less than one are seldom toxic, while SEM/AVS ratios greater than one more often result in sediment toxicity (e.g., Berry et al., 1996; Hansen et al., 1996). An excess of AVS usually results in low pore water Cu, Pb, Cd, Zn, and Ni concentrations because sufficient sulfide is available to form sparingly soluble metal sulfides from these metals (e.g., CuS). Conversely, SEM/AVS ratios greater than one suggest that free sulfide concentrations are not high enough to bind all available Cu, Pb, Cd, Zn, and Ni as insoluble metal sulfides. In this instance, the bioavailable fraction of these metals may be greater, although other phases such as organic matter or ferric- and manganese-oxide phases may act to keep the bioavailable fraction of these metals relatively low. Consequently, sediments with SEM/AVS ratios greater than one are not necessarily toxic.

The AVS approach to assessing toxicity due to the affected metals (Cu, Pb, Cd, Zn, Ag, and Ni) has been criticized. Lee et al. (2000a) found that the bioavailability of Cd, Ni, and Zn to four benthic invertebrate species was controlled more by feeding behavior and dietary uptake (ingestion of sediment particles) rather than sediment pore water concentrations. Boothman et al., (2001) documented that fine scale vertical and temporal variations of AVS and SEM can occur in sediments, and concluded that these variations should be considered when assessing bioavailability. Similarly, Lee et al. (2000b) observed fine scale (≤ 1cm) variations in pore water concentrations of Cd, Ni, and Zn in laboratory microcosms, and concluded that these concentrations were influenced by diffusion as well as AVS. Additionally, the presence of excess AVS in sediments can be accompanied by toxic levels of dissolved H_2S in pore waters. Wang and Chapman (1999) reviewed the biological implications of sulfide toxicity in sediments and concluded that they are poorly understood and often ignored in sediment toxicity assessments and experiments. Finally, AVS are unstable in the presence of oxygen, so other phases such as organic matter and various metal oxide phases act to govern trace metal speciation and bioavailability in oxic sediment environments (Chapman et. al., 1998).

Diagenesis refers to the sum total of physical, chemical, and biological processes that act to change sediment after deposition (Berner, 1980). Diagenetic modeling has been used for over 30 years to help understand and decipher the effects of diagenetic processes in sediments, but model applications have been done far more frequently for oceanic than fresh water environments (Boudreau, 1999). A particularly important application of diagenetic modeling is to rationalize observed pore water concentration profiles of chemical species in sediments. Sediment pore waters sensitively reflect diagenetic changes in sediments. Hence, since pore water is often the dominant route of exposure of benthic species to toxic substances, a diagenetic model that can match observed pore water profiles is also a potentially powerful but underutilized tool to help assess bioavailability.

Diagenetic modeling can also be used to determine the fluxes of contaminants and nutrients across the sediment water interface (Di Toro, 2001), and such fluxes can be a dominant source (flux from sediment) or sink (flux into sediment) term when calculating, for example, nutrient budgets. Garland et al. (2000) employed diagenetic modeling to help quantify the release of phosphorus from Lake Pepin sediments. They determined that internal loading (i.e., phosphate release from sediments) represented 50% of the total phosphorus loading to Lake Pepin. Reckhow and Chapra (1999) reviewed available nutrient loading models and approaches and found that sediment water exchange phenomena are typically addressed in a "primitive" fashion. They recommended that more sophisticated diagenetic models should be integrated into nutrient/food-web models. Soetaert et al. (2000) reviewed the various approaches that have been used to couple benthic and water column diagenetic models.

Previous investigations of sediment chemistry within the Illinois River watershed and in Peoria Lake in particular, have focused on total concentrations of various constituents. As discussed above, total sediment concentrations of potentially toxic chemical constituents by themselves are often not the most reliable indicators of actual bioavailability and toxicity. Rather, other measures such as pore water concentrations and AVS determinations should also be employed as initial screening measures. There appears to have been only a few studies that have included such measures of bioavailability and toxicity conducted along the Illinois River or Peoria Lake in particular. Sparks and Ross (1992) attempted to identify the toxic substances that may have been responsible for the rapid decline in several species of aquatic organisms in the upper Illinois River during the mid-1950s. Toxicity tests with both the fingernail clam (*Musculium transversum*) and water flea (*Ceriodaphnia dubia*) using pore waters from various locations between river miles 6 and 248 strongly implicated ammonia as the species primarily responsible for the observed acute toxic effects. In an earlier and less extensive study, Schubauer-Berigan and Ankley (1991) concluded that ammonia, metals and non-polar compounds were responsible for the toxicity of sediment pore waters from the Cal Sag Channel in Illinois. Frazier et al. (1996) found total ammonium (NH_4-N) concentrations ranged from 0.07 to 4.0 mg/L in winter, and 0.07 to 10 mg/L in summer in pore waters from four sites in pool 8 of the upper Mississippi River. However, these concentrations were apparently not lethal to fingernail clams in the study area.

The overall objective of this study was to provide a comprehensive assessment of ammonia, Cu, Pb, Cd, Zn, and Ni concentrations in the pore waters of Peoria Lake sediments, as well as AVS and SEM concentrations in these same sediments. To the knowledge of the Principal Investigators, this study is among the first along the entire Illinois River watershed that emphasized the collection, determination, and interpretation of sediment pore water, as well as AVS and SEM concentrations. This will help provide a more complete assessment of potential environmental impacts associated with the proposed dredging and other restoration efforts within Peoria Lake. We also envision that the results of and expertise gained from this study will be useful in future work related to sediment chemistry and contamination issues in other portions of the Illinois River Watershed and other watersheds within the State.

METHODOLOGY

Sample Collection

All sample containers were cleaned with acid to reduce metal contamination before going out on the river. Polyethylene bottles and centrifuge tubes were filled with 8% HCl, soaked at least 48 hours, and rinsed several times with deionized water. The peristaltic pump tubing and syringe filters were cleaned by pumping 8% HCl and then deionized water through them. Commercially cleaned dissolved organic carbon (D.O.C.) vials and Teflon®-lined septa and the AVS jars (I-Chem) were used as-received. The sediment section rings and caps were soaked in 8% HCl and rinsed with deionized water.

Ten sites in Peoria Lake were chosen for sediment sampling (Figure 1). The sites spanned from river mile 164, near downtown Peoria, to 179, near Chillicothe. There were two sites at river mile 164. Site 164W was near the eastern side of the navigation channel while site 164E was farther east near the entrance to Eastport Marina. Sites 171E, 171M, and 171W formed an east-west transect at river mile 171. Site 171W was near the western side of the navigation channel, site 171E was near the eastern shore, and site 171M was approximately halfway between the other two sites. Sites 171M and 171E were in the Woodford-Tazewell-Peoria State Fish and Wildlife Area. There were also sampling sites at river miles 165.5, 169, 175, and 177. Sediment cores and overlying water samples were collected from all ten sites in April 2000 and again in October 2000.

The site numbering system was the same as that of the vibra-coring stations given in Table 1 of Cahill (2001) who used a global positioning system (GPS) to identify site coordinates. We utilized GPS to locate near the vibra-coring stations of Cahill (2001). The actual GPS coordinates for our stations, as well as those from Cahill (2001) are given in Appendix A (Table A-1).

At each site the river-water quality near the sediment-water interface (within about 15 cm) was characterized. The temperature, pH, conductivity, and dissolved oxygen concentration were measured using a multi-probe sonde (YSI model 600R with model 610-DM data logger). The probes were calibrated daily according to manufacturer's instructions prior to data collection.

After the river-water-quality parameters were recorded at a site, two sediment cores were collected. One core was for pH measurements and the other was for extrusion and further processing. The sediment corer (Aquatic Research Instruments, Lemhi, ID) consisted of a PVC coring head and a removable polycarbonate core tube (9.5 cm ID, 50 cm long). The head was attached to an aluminum rod and had a one-way check valve and ball valve vacuum release. This valve let air and water escape as the tube was being pushed down through the sediment, but kept the sediment core and overlying water in the tube when the sampler was pulled up. The sediment sampler is based on the design of Jakoke (1988).

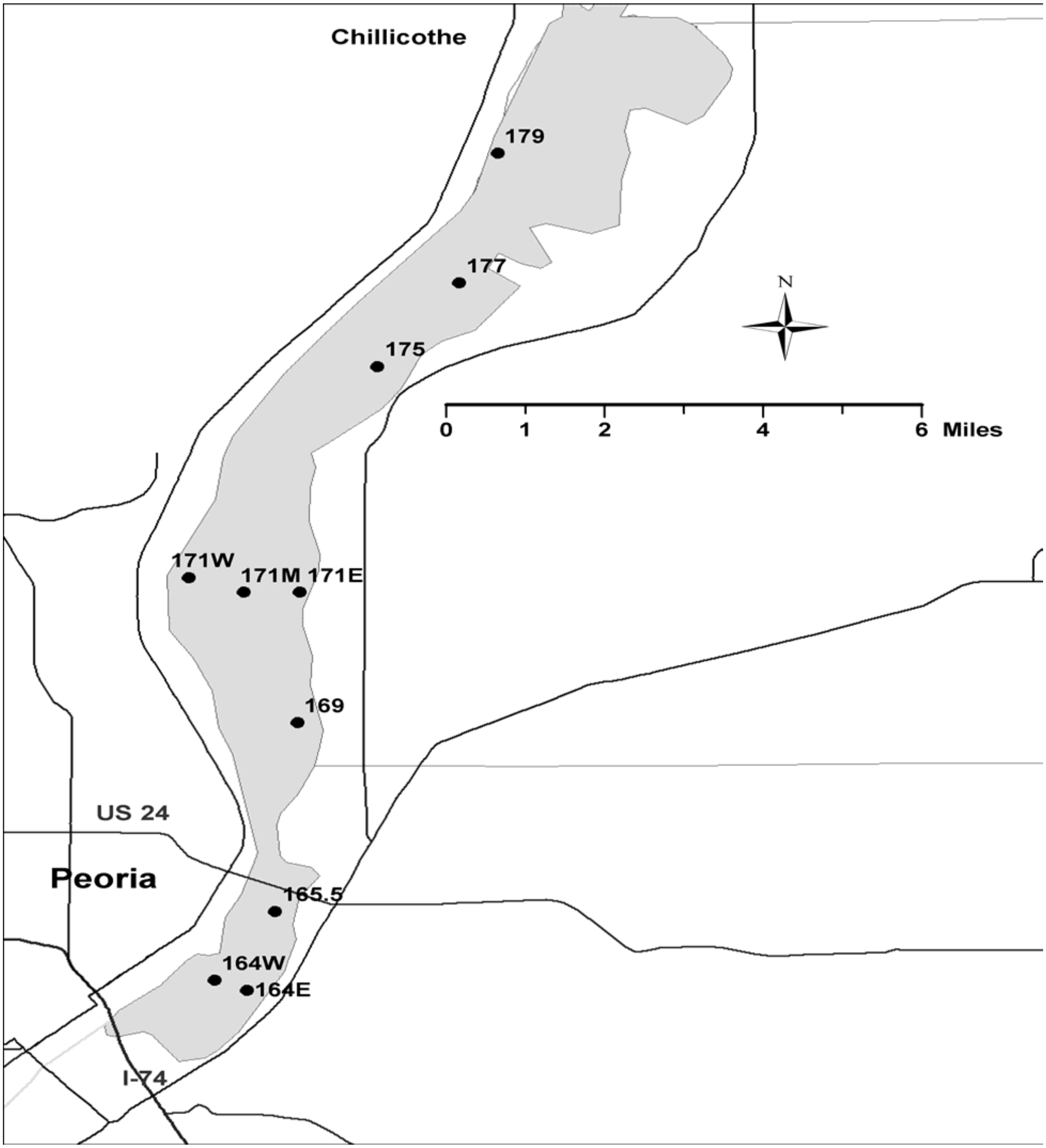

Figure 1. Peoria Lake Sampling Stations

Sediment sampling involved two people. One person pushed the sampler into the sediment and pulled it up until the bottom of the core tube was a few centimeters below the water surface. The other person inserted a custom-fit polyethylene stopper with an o-ring (also from Aquatic Research Instruments) into the bottom of the tube for proper sealing before it emerged from the water. After the stopper was in place, the head was disconnected and the stopper was pushed up through the tube with the aid of an extrusion rod until all of the overlying water was forced out the top. The core was extruded into a series of polycarbonate rings that were cut from the same stock as the core barrels (9.5 cm ID) and were 6 cm long. A ring was placed on top of the core barrel and held in place by another polycarbonate ring that had been slit lengthwise. The sediment was pushed up until its surface was even with the top of the ring. The slit ring was then removed and a broad spatula (enclosed in a plastic bag) was inserted between the top of the core tube and the bottom of the ring to slice off the 6 cm sediment section. The top of the sediment-filled ring was then sealed with a tight-fitting polyethylene cap. Next, the section was turned so the bottom was facing up, the spatula was removed, and a second polyethylene cap sealed the bottom of the sediment section. The caps were sealed to the ring with duct tape, a unique identification number was written on one of the caps with indelible marker, the identification number was recorded, and the rings were sealed in individual zip-lock® bags and stored in a cooler with ice. The process was repeated until either the entire sediment core had been extruded (short cores) or five sections (rings) had been processed and stored. Extrusion was done as quickly as possible to minimize sediment exposure to air. This minimized the oxidation of reduced species such as ferrous iron or sulfide.

For each station a second core for pH measurements was collected and sealed with polyethylene end caps. The core tube for pH and temperature measurements had pairs of holes drilled every 2 cm. The holes were covered with athletic tape for core collection. Temperature and pH were measured using an Orion portable pH meter, an Orion temperature probe, and an Orion Ross^{TM} Sure-Flow$^{®}$ semi-micro pH electrode with a flushable junction (Thermo Orion, Beverley, MA, model 8175BN). Two holes were uncovered at each measuring depth, the combination pH electrode was inserted into one hole, and the temperature probe into the other. The pH was monitored and recorded along with the temperature when the rate of change was less than about 0.02 pH units per minute. The junction was flushed with filling solution after every measurement to prevent clogging and attendant problems of drifting readings. The pH electrode was calibrated (with automatic temperature compensation) with NBS traceable buffers (pH 7.00 and pH 4.00) before each core was measured. Electrode drift was monitored by re-measuring a pH 7.00 buffer solution after pH measurements were completed on each core.

At each station, filtered river water samples were collected for determination of metals, ammonia, and organic carbon. The samples were collected through a polyethylene tube. One end of the tube was weighted so that it was suspended above the sediment surface at a height that varied between about 3 and 15 cm. The other end was connected to a silicone tube in a peristaltic pump. The silicone tube was connected to an in-line filter. For the April 2000 sampling trip separate 25 mm syringe filters were used for metals and ammonia (0.22 µm, glass prefilter/acetate Cameo$^{®}$ filters from Osmonics, Inc.), and dissolved organic carbon (1.0 µm, glass filters from Gelman Sciences, Inc., Ann Arbor, MI). For the October 2000 sampling trip, all river water samples were filtered using high capacity filter capsules designed primarily for groundwater sampling of dissolved trace metals (0.45 µm, also from Gelman Sciences, Inc.) . The acid preservatives had been added to the sample containers before sampling. Appendix B (Table B-1) lists the sample containers, approximate filtered volumes collected, and acid preservatives used.

Blank samples for metals, ammonia and organic carbon were processed in the laboratory by filtering and preserving distilled-deionized water using procedures identical to those followed for our pore water and river water samples. As such, these blanks provide assessment of the sum total of possible contamination levels. These blank data are tabulated at the beginning of the appropriate tables in Appendix A.

Sediment and Pore Water Processing

The sediment samples were taken to the ISWS Peoria laboratory after collection. Batches of sediment sections (~10) were sealed in glove bags® (Instruments for Research and Industry, Cheltenham, PA). Each glove bag was evacuated and then filled with nitrogen (N_2). This process was repeated three times. The N_2-filled glove bags were stored at 4°C until they could be processed further. This minimized exposure of the core sections to air.

Sediment processing was done in a N_2 atmosphere in glove bags® (Instruments for Research and Industry). As with the other precautions taken in collecting and storing the core sections, this was done to avoid exposure of the sediments to air. Two sediment sections, eight 50 cm^3 centrifuge tubes, and four 4-oz. (120 cm^3) glass jars were put in a glove bag (the "dirty" glove bag). The ID numbers of the sediment sections, centrifuge tubes, and AVS jars were recorded in the project notebook. The glove bag was alternately evacuated and filled with N_2 three times. For each section, the centrifuge tubes were filled by alternately scooping sediment out of the ring into a centrifuge tube and tapping the tube on the bench top to force the sediment to the bottom of the tube. The tubes were filled completely (4 per sediment section) and then tightly capped. Next, the AVS jars were filled completely and tightly capped. After all the centrifuge tubes and jars had been filled, the AVS jars were placed in a freezer. The centrifuge tubes were transferred to a high-speed tabletop centrifuge (Damom/IEC model HT) and centrifuged at 12,000 rpm for 30 minutes. The centrifuge was kept in a walk-in cooler to avoid excessive heating during centrifugation. Soft or "soupy" sediments yielded 15-20 mL of supernatant per tube after centrifuging. Firm or "dry" sediments yielded ~10 mL. Sandy sediments yielded essentially no supernatant. Centrifugation is the generally preferred ex-situ method for isolating pore water (Carr et al., 2001;U.S.EPA, 2001g).

After centrifuging, the centrifuge tubes were transferred to another glove bag (the "clean" glove bag) with two acid-cleaned, numbered 2-oz. (60 mL) HDPE bottles, and the glove bag was alternately evacuated and filled with N_2 three times. The "clean" glove bag had a 1/8-in. (0.3 cm) OD Teflon® tube sealed into the side. This tube was connected to a peristaltic pump. The supernatant from one sediment section (4 centrifuge tubes) was decanted into one of the 2-oz. bottles. The tube was inserted into the bottle and an appropriate syringe filter (25mm O.D.) was attached to the pump tubing. April pore water samples for metals and ammonia were filtered through separate 0.22 µm Cameo glass prefilter/acetate filters (Gelman), and organic carbon pore water samples were filtered through 1.0 µm glass fiber filters (Gelman). October pore water samples for metals were filtered with 0.2 µm Puradisc® polypropylene syringe filters (Whatman). Use of these filters resulted in lower dissolved metals blanks, especially for Zn and Cu. October pore water samples for ammonia and organic carbon were filtered as in April. A few mL of filtrates were run to waste before appropriate volumes of filtrate were collected (given in Table B1). The bottles that were intended for metals analyses contained Optima® high-purity HNO_3 (Fisher) as a preservative, and the bottles that were intended for ammonia and organic carbon analyses contained reagent-grade H_2SO_4. Duplicate samples for metals or ammonia were collected for approximately 20% of the sediment sections, and dissolved organic carbon duplicates were collected on about 10% of the sediment sections. After filtration the ID numbers of the centrifuge tubes, 2-oz. bottles, metals and ammonia bottles, and D.O.C. vials were recorded and the process was repeated for the centrifuge tubes from the other sediment section. All filtered samples were stored at 4°C.

AVS and SEM Methods

Acid-volatile sulfide (AVS) was determined by passive distillation (Gagnon et al., 1995). The distillation apparatus consisted of a 250-mL standard-taper three-neck flask, a magnetic stirrer, an egg-shaped stirring bar, and two 125-mL gas washing bottles. The gas washing bottles were connected in series to one side neck of the flask by a standard-taper fitting and a Teflon® tube. The other side neck was connected to a N_2 line by a standard-taper fitting. The N_2 flow rate was controlled by a needle valve and measured with a flowmeter. The middle neck was for sample introduction and was closed by a standard-taper stopper. Silicone grease was used to seal the fittings and stoppers on the flask and the tops of the gas washing bottles to the bottoms.

The AVS procedure followed that of Chanton and Martens (1985). A frozen sediment sample was thawed. A 15 mL aliquot of 9M HCl/20% $SnCl_2$ was added to the flask and 100 mL of 1.7M NaOH/0.15M Zn acetate was added to each of the gas washing bottles. The purpose of the $SnCl_2$ was to prevent the liberation of H_2S from any pyrite in the sediment (Chanton and Martens 1985). The fittings on the side necks of the flask were secured with wire and the stopper was secured with a Keck clamp. The system was purged with high-purity N_2 at a flow rate of 100 cm^3/min for 10 min. After purging, the stirrer and N_2 flow were turned off and five cm^3 of thawed sediment was added to the flask using a plastic syringe with the tip cut off. The middle stopper was secured with wire and the stirrer and N_2 were turned back on. The N_2 flow rate was adjusted to 60 cm^3/min. and the distillation continued for 3 hr. After distillation the gas washing bottles were disconnected from the system and the N_2 and stirrer were turned off. Eighteen mL of concentrated HCl was added to the downstream bottle to neutralize the NaOH and immediately after that standardized I_2/KI solution was added to oxidize any sulfide. The I_2/KI solution was repeatedly drawn into and out of the gas dispersion tube to oxidize any sulfide trapped inside. The contents of the gas-washing bottle were transferred to a beaker and the process was repeated for the other gas-washing bottle. The excess I_2 was back-titrated with standard sodium thiosulfate (Fisher) (Clesceri et al., 1998).

The AVS distillation involves transferring gaseous H_2S from the flask to the solution in the gas scrubbing bottles. If there were any leaks in the system, then some H_2S would be lost. Leaks occurred frequently when the joints were sealed with just silicone grease or silicone grease plus Keck clamps. The authors suspect that CO_2 liberated by HCl from carbonate minerals in the sediments formed $ZnCO_3$ or $Zn_3(CO_3)_2(OH)_2$ in the glass frits and created back pressure. Securing the fittings with wire eliminated most of the leaks. Stopping the stirring and N_2 flow during sediment addition minimized H_2S losses during sediment addition. The authors found that a significant fraction of sulfide was trapped inside the gas dispersion tubes. For some samples the solution in the gas dispersion bottle was yellow after adding I_2/KI solution and mixing, indicating there was excess I_2. However, the yellow color disappeared after the solution was drawn into the gas dispersion tube and more I_2/KI solution had to be added.

Sub-sampling the thawed sediment samples was problematic because freezing caused some separation of sediment solid phases and water. Although all sediment samples appeared to be homogeneous when they were first packed into the jars, many samples had a layer of water on top when they were thawed. In effect, this phenomenon was an example of ‘freeze-thaw conditioning’, whereby water is separated from the sediment solids as ice crystals form (e.g., Martel, 1999). Consequently, for each AVS determination an attempt was made to homogenize the sample after thawing. However, in some cases it was difficult to collect duplicate samples having the same consistency.

Some sediment sections were analyzed in duplicate and some others were spiked with Na_2S. For the spikes, a 1-10 mM Na_2S solution was prepared and standardized (Clesceri et al., 1998) immediately before the distillation. A small volume of the Na_2S solution was added immediately after the sediment was added. AVS blanks were measured by performing the procedure with reagents only, no sediment.

Simultaneously extracted metals (SEM) had to be extracted in a separate flask. The reagent-grade $SnCl_2$ used in the AVS distillations may have contained significant quantities of other metals according to the manufacturer’s specifications. Therefore, SEM was determined in parallel with AVS in a separate flask. The SEM apparatus consisted of a flask and stirring bar that were identical to those used for AVS. Fifteen mL of 9M trace-metal-grade HCl (Baker) were added to the flask and the flask was purged with high-purity N_2 for 10 min. Then 5 cm^3 of thawed sediment were added and the mixture was stirred for 3 hr. While the sediment was being stirred, a 25 mm, 0.22 μm Cameo glass fiber prefilter/acetate syringe filter was cleaned by pumping 100 mL of 8% HCl followed by 100 mL of deionized water through it. After the 3 hr. distillation/extraction, 120 mL of deionized water was added to the flask and the contents were stirred. The suspension was allowed to settle and a portion of the supernatant was filtered into two 1-oz. (30 mL) acid-cleaned HDPE bottles. The sediment sample and bottle ID numbers were recorded. For selected sediments, both bottles were submitted for analysis. SEM blanks were measured by performing the procedure without added sediment.

Pore Water, River Water and Sediment Solid Characterizations

Dissolved Fe in pore water samples from sites 165.5 and 177 (April and October) was determined by the phenanthroline colorimetric method (Clesceri et al., 1998). The reagent (from CheMetrics, Calverton, VA) contained a reductant, so total dissolved Fe was measured. Selected samples were analyzed in duplicate. Other selected samples were spiked with standard Fe solution. Blanks were run using deionized water instead of pore water.

Ammonia concentrations (as well as a few dissolved nitrate and phosphate concentrations) in pore water and river water samples were determined by the ISWS Analytical Chemistry and Technology Unit. Metals (Ni, Cu, Zn, Cd, and Pb) and D.O.C. in pore water and river water, SEM (Ni, Cu, Zn, Cd, Pb, Fe, and Mn), HNO_3-extractable metals in sediments (Ni, Cu, Zn, Cd, and Pb), and total organic carbon (T.O.C.) in sediments were determined by the WMRC laboratory staff. The metals were determined by inductively coupled plasma mass spectrometry (ICP-MS). Calcium (Ca) causes a low-level interference for nickel (Ni) in ICP-MS (Grotti et. al., 1999). Therefore, the WMRC ICP-MS chemists also determined Ca in sediment pore waters and corrected the Ni concentrations for the Ca interference. More information on this correction procedure is given in Appendix C. The mineralogy of selected sediment samples was characterized by x-ray diffraction at the State Geological Survey (ISGS). More information on the x-ray diffraction methods used is given in Appendix D. The samples were subject to the QA/QC programs of the ISWS, WMRC, and ISGS laboratories.

RESULTS

The measurements and analyses of Peoria Lake sediments, pore waters and overlying waters are described in separate sections. For each parameter a typical plot of concentration vs depth and a box-and-whisker plot summarizing all concentrations are presented. All measurements and analytical results are presented in Appendix A.

Sediment Appearance and Mineralogy

There was a thin (< 5 mm) flocculent brown layer at the sediment-water interface. Deeper sediments had a dark brown to black color. The sediments at all sites except 171E and 179 consisted of fine-grained materials and contained roughly 79% clay minerals, including 43% smectites, 21% illite, 4% kaolinite, and 9% chlorite. The non-clay minerals included approximately 14% quartz, 4% feldspars, and 3% calcite and dolomite. At sites 171E and 179, the sediments were mostly sandy. Appendix D presents the details of sediment mineralogy.

Sediment pH and Temperature

The sediment pH values at site 164W decreased with depth in the sediment and the October pH values were 0.1-0.2 pH units lower than the April values at all depths (Figure 2). In Figure 2 and subsequent figures depicting surface water values, the surface water depth is given as minus 3 cm which represents 3 cm above the sediment surface. This particular depth was chosen for convenience only and reflects the variable depth above the sediment surface (~ 3 to 15 cm) from which surface water samples were collected. The river water pH was 0.5-0.6 pH units higher than the shallowest sediment pH value. Peoria Lake is only 2-3 feet deep at most places except in the navigation channel, so it was assumed that the overlying water was well-mixed. The pH values for all sites displayed trends similar to those of site 164W (Figure 3). The median pH values decreased with increasing depth in the sediment, and were close to the average at most depths. At most depths the October median pH values were lower than the April median values. The median river pH values were higher than any median sediment pH values. The pH data for all sampling stations are presented in Figures A-1a and A-1b in Appendix A.

In April, the river was warmer than the sediment and the sediment temperature generally decreased with depth, while in October the opposite was true (Figure 4). In October, the sediment was warmer than the river and the temperature increased with depth.

The complete pH and temperature data set is given in Table A-2 of Appendix A. Also included in this Table are the pH 7.00 ‘buffer check’ values, which were measured right after the sediment core pH values were taken. In most cases the buffer check reading was 7.00 ±0.03. When the buffer check differed from the accepted value by more than 0.05 pH units the pH electrode was recalibrated. Also shown in Table A-2 are ‘interpolated pH’ values. These latter pH values are interpolated estimates at the average sediment depth from which each core section was collected. These values are useful when comparing sediment pH values with other data. Note that sediment temperature was not measured on several cores taken in April because the temperature probe was not working correctly. However, the pH electrode was calibrated at approximately the temperature of the sediments, so it was felt that the measurements were reasonably accurate. Also, pH buffer checks were sometimes not performed because of time constraints.

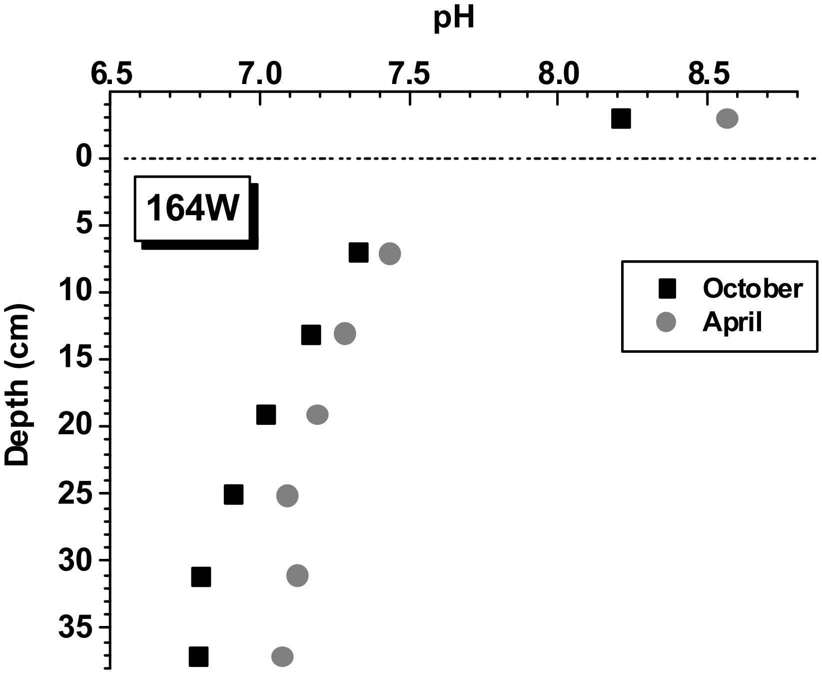

Figure 2. Profiles of pH for site 164W in April and October 2000. The river water pH values are plotted at 3 cm above the interface for convenience. It was assumed that the river was well-mixed.

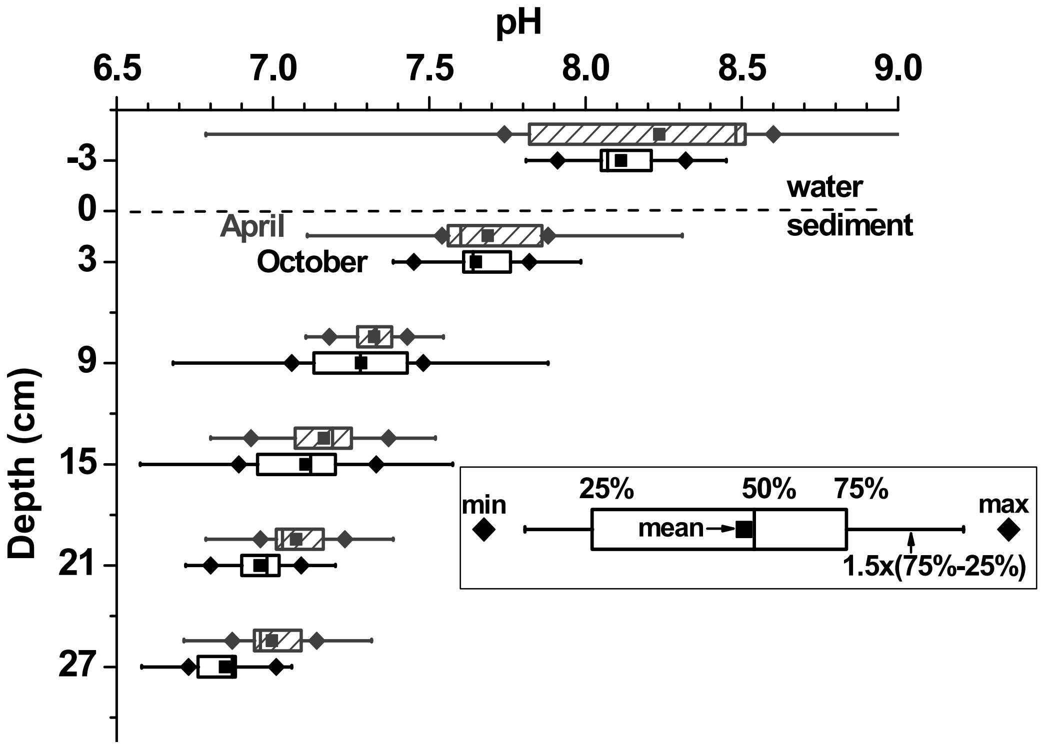

Figure 3. Summary of sediment pH values for all stations. Each box-and-whisker object summarizes the pH values of all stations at one depth for one sampling event. The pH values are interpolated for the average depths of the sediment sections (e.g., 9 cm for the 6-12 cm sections.) The "whiskers" (the lines outside the boxes) show 1.5 times the difference between the 25th and 75th percentiles. Points outside the whiskers can be considered statistical outliers.

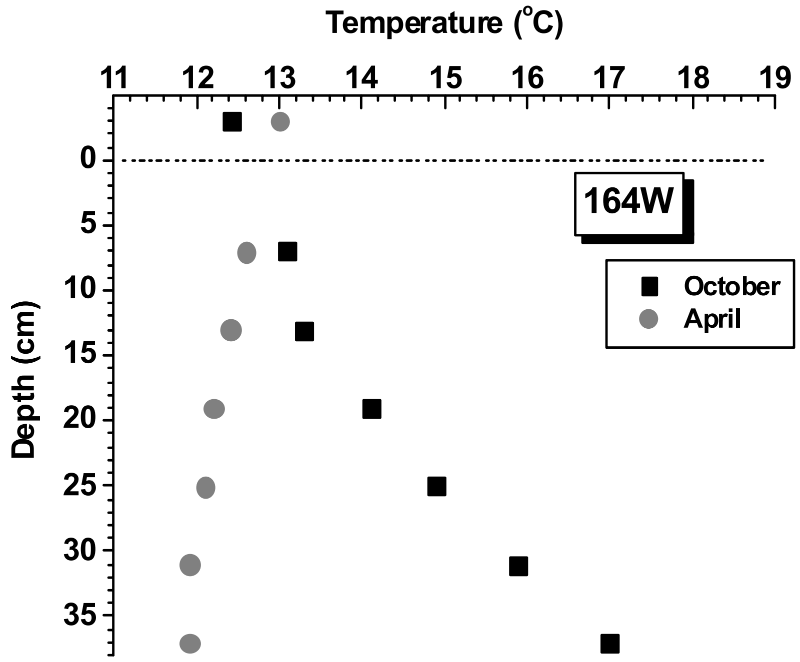

Figure 4. Temperature profiles in the sediment at site 164W in April and October 2000.

Dissolved Ammonia in Sediment Pore Water

The NH_4-N concentration in the river water at site 177 was slightly above the detection limit in April 2000. The NH_4-N concentrations in the sediment were all greater than that in the river and increased with depth (Figure 5). The concentrations in the three deepest sections were higher in October than in April. The primary source of ammonia in sediment pore water is typically the solubilization and anoxic metabolism of particulate organic nitrogen (Berner, 1980, DiToro, 2001). Therefore, the higher sediment temperatures in October may be the reason for the higher ammonia concentrations.

The NH_4-N concentrations of all sites displayed trends similar to that of site 177 (Figure 6). Overlying water column values were usually less than the analytical detection limit of 0.07 mg/L. Mean and median pore water concentrations, however, increased from about 1-2 mg/L NH_4-N at an average sediment depth of 3 cm, to about 10 to 20 mg/L at 27 cm average depth. The mean and median NH_4-N concentrations below 15 cm average sediment depth were higher in October than in April, possibly because of greater microbial activity during this period due to the higher sediment temperatures. The dotted line in Figure 6 indicates the Chronic Criterion Concentration (CCC) for NH_4-N as defined by the U.S. EPA (U.S. EPA, 1999a). The significance of the CCC for NH_4-N in relation to our pore water NH_4-N concentrations is discussed below.

Tables A-3a and A-3b in Appendix A present the ammonia concentrations for April and October 2000 and Figures A-2a and A-2b show the ammonia profiles at all of the sampling sites.

Quality Assurance/Quality control (QA/QC) data for ammonia are not listed in tabular form in Appendix B because the pore water samples were analyzed at the ISWS as part of a much larger set of analyses. However, QA/QC data specific to the pore water samples was extracted from the larger QA/QC data set. Relative precision of duplicates (RPDs) averaged 2.6%, and analytical spike recoveries ranged from 55 to 160% with an overall average of 99%, for both the April and October samples.

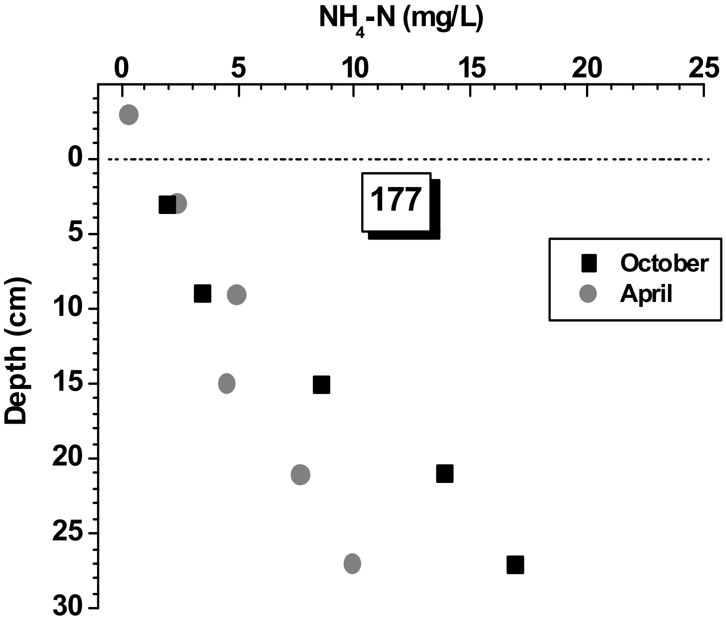

Figure 5. Dissolved ammonia concentrations in sediment pore water at site 177 in April and October 2000.

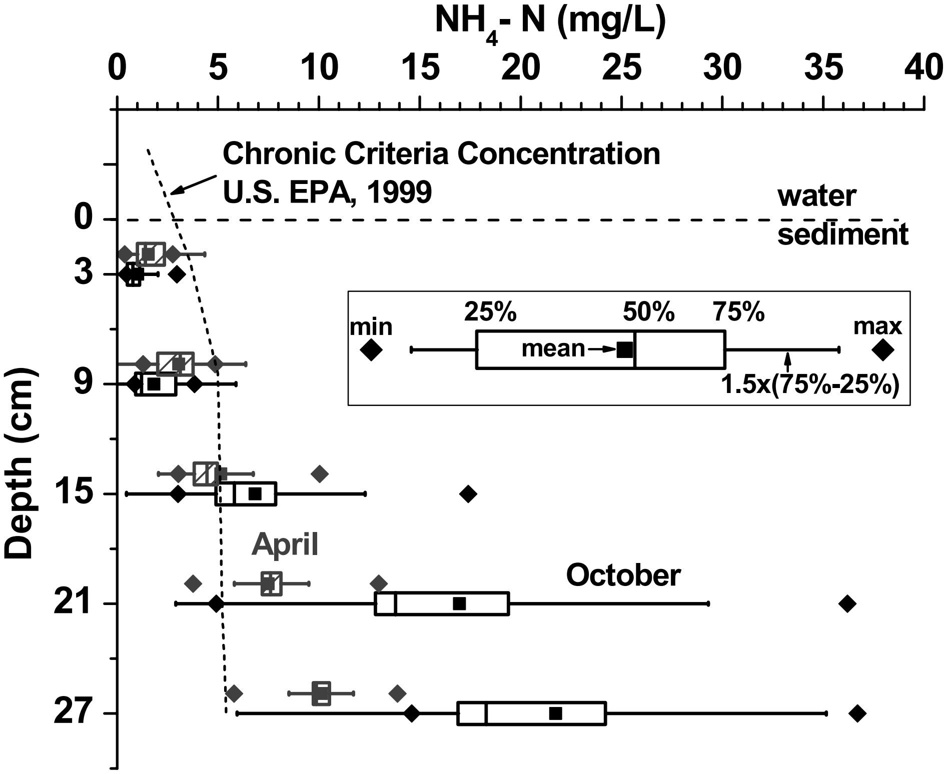

Figure 6. Summary of NH_4-N concentrations in Peoria Lake sediment pore water in April and October 2000.

Dissolved Metals

Dissolved calcium (Ca) concentrations in sediment pore water at Site 164E increased with depth and the October concentrations were lower than the April concentrations at all depths (Figure 7). There was good agreement between duplicates for 15 cm average depth. These trends were consistent with sediment pH values, which decreased with depth and which were lower in October than in April. Dissolved Ca concentrations were probably higher in deeper pore waters because of the lower pH values and resulting higher solubilities of calcite ($CaCO_3$) and/or dolomite ($CaMg(CO_3)_2$). At all sites, the mean and median Ca concentrations increased from 50-60 mg/L in the surface water to 120-140 mg/L at 27 cm average sediment depth (Figure 8). The pore water Ca concentrations at 3 and 9 cm average sediment depth were somewhat greater in April than October, while the reverse was true at 21 and 27 cm average sediment depth. There were some outliers in the deeper layers.

Tables A-4a and A-4b in Appendix A present the Ca concentrations for April and October 2000, and Figures A-3a and A-3b show the Ca profiles at all of the sampling sites.

Calcium affected nickel (Ni) determinations in pore waters by ICP-MS through formation of small amounts of calcium oxide (CaO) in the plasma. Some combinations of Ca and O isotopes produce oxides with the same masses as some Ni isotopes. A correction procedure based on Ca concentrations and oxide levels in the plasma was developed (Appendix C). The correction is significant, generally amounting to between 25 and 50% of the uncorrected dissolved nickel concentration (1 and 4 µg/L). Tables A-4a and A-4b include both the uncorrected and Ca-corrected dissolved nickel concentrations.

Quality assurance/quality control (QA/QC) parameters associated with calcium analyses conducted by WMRC personnel included analytical duplicates and analytical spikes. Analytical spike recoveries ranged from 95%-100% and duplicate samples yielded relative percent differences from 0%-6%.

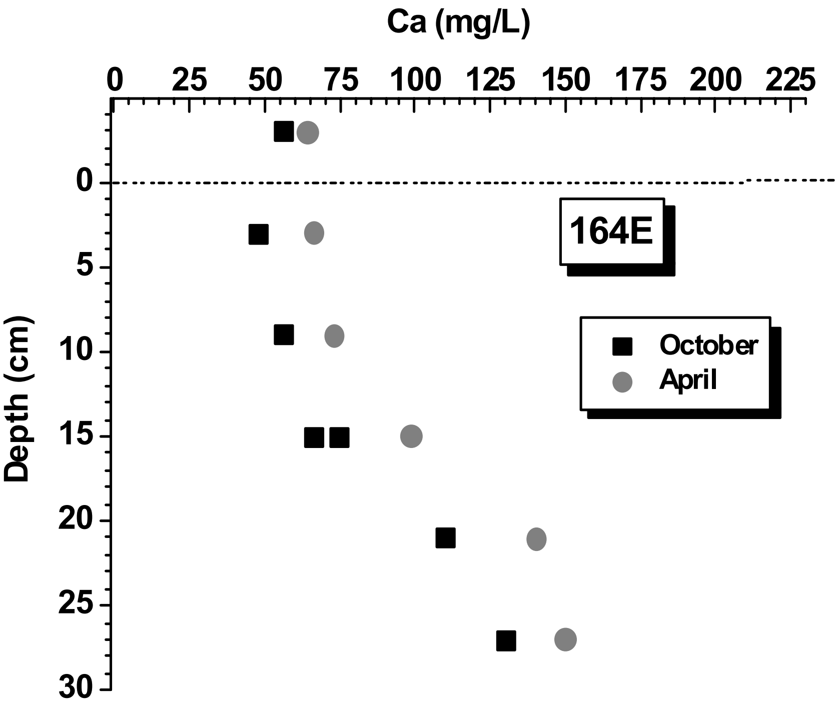

Figure 7. Dissolved calcium concentrations in sediment pore water at site 164E in April and October 2000.

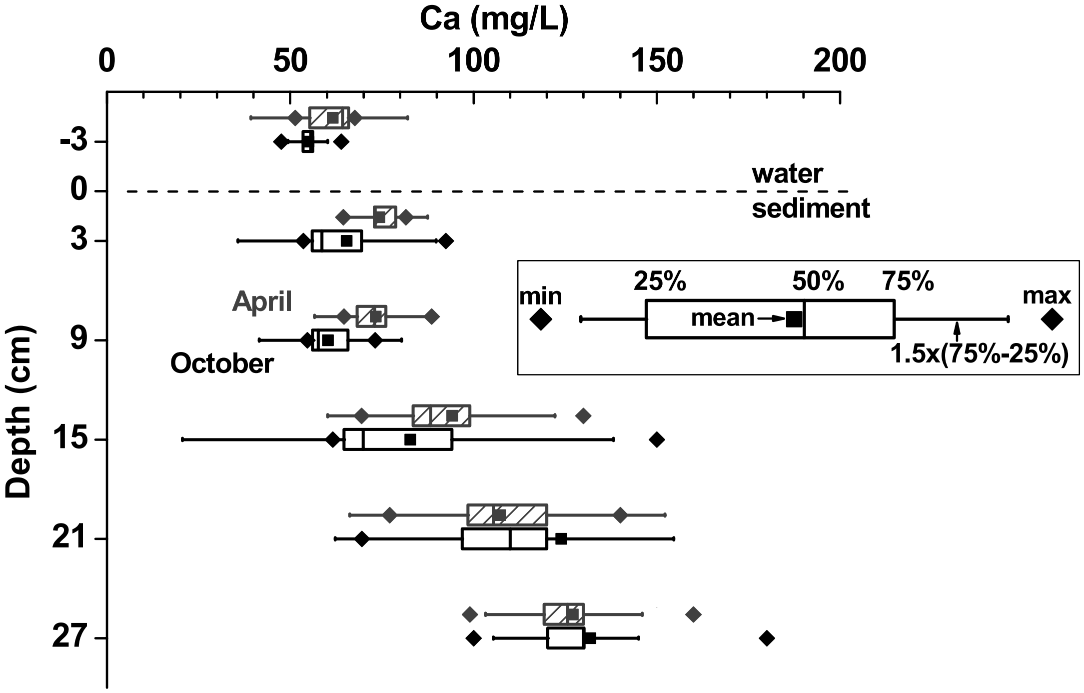

Figure 8. Summary of dissolved calcium concentrations in Peoria Lake sediment pore water.

Dissolved Ni concentrations in sediment pore water at site 171W were higher in October than in April (Figure 9). Nickel was the only metal that was detected at all depths at site 164E and it was the only metal that was consistently detected in pore water at the other sites in both April and October. River water and pore water concentrations of dissolved Cd, Cu, Pb, Ni, and Zn were always less than 15 µg/L. Moreover, of these potentially toxic metals, only Ni was consistently above the analytical detection limits of 0.05 to 0.2 µg/L. Dissolved nickel concentrations at almost all depths at all sites were higher in October than in April (Figure 10). Mean and median river water and pore water Ni concentrations ranged from about 0.5 to 6 µg/L, and both river water and especially pore water concentrations were noticeably greater during our October sampling period than those found the previous April. There were outliers at nearly all depths. The reasons for the differences between April and October Ni concentrations are unknown, but the higher October concentrations may have been related to the lower pH values (Figure 3).

The dissolved concentrations of Cd, Cu, Ni, Pb, and Zn in the overlying river water were generally greater than those in the pore waters. Figure A-4g in Appendix A gives dissolved Cu profiles for those stations where concentrations were mostly above method detection limits for both April and October. River water dissolved Cu concentrations were 1-2 µg/L (equivalent to ppb plotted in Figure A-4g), while pore water concentrations were generally less than 1µg/L. QA-QC data for dissolved Cd, Cu, Pb, Ni, and Zn as supplied by WMRC personnel are given in Tables B-3 and B-4.

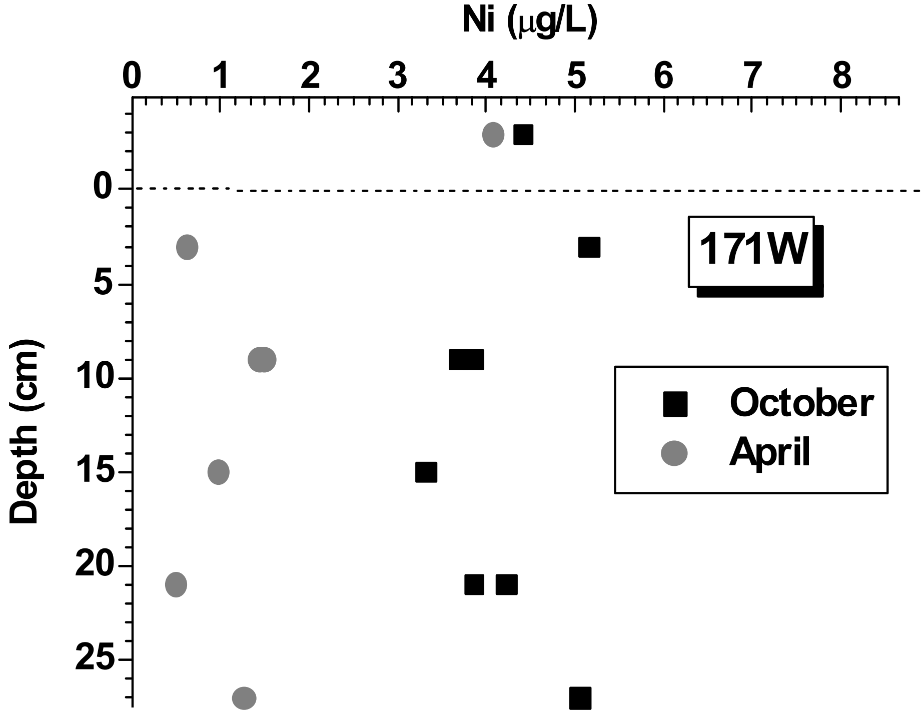

Figure 9. Dissolved nickel profiles in sediment pore water at site 171W in April and October 2000.

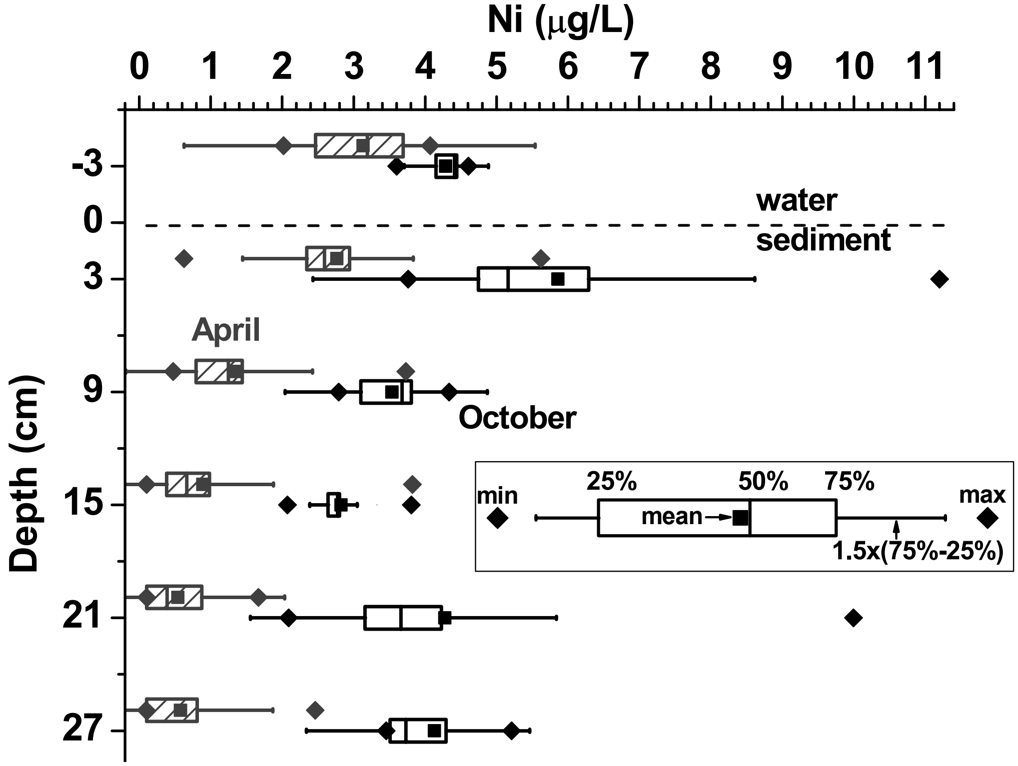

Figure 10. Summary of dissolved nickel concentrations in Peoria Lake pore sediment pore water.

Figures 11 and 12 show the dissolved Fe concentrations at sites 165.5 and 177 in April and October. Agreement between duplicates was very good. As a result, the symbols for the duplicates plot on top of one another. At both sites the Fe concentrations increased with depth. This is consistent with the pH, which decreased with depth. The solubilities of both siderite ($FeCO_3$) and mackinawite (FeS) increase with decreasing pH. However, the April Fe concentrations were generally greater than the October concentrations, which is inconsistent with the lower pH values measured in October. At Site 165.5 the April Fe concentrations were up to 12 mg/L higher than the October concentrations. At Site 177, on the other hand, the April Fe concentrations were no more than 3 mg/L higher than in October.

River water samples were not analyzed for dissolved Fe. However, U.S. Geological Survey analyses of river water samples from several sites along the Illinois River typically find dissolved Fe concentrations are less than 10 μg/L.

Tables A-4a, A-4b, and A-5 in Appendix A present the dissolved metal concentrations in April and October. Figures A-4a through A-4g show the profiles of dissolved metals at all sampling sites.

Nitrate and Phosphate

Concentrations of dissolved nitrate and phosphate were only measured at site 165.5 in October. These data are given in Table A-6 of Appendix A. Dissolved NO_3-N was always below the method detection limit of 0.12 mg/L in pore water, while the river water value was 1.80 mg/L. This river water value was typical of the relatively low NO_3-N concentrations in this portion of the Illinois River during the late-summer and early fall. In any case, there was a driving force for nitrate diffusion into the sediment. In contrast, dissolved phosphate was greater in sediment pore water (1.26 mg/L as P at 3 cm average depth) than in the overlying surface water (0.28 mg/L). Therefore, the sediments may serve as a source of P to the river.

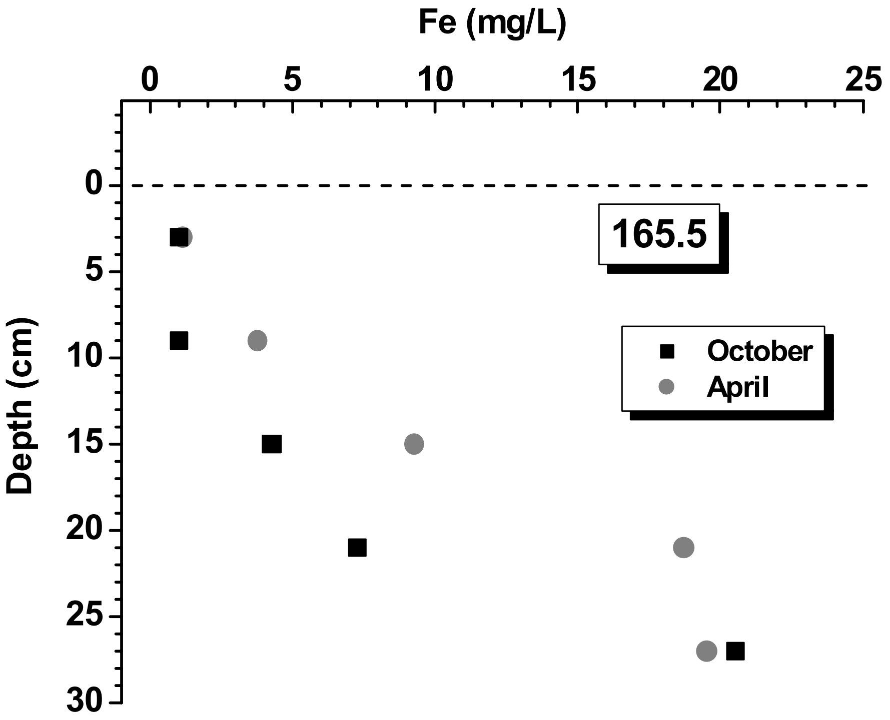

Figure 11. Dissolved iron concentrations in sediment pore water at site 165.5 in April and October 2000.

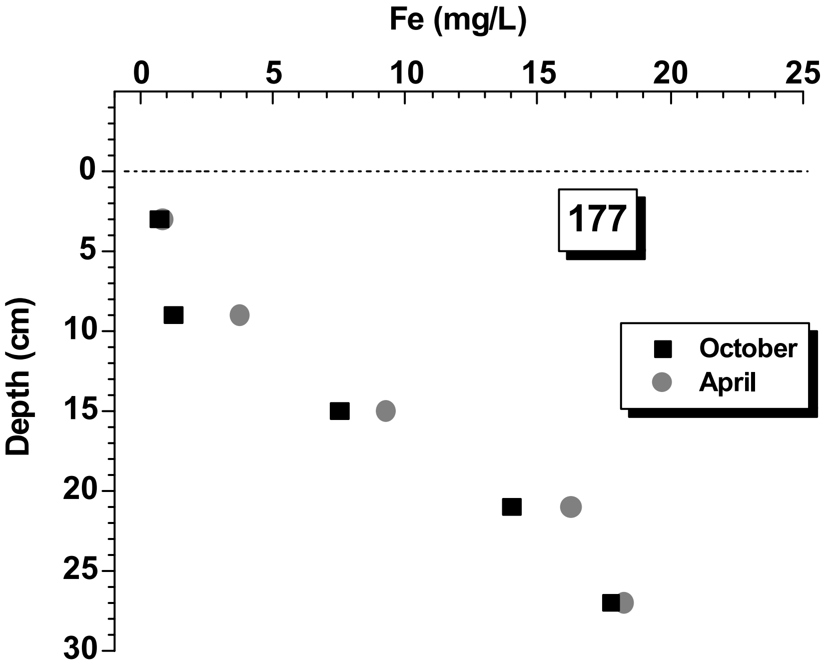

Figure 12. Dissolved iron concentrations in sediment pore water at site 177 in April and October 2000.

Acid-Volatile Sulfide

Acid-volatile sulfide AVS was detected at all depths at site 175 (Figure 13). Consequently, the sediments at Site 175 are strongly reducing at all depths except perhaps a thin layer at the sediment-water interface, since AVS phases are unstable in the presence of oxygen. The difference between duplicate AVS determinations was generally less than 15 µmol/g. The differences between duplicates may have been due to a combination of imprecision of the method, sample heterogeneity, and difficulty taking sub-samples, as explained in the Methodology section. In some cases the difference between April and October AVS values was approximately as large as the difference between duplicate determinations. However, in a few cases, such as the average depth of 15 cm at Site 175, the differences were larger. There was good agreement between April and October samples except for 15 cm average depth. AVS generally increased with depth in the top four sections and decreased somewhat from the fourth to the fifth section.

All six sites for which AVS was measured in both April and October samples showed little change in AVS. For sites 165.5 and 179 the April and October AVS profiles were essentially the same. That is, the differences between the April and October AVS concentrations were in the range of differences between duplicates. For sites 171E, 175W, and 177, there was a large difference in April and October AVS values at one depth and agreement at the other depths.

Tables A-7a and A-7b present the AVS concentrations in all sediment samples. Figure A-5a shows the AVS profiles for April and October. Figure A-5b shows the AVS profiles for the sites that were only analyzed in April. The AVS concentrations at sites 171E and 179, the sites with sandy sediments, were consistently lower than at the other stations. The lower AVS concentrations at these sites may have been due to a lower interfacial area for AVS to accumulate.

Simultaneously Extracted Metals

The Cd concentrations were lowest of the HCl-extractable metals (SEM) at all depths at site 175, Zn was the highest, and Cu, Ni, and Pb were intermediate (Figure 14). There was good agreement between replicates. The October profiles (Figure 15) were essentially identical to the April profiles. Iron and Mn were also determined in the 9M HCl extracts and these metals were much more abundant than Cd, Cu, Ni, Pb, and Zn. Iron accounted for 0.5-1.5% of the sediment dry weight, while Mn accounted for about 0.05%. The Cd, Cu, Ni, Pb, and Zn concentrations generally increased with depth while the Fe and Mn concentrations were essentially independent of depth.

The total molar concentrations of HCl-extractable Cd, Cu, Ni, and Zn were less than the AVS concentrations in all sediment samples collected in April 2000 (Figure 16). Even the sandy sediments had some AVS. The median AVS increased from 13 µmol/g in the 0-6 cm depth interval to 24 µmol/g in the 12-18 cm interval and was 21-24 µmol/g from 12-30 cm. There were some outliers for both AVS and SEM.

Over 95% of the SEM:AVS ratios were less than or equal to 0.5 and all values were less than 1.0 (Figure 17). Therefore, the sediments are not expected to be toxic to sediment-dwelling organisms based solely on their metal contents (Hansen et al. 1996). There was a large excess of Fe over AVS in all samples (Figure 18). Most of the excess Fe was probably present as $FeCO_3$ (siderite).

Tables A-7a and A-7b in Appendix A present the AVS and SEM data for April and October 2000. Figures A-5a and A-5b show the AVS profiles for April and October. Figures A-6 through A-9 show profiles of HCl-extractable metals, including Cd, Cu, Ni, Pb, and Zn (SEM) and Fe and Mn. Tables B-5 and B-6 in Appendix B give the QA/QC results for the April and October SEM analyses.

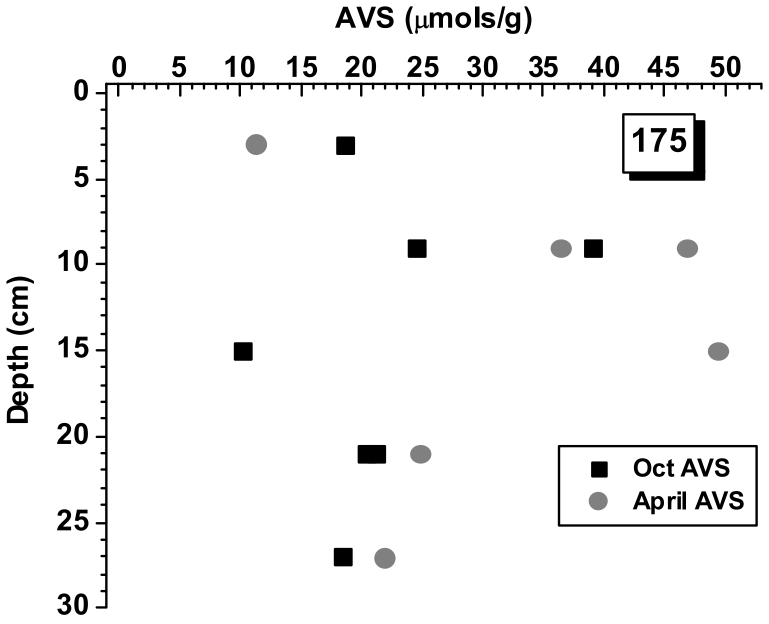

Figure 13. Profiles of acid-volatile sulfide in sediment at site 175 in April and October 2000.

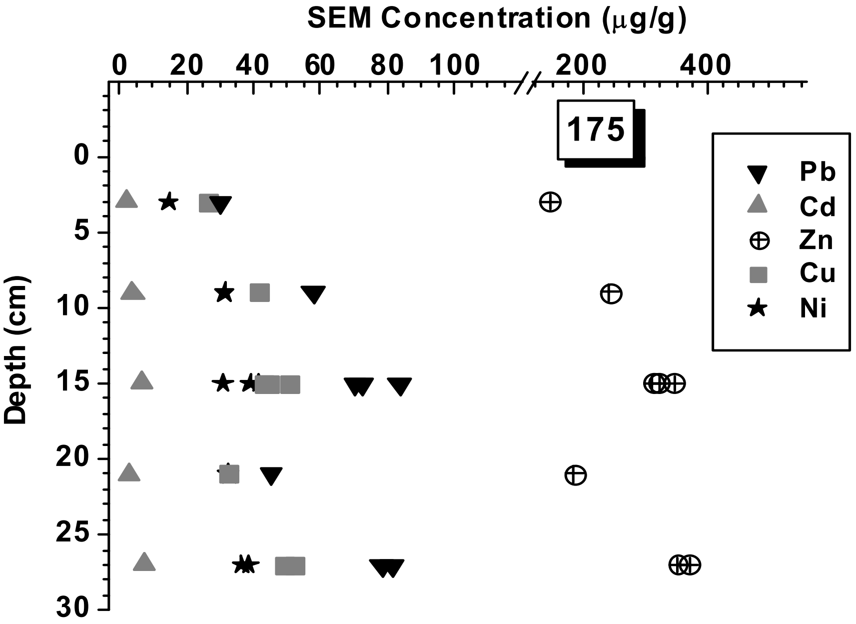

Figure 14. Profiles of simultaneously extracted metals in sediment at site 175 in April 2000.

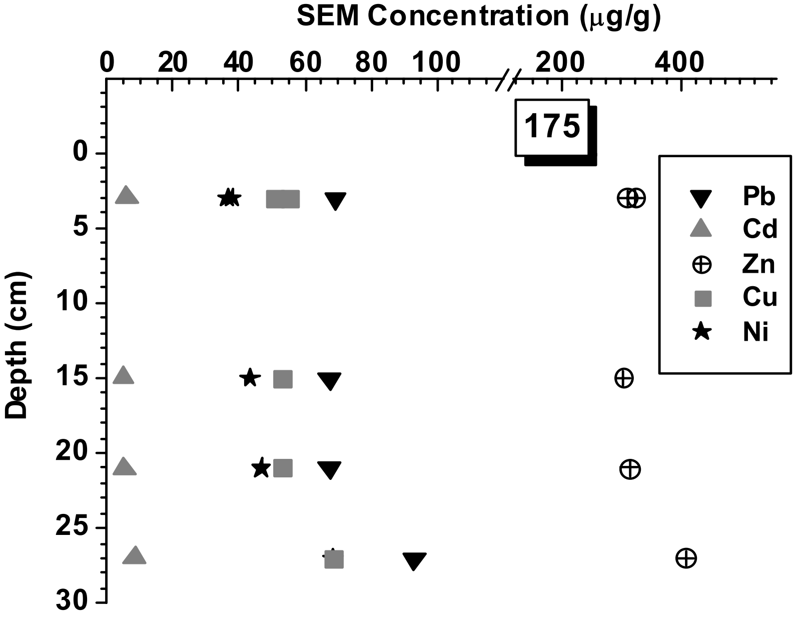

Figure 15. Profiles of simultaneously extracted metals in sediment from site 175 in October 2000.

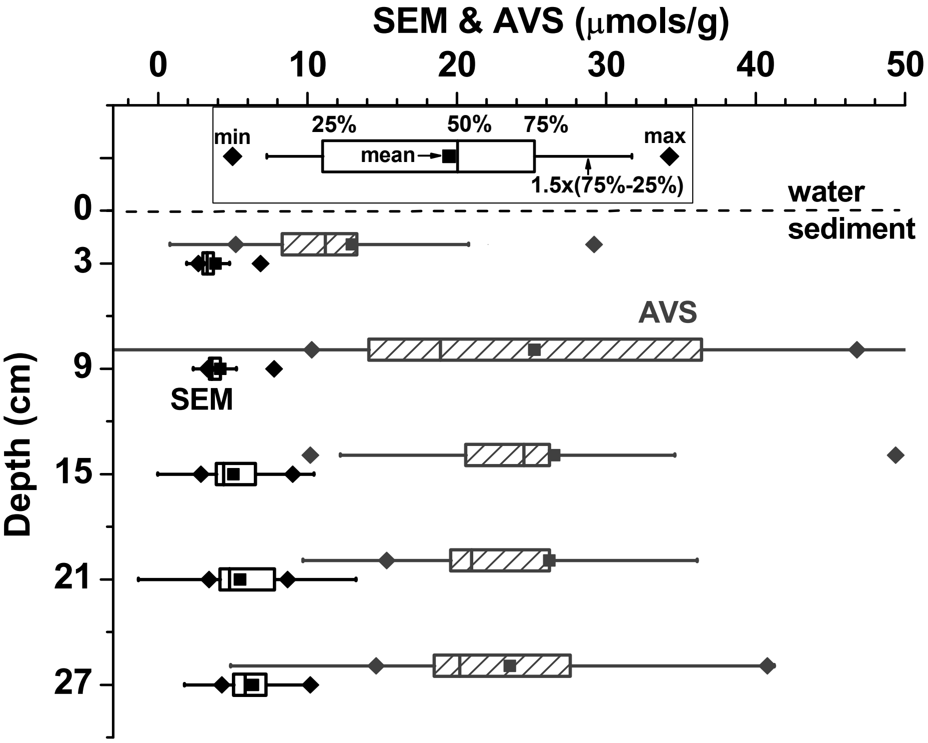

Figure 16. Summary of acid-volatile sulfide and simultaneously extracted metals in sediment collected in April 2000. SEM is the molar concentration sum of Cd, Cu, Ni, Pb, and Zn.

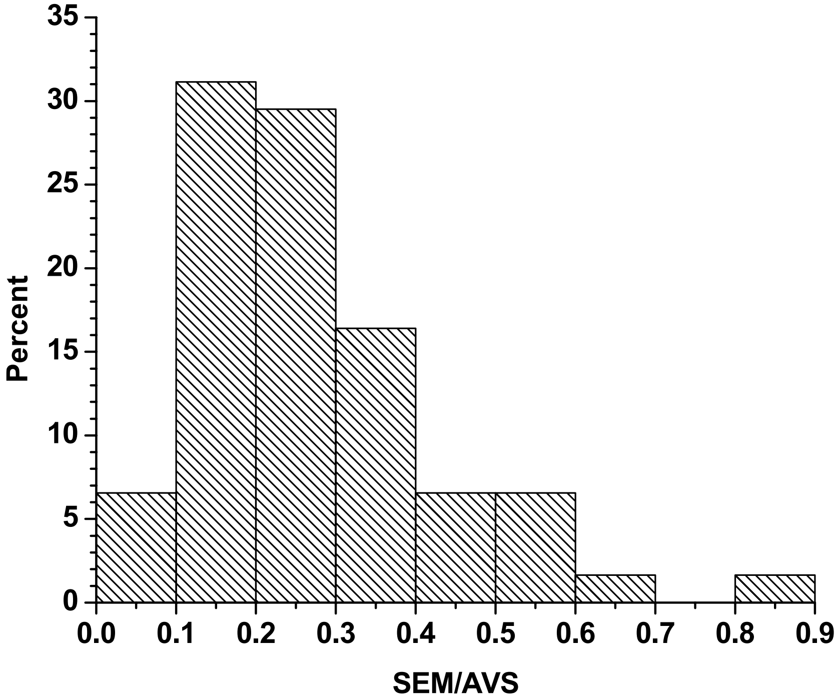

Figure 17. Frequency distribution of SEM:AVS ratios in Peoria Lake sediments.

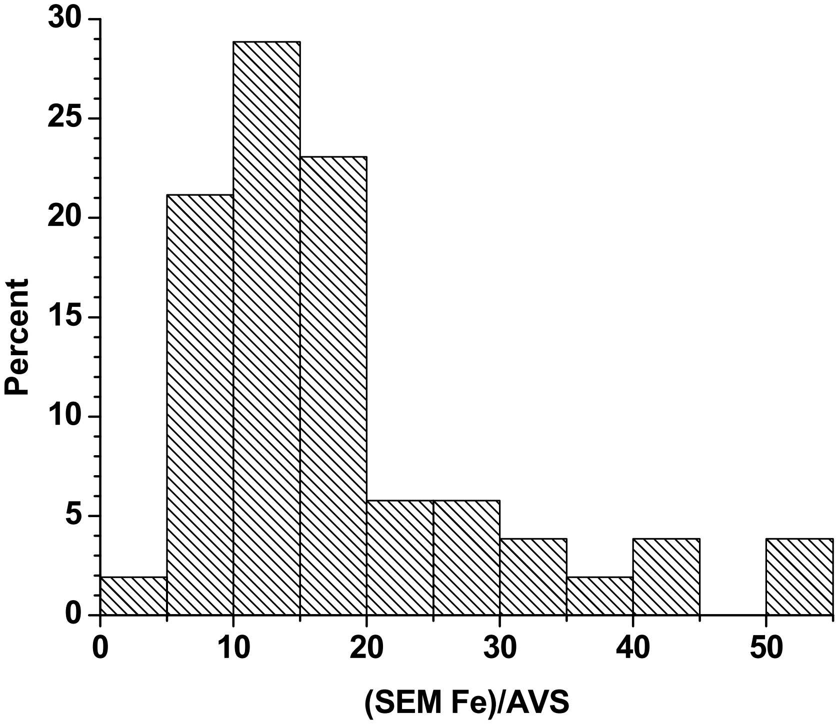

Figure 18. Frequency distribution of HCl-extractable Fe to AVS ratios in Peoria Lake sediments.

Total Recoverable Metals

Figure 19 shows the concentrations of total recoverable metal (extractable by hot HNO_3) in sediments from Site 175. At all depths the Zn concentrations were considerably higher and the Cd concentrations considerably lower than the Cu, Ni, and Pb concentrations, similar to SEM. Except for the deepest average depth, the concentrations of all five metals increased with depth. This was also the case at sites 164E, 169, 171M, 171W, 175, 177, and 179. In contrast, the total recoverable metals concentrations at sites 164W, 165.5 and 171E were essentially independent of depth.

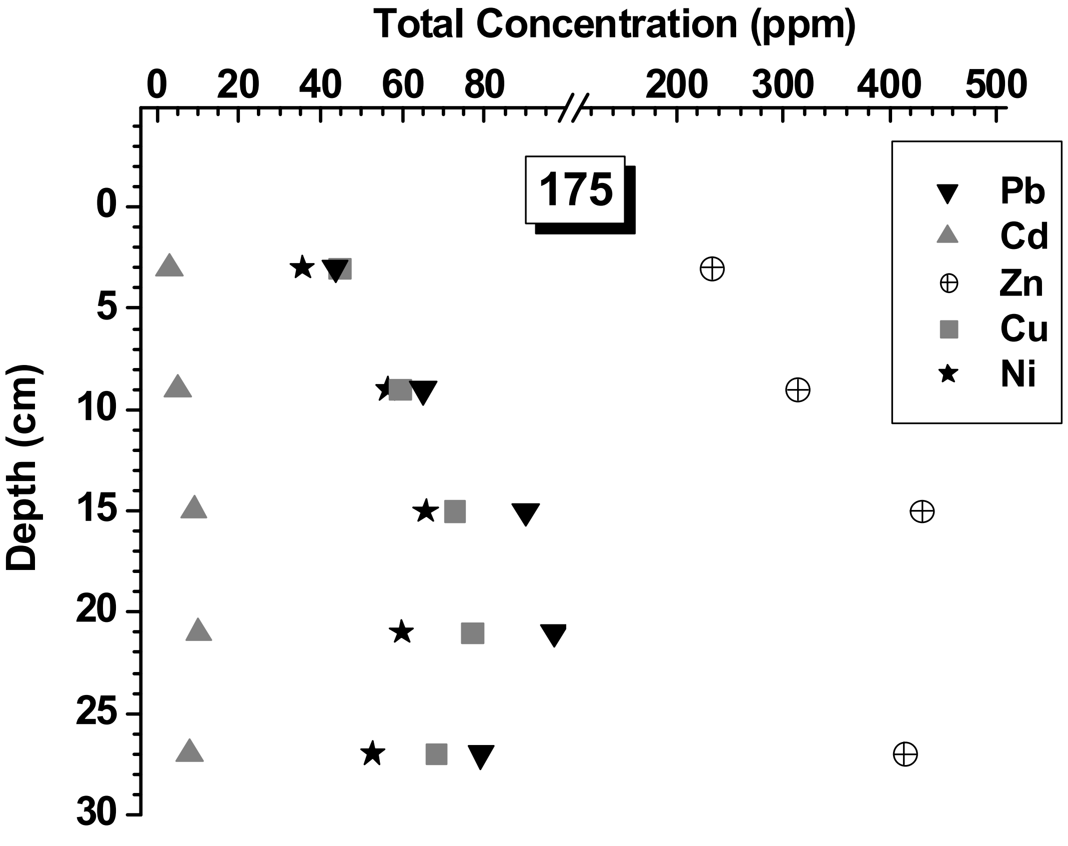

Figure 19. Profiles of HNO_3-extractable metals in sediments at site 175 in April 2000.

The total recoverable metal concentrations from sediment samples collected in April 2000 are summarized in Figure 20. The concentrations of Cd were considerably lower, and those of Zn considerably greater, than those of Ni, Cu and Pb. The mean and median recoverable metal concentrations tended to increase slightly with depth. The concentrations of these metals may have been lower in shallower (more recent) Peoria Lake sediments because point sources of these metals have been reduced since the 1960s. These same trends are even more readily apparent in the deeper sediment cores analyzed and discussed in Cahill (2001). Also given in Figure 20 are the "Probable Effect Concentrations" (PEC) for these metals as defined by MacDonald et. al., (2000). These PEC values represent the total metal concentrations above which toxic effects are "probable" in a wide variety of aquatic organisms exposed to these concentrations. Total recoverable Cu and Pb never exceeded their PEC values in any sediment section from this study. However, both mean and median Cd and Ni concentrations exceeded their respective PEC values of 5 and 49 μg/g at average sediment depths greater than 15 cm. A few deeper sediment sections also exceeded the PEC value for Zn.

HCl-extractable Cd, Cu, Ni, Pb, and Zn were less than the amount of HNO_3-extractable metal in most core sections. Cold HCl dissolves mackinawite (FeS) and related minerals but not pyrite (FeS_2), which is thermodynamically more stable than FeS and is found in many sulfidic sediments. Nitric acid dissolves FeS_2 and HCl- and HNO_3-extractable metals are sometimes called "reactive" and "pyrite-associated" metals (Morse 1995). However, Cooper and Morse (1998, 1999) found that Cu and Ni monosulfides are incompletely dissolved by 1M and 6M HCl while Cd, Pb, and Zn monosulfides can be completely dissolved by 1M HCl. Therefore, at least for Cu and Ni, it may not be possible to determine whether Cu or Ni is associated primarily with FeS or FeS_2 based on chemical extractions.

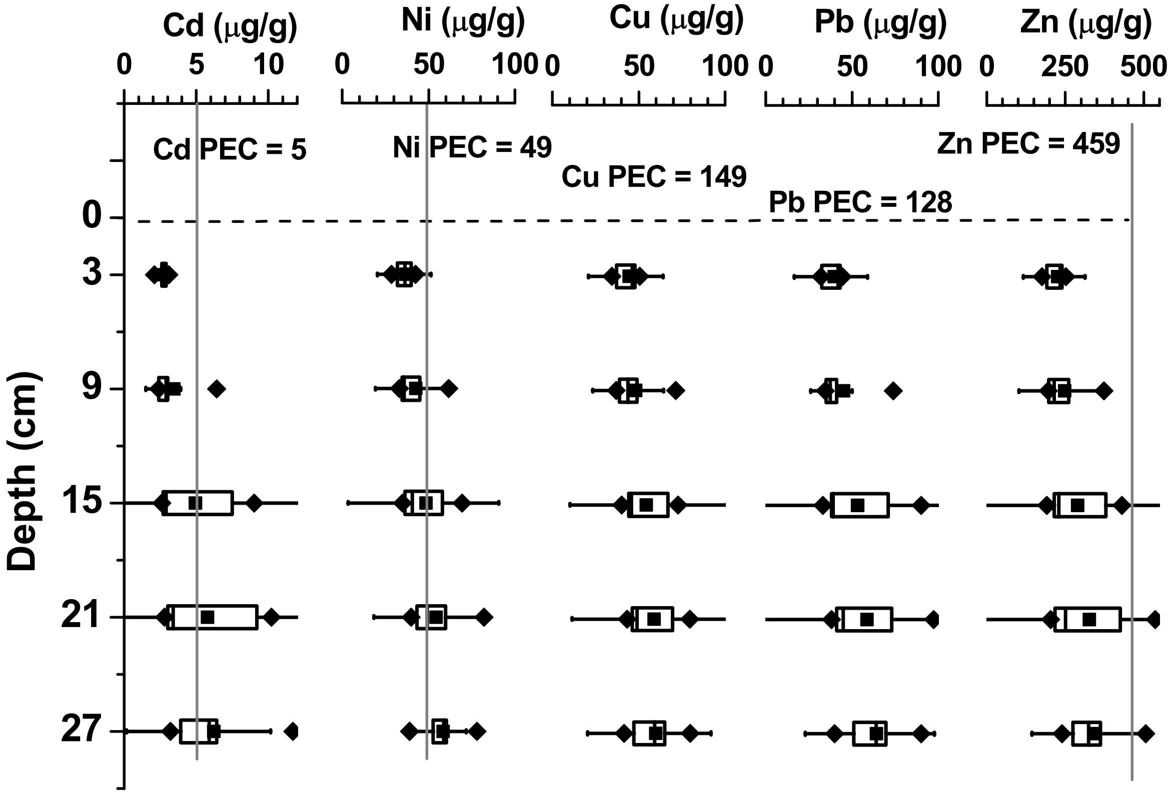

Figure 20. Box plot summary of HNO_3-extractable metals in sediments in April 2000. Probable effect concentrations (PEC) are shown as vertical lines for Cd, Ni, and Zn.

Figure 21 summarizes the ratios of HCl- and HNO_3-extractable metals for all core sections collected in April 2000 in box plot form. For Cd, Pb, and Zn, the metals whose sulfides are soluble in HCl, median ratios were greater than 0.8. Apparently these metals were mostly in monosulfide forms. There were some low outliers for all three metals and these may have been sediments with predominantly pyritic metals. For some samples the ratio was greater than one, which probably reflects the imprecision of the extractions. For Cu and Ni the median ratios were between 0.6 and 0.7 and all ratios were less than one. This may have been due to pyritic metals or to the low solubilities of Cu and Ni sulfides and the consequent difficulty of extracting these metals with HCl.

Table A-8 in Appendix A presents the total recoverable metals concentrations in all samples along with comparable data from samples analyzed by the Illinois State Geological Survey. Additional analyses provided by the Illinois State Geological Survey are given in Table A-9. Figures A-10a and A-10b show the profiles of total recoverable metals at all sites. Table B-7 gives the total recoverable metals QA/QC data.

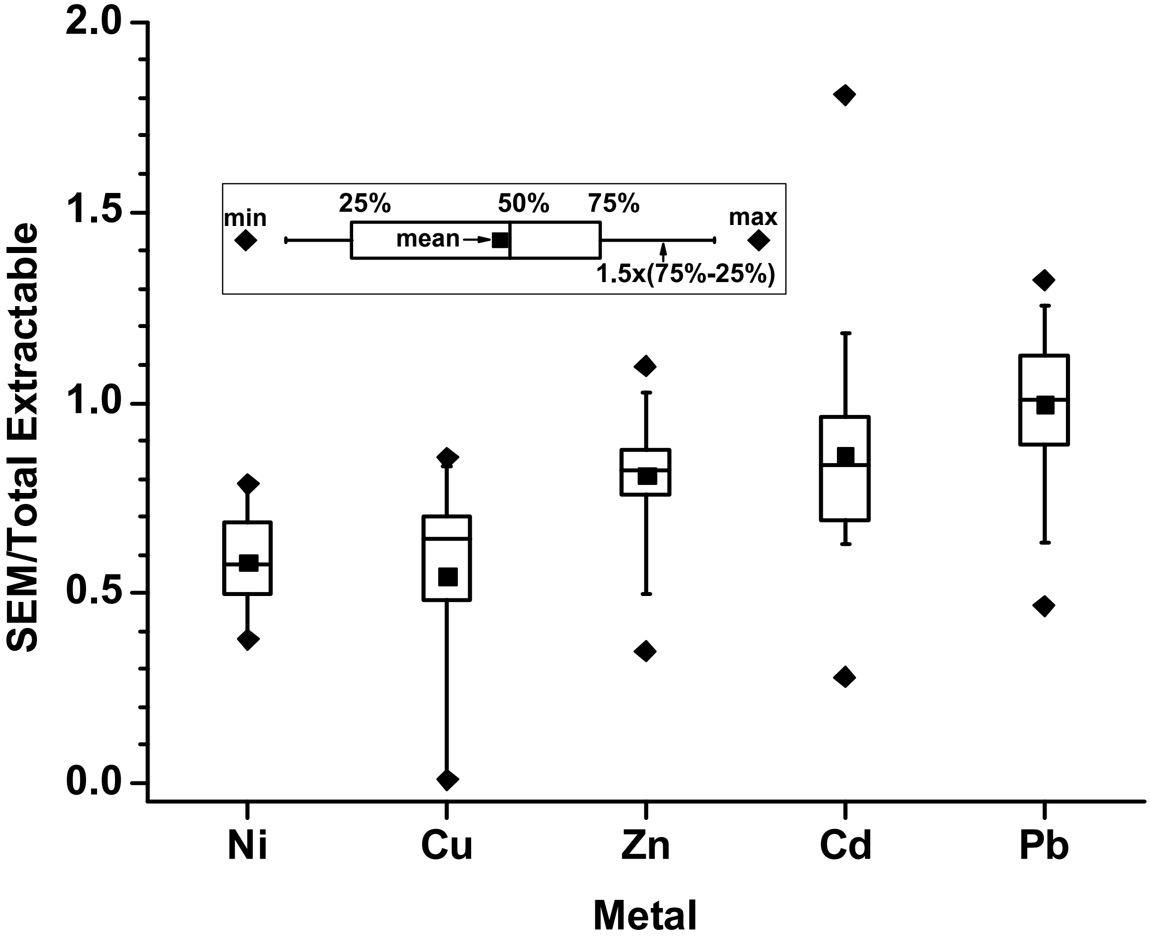

Figure 21. SEM to Total Extractable Metals Ratios in Peoria Lake sediment in April, 2000.

Dissolved Organic Carbon

The DOC concentrations in sediment pore water at site 171W increased with depth from about 9-10 mg/L at 3 cm average sediment depth to about 15-16 mg./L at 27 cm average sediment depth (Figure 22). The river water DOC values were lower than the pore water values. Thus, DOC may be diffusing from the sediments to the river.

Figure 23 summarizes the pore water DOC data in a box-and-whisker plot. As for the DOC profile of Site 171W, the median concentrations increased with depth and there were small differences between the April and October median concentrations at all depths. The pore water DOC boxes are relatively long, which signifies that there was considerable site to site variation in DOC concentrations at a particular depth.

Complete DOC data sets are given in Tables A-10a (April) and A-10b (October), and corresponding profiles are in Figures A-11a and A-11b. QA/QC data for DOC are given in Tables B-8 and B-9 of Appendix B.

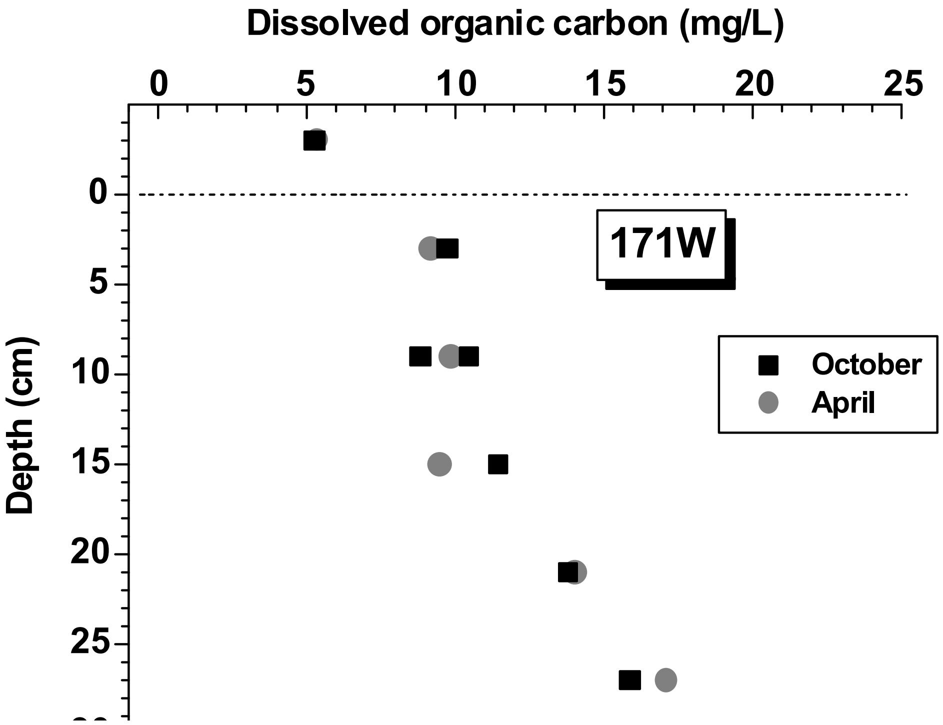

Figure 22. Depth profiles of dissolved organic carbon in sediment pore water at site 171W in April and October 2000.

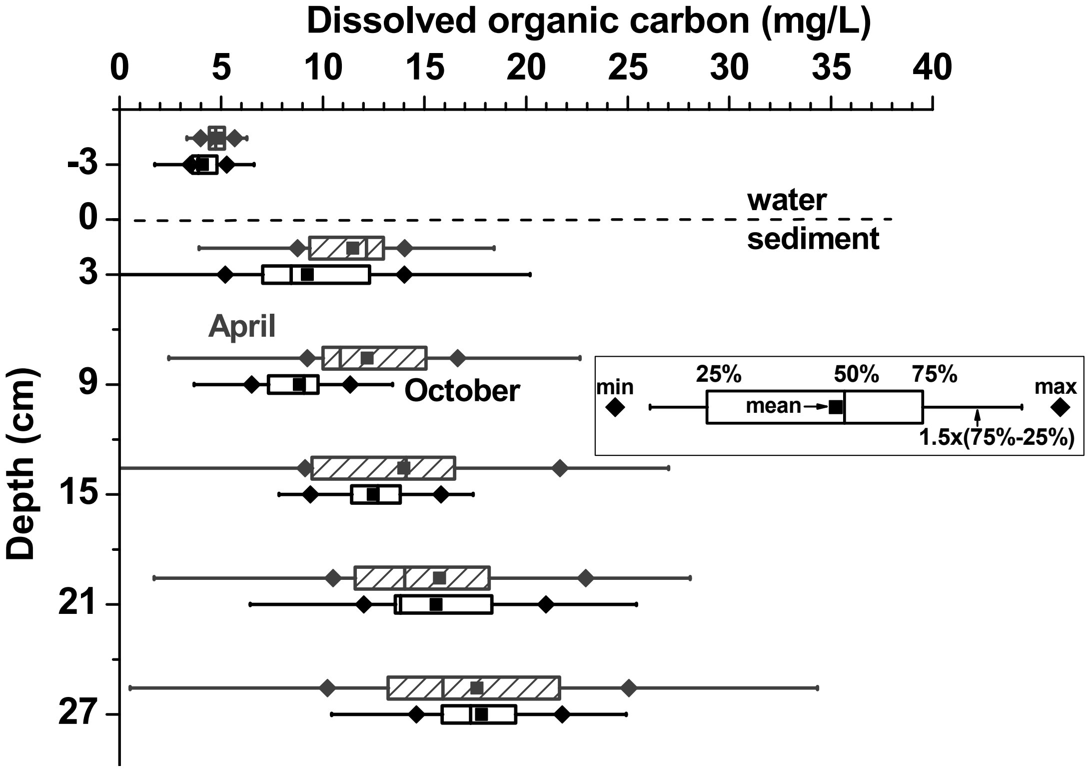

Figure 23. Summary of dissolved organic carbon concentrations in sediment pore water.

Total Organic Carbon

TOC comprised 2-3% of the sediment dry weight at site 175 (Figure 24). TOC decreased slightly with depth, unlike DOC which increased with depth. Table A-11 of Appendix A contains the complete April data set, and corresponding profiles are given in Figures A-12a and A-12b. QA/QC data for the TOC analyses are given in Table B-10. Total organic carbon was not determined for the October samples.

The TOC concentrations at all sites were relatively constant with depth (2.5 to 3.5%) (Figure 25), although there was some station-to-station variability at all depths. The primary source of this variability is the relatively lower TOC concentrations at stations 171E and 179, which contained considerably more sand than the other sediment stations. The minimum values for 3 and 9 cm average depth appeared to be statistical outliers.

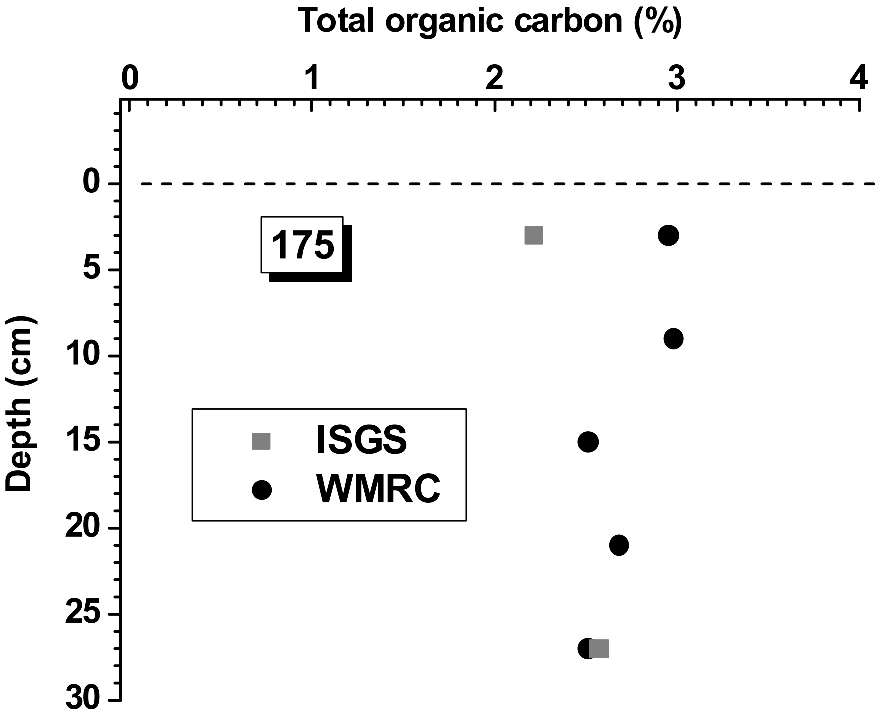

Figure 24. Profile of total organic carbon in the sediment at site 175 in April 2000.

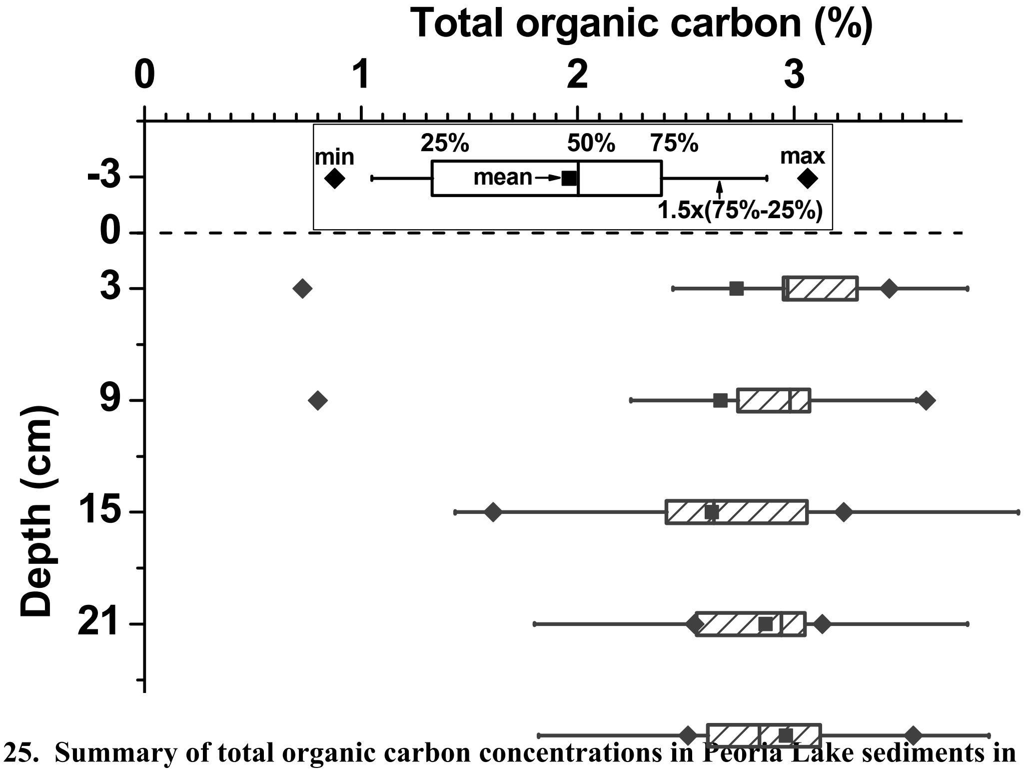

Figure 25. Summary of total organic carbon concentrations in Peoria Lake sediments in April 2000.

DISCUSSION

General Diagenetic Trends in Peoria Lake Sediments

Diagenesis refers to the sum total of physical, chemical and biological changes that occur in sediments after they are deposited (Berner, 1980). In most recently deposited sediments, including those of Peoria Lake, the sequence of chemical diagenetic reactions that occur are driven by the microbially mediated solubilization and oxidation of organic matter (Nealson, 1997; DiToro, 2001). An idealized form of organic matter solubilization is (DiToro, 2001):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)_{(s)} \rightarrow 106CH_2O_{(aq)} + 16NH_{3(aq)} + H_3PO_{4(aq)} \qquad (1)$$

In this equation, the organic carbon component of organic matter is represented as "CH_2O", and the composition of particulate organic matter follows the ideal Redfield ratio (106C:16N:1P), which is usually appropriate for 'fresh' or recently deposited particulate organic matter.

Available particulate and soluble organic matter are oxidized in sediments by a succession of microorganisms that reduce various electron acceptors usually in order of decreasing reduction potentials (Nealson, 1997). Consequently, with increasing depth, sediments generally become more reducing. Organic matter oxidation first occurs by the reduction of dissolved oxygen. Since dissolved oxygen concentrations in water are rather limited (typically < 10 mg/L), undisturbed sediments typically become anoxic at some depth. In eutrophic water bodies such as Peoria Lake, this occurs within a few centimeters of the sediment surface because of the abundant supply of oxidizable organic matter.

Table 2 lists the general sequence of oxidation-reduction (redox) reactions involving organic carbon, and Figure 26 presents concentration profiles of some major redox-sensitive species in a typical freshwater sediment. Most of these profiles are the result of a reaction listed in Table 2. For example, the methane fermentation reaction (last entry of Table 2), results in the production of methane ($CH_{4(g)}$), at depth in Figure 26.

Table 2. General sequence of redox reactions in natural environments involving organic carbon (CH_2O). Taken from Stumm and Morgan, 1996, Table 8.8.

O_2 consumption (respiration)	
$\frac{1}{4}\{CH_2O\} + \frac{1}{4}O_2$	$= \frac{1}{4}CO_2 + \frac{1}{4}H_2O$
Denitrification	
$\frac{1}{4}\{CH_2O\} + \frac{1}{5}NO_3^- + \frac{1}{5}H^+$	$= \frac{1}{4}CO_2 + \frac{1}{10}N_2 + \frac{1}{2}H_2O$
Nitrate reduction	
$\frac{1}{4}\{CH_2O\} + \frac{1}{8}NO_3^- + \frac{1}{4}H^+$	$= \frac{1}{4}CO_2 + \frac{1}{8}NH_4^+ + \frac{1}{8}H_2O$
Production of soluble Mn(II)	
$\frac{1}{4}\{CH_2O\} + \frac{1}{2}MnO_2(s) + H^+$	$= \frac{1}{4}CO_2 + \frac{1}{2}Mn^{2+} + \frac{1}{8}H_2O$
Fermentation	
$\frac{3}{4}\{CH_2O\} + \frac{1}{4}H_2O$	$= \frac{1}{4}CO_2 + \frac{1}{2}CH_3OH$
Production of soluble Fe(II)	
$\frac{1}{4}\{CH_2O\} + FeOOH(s) + 2H^+$	$= \frac{1}{4}CO_2 + \frac{7}{4}H_2O + Fe^{+2}$
Sulfate reduction, production of H_2S	
$\frac{1}{4}\{CH_2O\} + \frac{1}{8}SO_4^{2-} + \frac{1}{8}H^+$	$= \frac{1}{8}HS^- + \frac{1}{4}CO_2 + \frac{1}{4}H_2O$
Methane fermentation	
$\frac{1}{4}\{CH_2O\}$	$= \frac{1}{8}CH_4 + \frac{1}{8}CO_2$

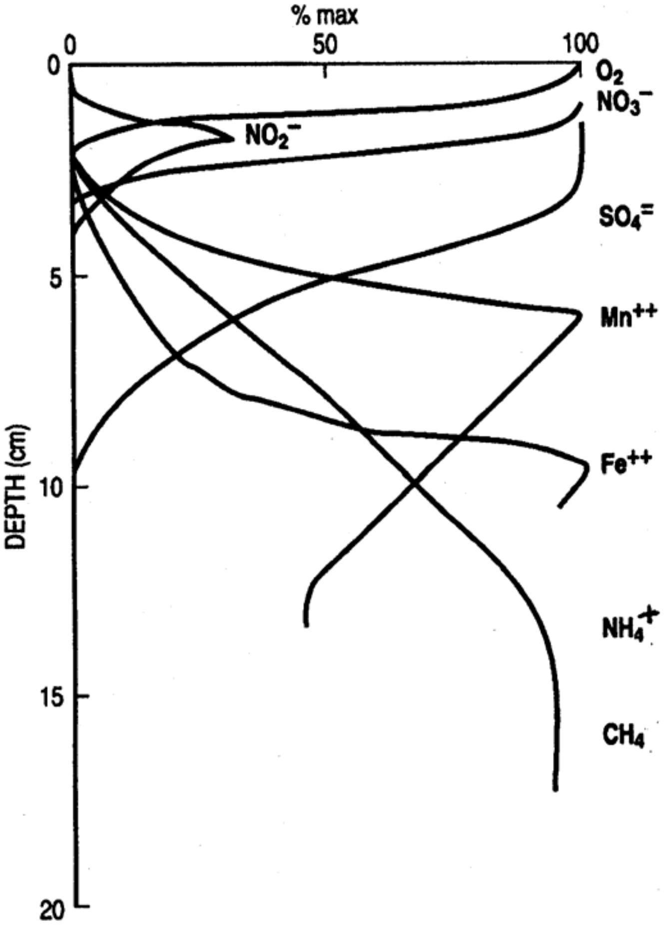

Figure 26. Vertical profiles of some major redox sensitive species in a typical freshwater sediment (from Nealson, 1997, figure 2).

Many of the general trends observed in Peoria Lake sediments can be qualitatively rationalized on the basis of reactions listed in Table 2. This is especially true for sediment pore waters because they are generally much more sensitive indicators of diagenetic processes than are sediment solids (Berner, 1980). All of the reactions in Table 2 produce $CO_{2(g)}$, and this is a primary reason why pH values are lower in Peoria Lake sediments than the overlying water (Figures 2 and 3). Moreover, the generally lower pH values observed in October 2000 are most likely related to warmer sediment temperatures (Figure 4). That is, warmer temperatures promote increased microbial activity which in turn results in a greater net production of dissolved carbon dioxide, and this decreases sediment pH values.

The high pore water concentrations of ammonia probably result from the solubilization of particulate organic matter (equation (1)), and the anoxic metabolism of particulate organic nitrogen (Berner, 1980; DiToro, 2001). The reduction of nitrate (which diffuses from the overlying water into the sediment or can be physically mixed into the upper sediment layers) could also be contributing. However, whether Peoria Lake sediments are a net sink or source of nitrate depends on whether nitrification of ammonia diffusing from sediments or nitrate reduction is the dominant process. In either case, Peoria Lake pore waters are probably generally devoid of nitrate except very near the sediment-water interface because it would be rapidly consumed. In fact, nitrate was below detection limits in the one set of pore water samples analyzed. Warmer sediment temperatures in October 2000 likely contributed to the generally higher pore water ammonia concentrations observed during this period (Figures 5 and 6). Pore water ammonia concentrations might also be influenced by cation exchange reactions with the abundant clay minerals present in Peoria Lake sediments. Cahill (2001) reported solid phase ammonia-N concentrations of up to 900 mg/kg in Peoria Lake sediments.

The calcite and/or dolomite present in Peoria Lake sediments is the likely source of the elevated pore water dissolved Ca concentrations (Figures 7 and 8). Moreover, Ca concentrations increase with depth, while pH decreases. Increased dissolution of calcite and/or dolomite at lower pH values is probably contributing to this increase in dissolved Ca concentrations.

In general, the concentrations of dissolved Cd, Cu, Ni, Pb, and Zn are low in Peoria Lake pore waters because sulfate reduction produces sulfide which forms sparingly soluble metal sulfide phases with these elements. Acid-volatile sulfides were detected in every sediment section analyzed, which shows that the zone of sulfate reduction commences within the top 6 cm of Peoria Lake sediments. This is a result of the extremely high sedimentation within Peoria Lake which rapidly buries and isolates organic carbon for microbial utilization. An important consequence of this compressed diagenetic profile is that detailed study of the upper few cm of Peoria Lake sediments will be necessary to determine the rates, relative importance and consequences (e.g., sediment-water exchange) of diagenetic processes within Peoria Lake itself. Pore water metal concentrations, as well as AVS and SEM concentrations, are compared to those found in other studies below.

In contrast to Cd, Cu, Ni, Pd, and Zn, dissolved Fe concentrations are much higher in Peoria Lake pore waters than in the overlying water column. This difference is dissolved Fe between overlying- and sediment pore waters is consistent with the difference in oxidation-reduction conditions. In the oxic (i.e., containing measurable dissolved oxygen) river water Fe exists predominately as insoluble ferric oxide phases, whereas in anoxic (i.e., no measurable dissolved oxygen) sediments, ferric oxide phases are reduced, which releases relatively soluble ferrous iron (Stumm and Morgan, 1996). A potentially important consequence of this is that the excess dissolved ferrous iron may limit the free sulfide concentrations to levels that are non-toxic to certain aquatic organisms.

Dissolved organic carbon concentrations are much higher in Peoria Lake pore waters than in the overlying water (Figures 22 and 23). This is a consequence of the solubilization and oxidation of particulate organic matter.

Ammonia in Pore Waters

There are few previous pore water ammonia data for Illinois River sediments. Sparks and Ross (1992) attempted to identify the toxic substances that may have been responsible for the rapid decline in several species of aquatic organisms in the upper Illinois River during the mid-1950s. Toxicity tests with both the fingernail clam (*Musculium transversum*) and water flea (*Ceriodaphnia dubia*) using pore waters from various locations between river miles 6 and 248 strongly implicated ammonia as the species primarily responsible for the observed acute toxic effects. The total ammonia concentrations in the pore waters used typically ranged between about 20 and 60 mg/L (as N). Unfortunately, Sparks and Ross (1992) were unable to precisely characterize ammonia toxicity because their pH measurements were unstable. Accurate pH measurements are required to determine the fraction of the total ammonia that exists in the highly toxic unionized form (i.e., NH_3). Still, their evidence for the importance of ammonia to pore water toxicity of Illinois River sediments is strong. In an earlier and less extensive study Schubauer-Berigan and Ankley (1991) determined a few pore water ammonia concentrations from surficial sediments (0-10 cm) at a site in the Cal-Sag channel near Chicago as part of their study of the toxicity of sediments and pore water at this site. They found that pore water NH_4-N concentrations ranged from 42 to 86 mg/L. These concentrations are higher than our measured values for Peoria Lake pore waters, which is not too surprising given that Cal-Sag channel sediments are almost certainly subject to higher loadings of organic matter. Schubauer-Berigan and Ankley (1991) concluded that their Cal-Sag channel sediments were highly toxic, with ammonia, metals, and nonpolar organic compounds all contributing to the observed toxicity.

Frazier et al. (1996) studied the vertical (to 12 cm depth) and temporal distribution of ammonia in pore waters from 4 sites in Pool 8 of the upper Mississippi River. Concentrations of NH_4-N generally increased with depth, and were higher when sediment temperatures were warmer. Both of these trends were also observed in this study. Total NH_4-N concentrations ranged from 0-4 mg/L in winter, to 0-10 mg/L in summer, which are similar to the concentrations at similar depth intervals in this study (2-3 mg/L at 3 cm and 6-9 at 9 cm from Figure 6 above). Frazier et al. (1996) also found that although the observed pore water ammonia concentrations were sometimes high enough to be toxic to fingernail claims based on laboratory studies, the concentrations were not lethal since fingernail clams were found at all sites in the study area. Similarly, Bartsch et al. (2003) found no relation between the survival and growth of juvenile mussels (*Lampsilis Cardium*) and pore water ammonia concentrations along the St. Croix riverway in Wisconsin.

Potential Ammonia Toxicity

The dotted line in Figure 6 indicates the Chronic Criterion Concentration (CCC) for NH_4-N as defined by the U.S. EPA (U.S. EPA, 1999a). This CCC value represents the dissolved NH_4-N concentration that should not be exceeded more than once every three years on average, when juvenile fish are present. The CCC value is temperature- and especially pH-dependent since both of these variables determine what fraction of total dissolved ammonia is present as the toxic NH_3 form. The line given in Figure 6 is calculated based on a temperature of 19 ^{o}C, and the mean pH values given in Figure 3. The equation used to perform this calculation is found in U.S. EPA (1999a). Mean and median pore water NH_4-N concentrations exceeded the CCC at and below 15 cm average sediment depth. Above 15 cm, pore water NH_4-N concentrations were generally less than the CCC. Furthermore, fingernail clams, which are indigenous to the Illinois River and which burrow to several centimeters depth in sediments, may be impaired at ammonia concentrations lower than the CCC (Sparks and Sandusky, 1981; U.S. EPA, 1999a; Augspurger et al. 2003). Consequently, pore water ammonia concentrations may be toxic to sensitive indigenous species in Peoria Lake.

AVS and SEM

Figures 27, 28, and 29 compare the SEM values, AVS values, and SEM:AVS ratios in Peoria Lake sediments from the present work with other published values for freshwater sediments. All references to Peoria Lake data are for the present work (Tables A-7a and A-7b, in Appendix A) unless otherwise noted.

Our AVS/SEM extraction procedure utilized 9M HCl (Chanton and Martens, 1985), while other investigators have typically used lower HCl concentrations, often 1M. A few studies have compared various HCl concentrations for extracting AVS and SEM. Allen et al. (1993) found that for some sediments the apparent AVS values were independent of the acid concentration for HCl concentrations equal to or greater than 0.5M but decreased to near zero as the HCl concentration decreased below 0.5M. Van den Berg et al. (1998) compared 1 and 6M HCl for extracting AVS and SEM from Meuse River (The Netherlands) sediments. The amounts of AVS, Zn, Cd, Pb, and Ni extracted were similar, but considerably more Cu was extracted, in general, with 6M than with 1M HCl. Cooper and Morse (1998b) observed that pyrrhotite (FeS), mackinawite (FeS_{1-x}), greenockite (CdS), galena (PbS), and sphalerite (ZnS) were highly soluble in 1 and 6M HCl, while covellite (CuS), chalcocite (Cu_2S), cinnabar (HgS), millerite (NiS), heazlewoodite (Ni_2S_3), and vaesite (NiS_2) were poorly soluble. Mikac et al. (2000) found that 1, 2, 3 and 6M HCl extracted similar amounts of Fe, Mn, Zn, Cd, Ni, and Pb from Seine River estuary sediments, but that the extraction of Hg increased from 1-5% in 1M HCl to 50-60% in 6M HCl.

Grabowski et al. (2001) collected sediment cores (~18cm long) from six sites on the Illinois, Mississippi, and Missouri Rivers near St. Louis in the Spring and Summer of 1998 (all 6 sites both times). Their SEM values were in the lower range of Peoria Lake values, with a median value of about 1.3 compared to about 4 µmol/g in Peoria Lake. There were no significant differences between their spring and summer SEM values. Their AVS values were 10 to 100 times lower than for Peoria Lake. Also, their summer AVS values were roughly 10 times greater than their spring values. No such distinct seasonal difference was noted for Peoria Lake AVS values between April and October 2000. Primarily as a result of much lower AVS values, the SEM:AVS ratios found by Grabowski et al. (2001) were much higher than those in Peoria Lake, with their median ratio being about 113 compared to 0.18 in Peoria Lake.

Dwyer et al. (1997) collected surficial sediment samples from 24 of the 26 navigational pools of the upper Mississippi River and one pool of the St. Croix River. Their highest SEM and AVS values were in the low range of the Peoria Lake values, but their median SEM (0.4 µmols/g) and AVS (1.9 µmols/g) were about 10 and 20 times lower than those for Peoria Lake, respectively. Their median SEM:AVS ratio was about 0.27, which is slightly higher than for Peoria Lake (0.18).

Ankley et al. (1993) collected surficial sediment samples from two bodies of water with relatively high Cu concentrations. Steilacoom Lake, WA was repeatedly treated with $CuSO_4$ to control nuisance algae. The Keweenaw watershed, MI was impacted by Cu mine tailings. The median Steilacoom Lake SEM value (1.3 µmols/g) was less than the median for Peoria Lake, while the median Keweenaw watershed value was considerably higher (15.1 µmols/g). The median Steilacoom Lake AVS value (1.94 µmols/g) was considerably lower than the corresponding Peoria Lake value (20.3 µmols/g), and the median Keweenaw watershed AVS value was lower still (0.06µmols/g). Median Steilacoom Lake and Keweenaw water SEM:AVS ratios were 0.83 and 327, respectively, both of which are greater than the median Peoria Lake value (0.18).

Hansen et al. (1996) collected surficial sediment samples from Turkey Creek, MO, which was impacted by strip mine tailings. Their median SEM (67.2 µmols/g) and AVS (44.2 µmols/g) were both higher than corresponding Peoria Lake values. Their median SEM:AVS ratio (1.20) was also considerably higher than that for Peoria Lake.

Besser et al. (1996a) collected surficial sediment samples from the Clark Fork River and Milltown Reservoir on the Clark Fork between Butte and Missoula, MT. Their median SEM value (12.5

µmol/g) was greater than the median for Peoria Lake, while their median AVS value(11.2 µmol/g) was lower. Their median SEM:AVS ratio (2.9) was also greater than for Peoria Lake.

Lacey et al. (2001) collected grab and core samples of sediment from Burlington Harbor in Lake Champlain, VT. Their median SEM value was very close to that of Peoria Lake (4.2 vs. 4.0 µmols/g), but their median AVS value was considerably less (2.6 vs. 20.3 µmols/g). Consequently, their median SEM:AVS ratio was about 10 times greater than for Peoria Lake (1.7 vs. 0.18).

Van den Berg et al. (1998) collected sediment cores from the Meuse River in The Netherlands. Their median SEM value was about 4 times higher (16.5 µmols/g) than that for Peoria Lake, and their median AVS value was about half (13.2 µmols/g) that of Peoria Lake. As a result, their median SEM:AVS ratio was about 8 times higher (1.34) than that for Peoria Lake.

Besser et al. (1996b) collected surficial sediment samples from two dredged areas of the Detroit River, MI. Their median SEM value was greater (11.5 µmols/g) than that of Peoria Lake, while their median AVS value was lower (5.3 µmols/g). Consequently, their median SEM:AVS ratio (1.8) was greater than that for Peoria Lake (0.18).

The top section of each Peoria Lake core had the lowest AVS value (Figure 16). This is in qualitative agreement with several previous studies. Van den Berg et al. (1999) found that AVS increased with depth in the top 10 cm at two of their three sites in the Meuse River, The Netherlands. Hare et al. (2001) found that AVS increased with depth in the top 2 cm of sediment in Lake Laflamme, Quebec, Canada, and was essentially independent of depth below 2 cm. Huerta-Diaz et al. (1998) found that AVS generally increased with depth in sediments taken from deep water sites in both Clearwater Lake, Ontario, and Chevreuil Lake, Quebec, Canada. Leonard et al. (1996) found that AVS was less at 1 cm depth than at 5 cm depth at nine sites in Lake Michigan.

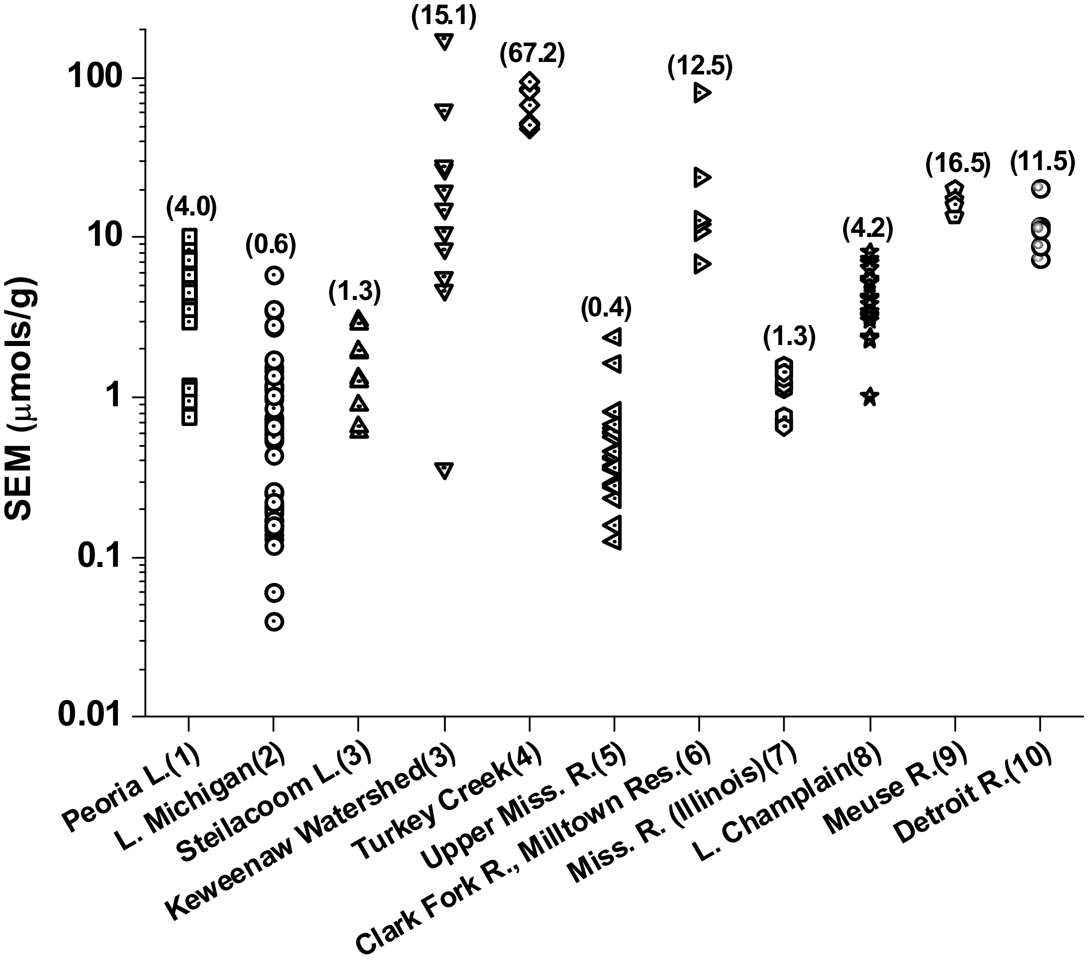

Figure 27. Comparison of SEM values for Peoria Lake with other published values for freshwater sediments. Parentheses enclose median values for each location. Literature sources are as follows: (1)This study, (2) Leonard et al. (1996), (3) Ankley et al. (1993), (4) Hansen et al. (1996), (5) Dwyer et al. (1997), (6) Besser et al. (1996a), (7)Grabowski et al. (2001), (8) Lacey et al. (2001), (9) Van den Berg et al. (1998), (10) Besser et al. (1996b).

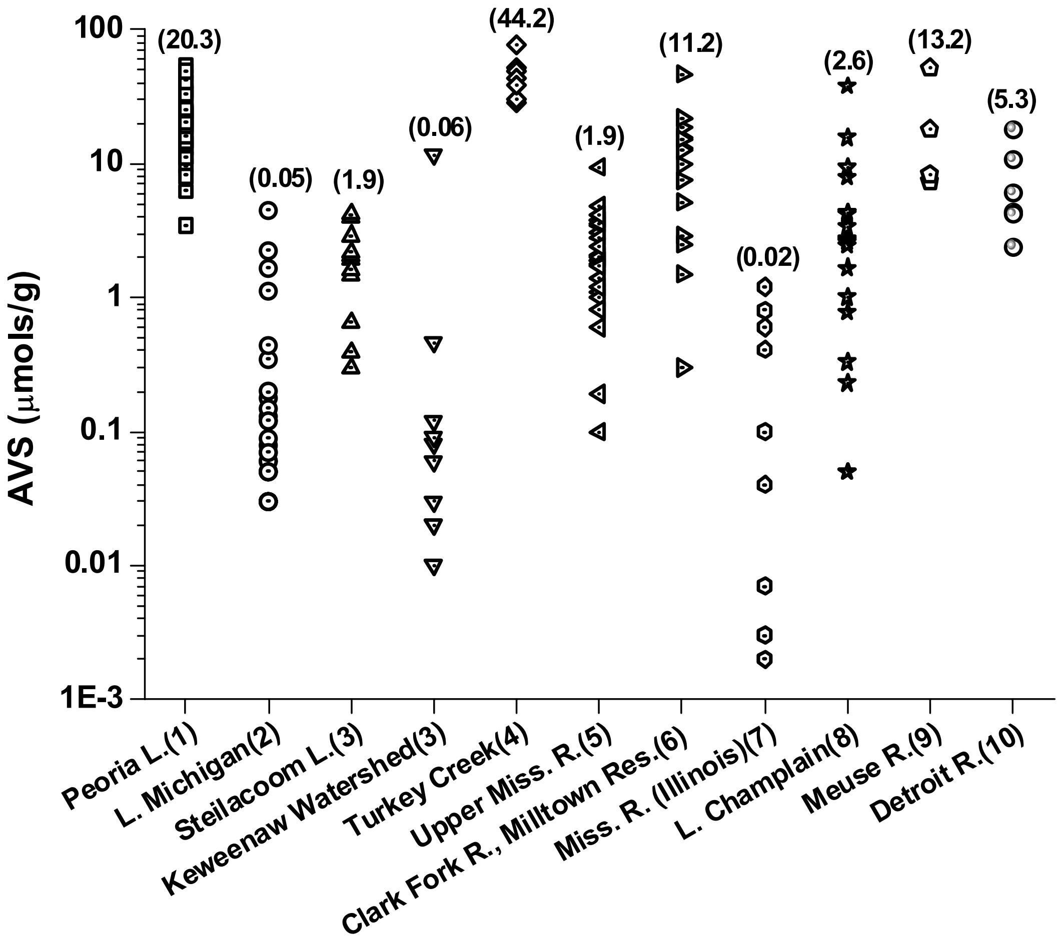

Figure 28. Comparison of AVS values for Peoria Lake with other published values for freshwater sediments. Parentheses enclose median values for each location. Literature sources are as follows: (1)This study, (2) Leonard et al. (1996), (3) Ankley et al. (1993), (4) Hansen et al. (1996), (5) Dwyer et al. (1997), (6) Besser et al. (1996a), (7)Grabowski et al. (2001), (8) Lacey et al. (2001), (9) Van den Berg et al. (1998), (10) Besser et al. (1996b).

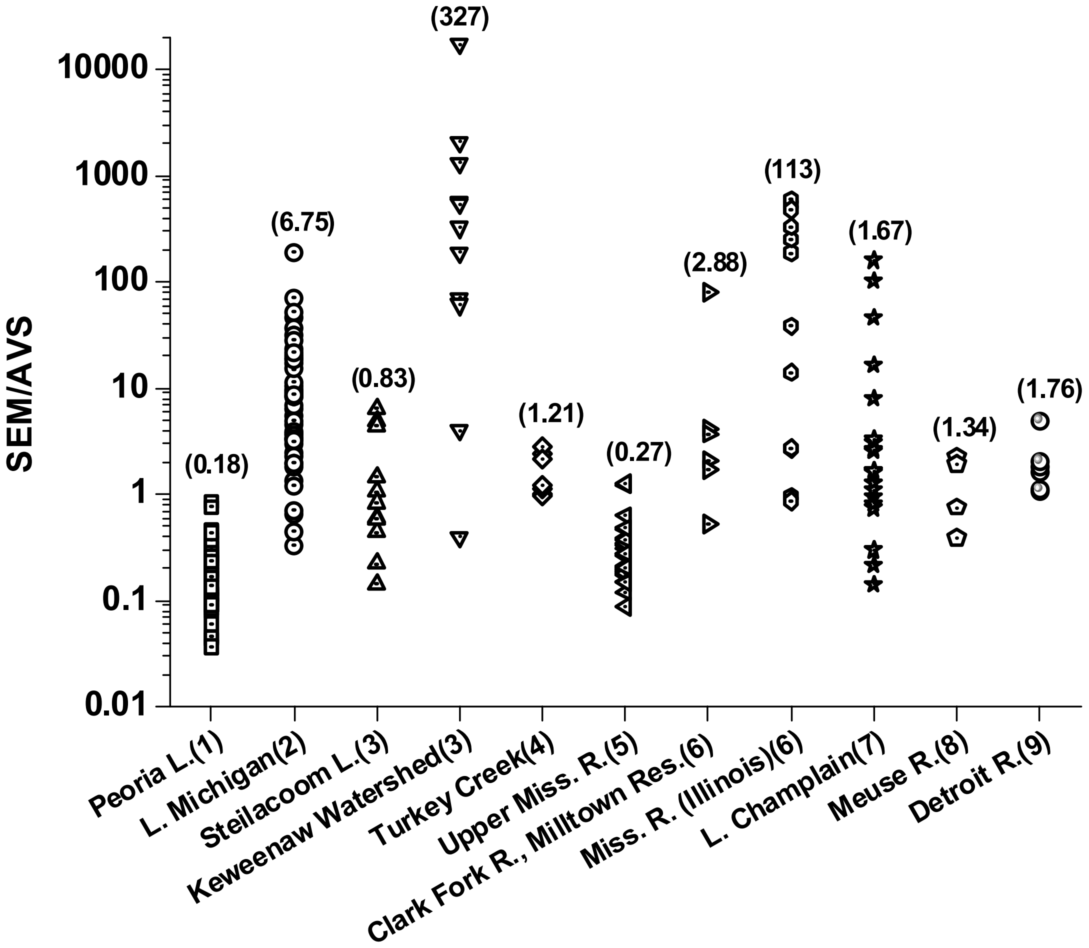

Figure 29. Comparison of SEM:AVS ratios for Peoria Lake with other published values for freshwater sediments. Parentheses enclose median values for each location. Literature sources are as follows: (1)This study, (2) Leonard et al. (1996), (3) Ankley et al. (1993), (4) Hansen et al. (1996), (5) Dwyer et al. (1997), (6) Besser et al. (1996a), (7)Grabowski et al. (2001), (8) Lacey et al. (2001), (9) Van den Berg et al. (1998), (10) Besser et al. (1996b).

Surface Water Metals

There have been few previous studies of dissolved Cd, Cu, Ni, Pb, or Zn concentrations anywhere along the main stem of the Illinois River. A notable shortcoming is the absence of a U.S. Geological Survey National Stream Quality Accounting Network (NASQAN) station anywhere within the Illinois River basin. The trace metal sampling protocols used at NASQAN sites since 1995 allow the accurate determination of low-level trace metal concentrations in contrast to earlier trace metal data from these sites, which were plagued by contamination problems (Taylor and Shiller, 1995).

An early previous study that includes water column trace metal data for Peoria Lake was conducted by Mathis and Cummings in 1969-1970 (Mathis and Cummings, 1971; 1973), well before "clean" trace metal protocols were widely practiced. These authors sampled sediments, water, and biota for selected trace metals at five stations near Peoria, including 2 within Peoria Lake itself. Shiller (1997) published dissolved trace metal data for a station near Valley City IL (near the mouth), that was sampled 3 times between June 1990 and April 1992. These samples were processed according to very stringent "ultra-clean" techniques. Comparisons of these data, as well as water column data from this study are presented in Table 3.

Table 3. Comparison of average dissolved trace metal data (in µg/L) for the Illinois River.

Metal	M&C[1]	Shiller[2]	This Study[3]
Cd	0.6		0.1
Cu	1.2	2.2	1.7
Ni	2.8	2.9	4.3
Pb	2.1	0.1	0.2
Zn	26	1.0	3.2

[1] Mathis and Cummings, 1971

[2] Shiller, 1997 Illinois R. at Valley City, IL 1990-1992

[3] This Study, October 2000

There is fairly consistent agreement in the dissolved Ni and Cu values between the three studies which span 30 years, and between the dissolved Pb concentrations in Shiller's and this study. Dissolved Zn was considerably higher in the Mathis and Cummings study and somewhat higher in the present study than that found by Shiller. Similarly, dissolved Cd was considerably higher in the Mathis and Cummings study than that found in this study, and dissolved Cd was not determined by Shiller.

A strict comparison of these data is not possible due to the different analytical protocols used, as well as possible real temporal and/or spatial variability in dissolved trace metal concentrations. In fact, both Mathis and Cummings (1971) and Shiller (1997) document such variability. Still, the Shiller (1997) study can be used as an approximate analytical benchmark for comparison, since the sampling and processing protocols most rigorously followed ultra clean techniques. On this basis, the elevated dissolved Zn and Cd values found by Mathis and Cummings may have been the result of contamination introduced at some stage of their sample processing procedures. This is also supported by the remarkably close agreement of their dissolved Ni and Cu values to those of the later studies. For these trace metals at least, it appears that dissolved concentrations have not changed significantly over the past 30 years. As such, the Mathis and Cummings (1971) study provides valuable historical information on dissolved trace metal concentrations in the Illinois River.

The sample collection and processing protocols for our trace metal samples were improved between our April and October samples. The most significant improvement was to change the filtration medium as detailed in the Methods section. As a result, trace metal blanks were lowered, especially for Zn which decreased from about 1 to 0.5 µg/L for our water column samples (see Tables 4a and 4b in Appendix A). In addition, the Mathis and Cummings (1971) and Shiller (1997) data prompted us to more closely examine our dissolved Ni data for possible sources of contamination. However, after a suggestion by Martin Shafer of the University of Wisconsin (personal communication), it was determined that dissolved Ca was enhancing dissolved Ni concentrations by the formation of CaO in the ICP-MS flame. This interference had been previously documented (Grotti et al., 1999), and John Scott and Jonathan Talbott of the WMRC determined dissolved Ca concentrations in our surface and pore water samples, which allowed this positive interference to be corrected for. Appendix D details this effort. In general, this correction varied between 1 and 4 µg/L, depending on the dissolved Ca concentration. This was a significant correction since dissolved Ni concentrations even before correction were generally less than 8 µg/L. In any case, our Ca-corrected dissolved Ni concentrations are much closer to the values of both Mathis and Cummings (1971) and Shiller (1997) than the uncorrected values. Tables 4a (April) and 4b (October) in Appendix A contain both uncorrected and Ca-corrected Ni concentrations.

Pore Water Metals

Pore water metals are determined much less frequently than total metals in sediments and pore water metals in freshwater sediments are determined less frequently than in marine and estuarine sediments. However, it was felt that comparison with freshwater sediments would be most appropriate.

Leonard et al. (1995) studied the toxicity of Cd in sediments from Pequaywan Lake, MN, a remote lake with relatively low metal concentrations. They collected sediment cores up to 80 cm deep and added Cd to some of the cores. The control core (no added Cd) is used for comparison with Peoria Lake. Ankley et al. (1993) studied Cu toxicity in sediments from Steilacoom Lake, WA, which had been treated with $CuSO_4$ to control algal blooms, and the Keweenaw Watershed, MI, which had been impacted by Cu mining. They collected surficial sediment samples from 11 sites in each study area. Hare et al. (2001) studied Cd accumulation by invertebrates in Lake Laflamme, a remote Canadian Shield lake in Quebec. They collected cores up to 10 cm deep. The control core (no added Cd) is used for comparison. Huerta-Diaz et al. (1998) performed detailed geochemical characterization of several elements, including Cd, Cu, Ni, Pb, and Zn in the sediments of Chevreuil and Clearwater Lakes, Quebec. These are Canadian Shield lakes that have been impacted by emissions from metal smelters. They collected triplicate cores up to 10 cm deep from a shallow and a deep water site in each lake. Cornett et al. (1989) measured concentrations of arsenic and Ni in the sediments of Moira Lake, Canada. They collected cores up to 30 cm deep from two sites in the lake. Van den Berg et al. (1999) studied the geochemistry of several metals, including Cd, Cu, Ni, Pb, and Zn in the Meuse River, The Netherlands. They collected cores up to 10 cm deep from three sites. Schubauer-Berigan and Ankley (1991) characterized the toxicity of sediment from the Cal-Sag channel, a tributary of the Illinois River near Chicago. They collected one surficial sediment sample. Leonard et al. (1996) collected surficial sediment samples from 44 sites in Lake Michigan. Zhang et al. (1995) collected 10 cm sediment cores from Esthwaite Water, England, and determined Zn, Cd, Ni, and Pb in the pore waters. Garban et al. (1996) collected 25-cm sediment cores from the Seine River, France, downstream from Paris. They reported pore water concentrations of Cd, Pb, and Zn in one of the cores. Moore et al. (1988) studied the sediments of Milltown Reservoir on the Clark Fork River near Missoula, MT. The river system had been impacted by copper mining. They collected cores up to 115 cm deep and reported Cu and Zn concentrations in the pore water of one core. Harrington et al. (1998) collected sediment cores from a section of Coeur d'Alene Lake in Idaho that was heavily contaminated by mine tailings. They reported pore water concentrations of Pb and Zn for one of their cores. Pore water metal concentrations were obtained from some of these publications by digitizing graphs.

The total concentrations of some sediment metals varied widely between the different water bodies (Table 4). Leonard et al. (1995) and Ankley et al. (1993) reported HCl-extractable metal concentrations, but not total metal concentrations. Huerta-Diaz et al. (1998) reported HCl-extractable (SEM) and HNO_3-extractable (pyrite-associated) metals but not total metals. Table 4 gives the sum of HCl- and HNO_3-extractable metals. Leonard et al. (1996), Schubauer-Berigan and Ankley (1991), and Zhang et al. (1995) did not report total metal concentrations. In most cases the ranges of HNO_3-extractable metals in Peoria Lake are comparable to those of the other water bodies in Table 4. The highest total Cu concentrations reported by Huerta –Diaz et al. (1998) and Leonard et al. (1996) were much higher than in Peoria Lake. The highest total Ni concentrations reported by Huerta-Diaz et al. (1998) and Cornett et al. (1989) were much higher than in Peoria Lake.

Table 4. Total metal concentrations in Peoria Lake sediments and other sediments for which pore water metal concentrations have been reported.

Total Concentration (µg/g)					**Location**	**Reference**
Cd	**Cu**	**Ni**	**Pb**	**Zn**		
0.2 – 12	4 - 80	8 - 82	7 - 97	32 – 536	Peoria Lake	This Study
10 - 29					Lake Michigan	Leonard et al. 1996
	14 - 1,113,000				Steilacoom Lake	Ankley et al. 1993
1 - 2					Lake Laflamme	Hare et al. 2001
1 - 6	26 – 1,140	34 - 758	4 - 141	6 - 260	Chevreuil and Clearwater Lakes	Huerta-Diaz et al. 1998
		59 - 965			Meuse River	Van den Berg et al. 1999
7 - 12	42 - 112	36 - 70	94 - 218	570 – 1,200	Seine River	Garban et al. 1996
1 - 2			25 - 100	450 - 1000	Seine River	Garban et al. 1996
	800 - 8000			2000 - 6300	Clark Fork River, Milltown Reservoir	Moore et al. 1988

Figures 30-34 compare pore water concentrations of Cd, Cu, Ni, Pb, and Zn, respectively, in Peoria Lake with the other published results. For concentrations that were reported as below detection, one half the detection limit was plotted. For studies that did not report detection limits, non-detects were not plotted in Figures 30-34. Many Cd concentrations for Peoria Lake pore waters were below the detection limit (0.02 µg/L), so these all appear as a single point in Figure 30. The maximum Peoria Lake Cd concentrations (0.1 µg/L) were less than the maximum Cd concentrations in all other pore waters compared except for Esthwaite Water (0.09 µg/L). The median pore water Cd concentration was lowest in Peoria Lake (0.01 µg/L), and greatest in the Seine River (3.12 µg/L).

The median Peoria Lake Cu concentration (0.16 µg/L) was less that for all other pore waters except Esthwaite Water (0.11 µg/L). All Steilacoom Lake and Seine River pore water Cu concentrations were greater than any found in Peoria Lake. Steilacoom Lake and the Milltown Reservoir on the Clark Fork River had the greatest median Cu pore water concentrations (41 and 31 µg/L, respectively).

Peoria Lake also had the lowest median Pb pore water concentration (0.1 µg/L). However, except for the single value from the Cal-Sag Channel, and the Seine River values, all other locations reported Pb concentrations that overlapped those for Peoria Lake.

Esthwaite Water had the lowest median Zn concentration (0.02 µg/L) followed by Peoria Lake (0.10 µg/L). The Seine River and Milltown Reservoir on the Clark Fork River had the greatest median Pb concentrations (120 and 346 µg/L, respectively). The highest Pb concentrations reported in Couer D'Alene Lake, the Meuse River, Esthwaite Water, and Lake Michigan pore waters were less than the highest concentrations in Peoria Lake.

Median dissolved Ni pore water concentrations were lowest for Esthwaite Water (1.0 µg/L) and Peoria Lake (2.38 µg/L). Moira Lake had the highest median value (35 µg/L, excluding the single Cal-Sag Channel value of 61 µg/L). There was considerable overlap of Peoria Lake pore water Ni concentrations with those from Chevreuil and Clearwater Lakes, the Meuse River, and Lake Michigan.

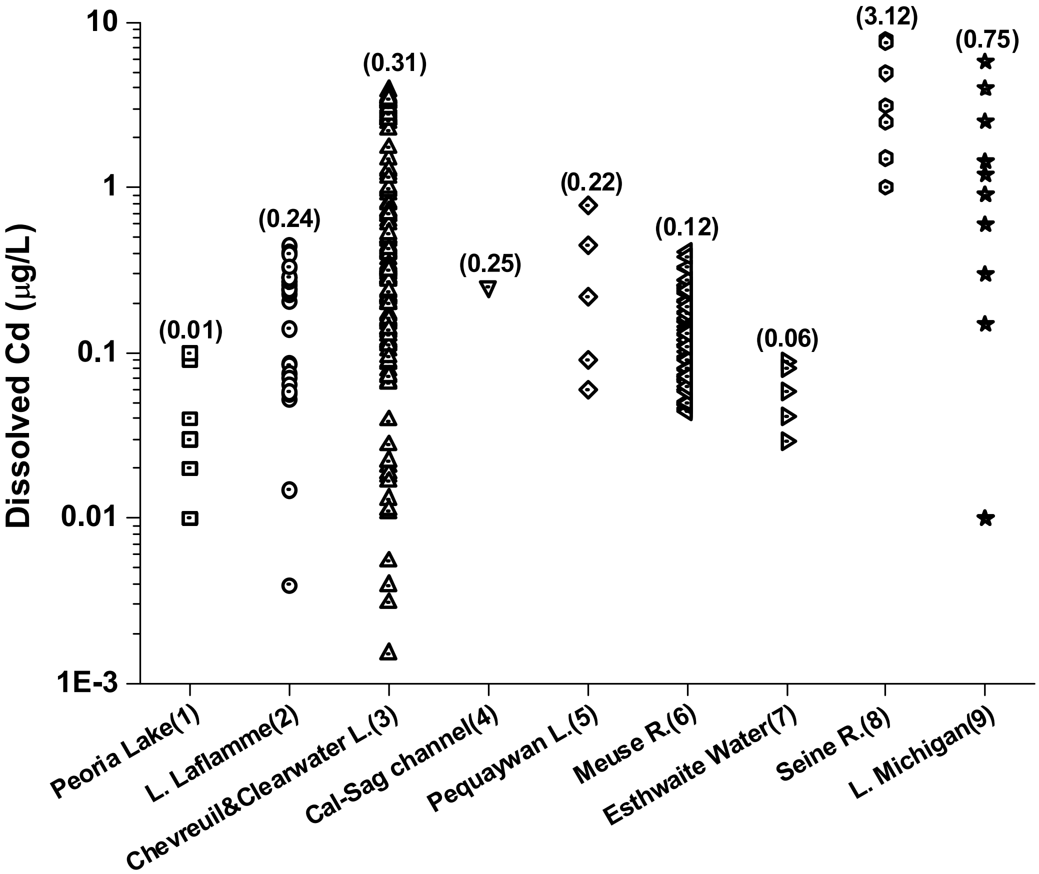

Figure 30. Comparison of dissolved Cd concentrations in Peoria Lake pore waters and other freshwater pore waters. Parentheses enclose median values for each location. Literature sources are as follows: (1)This study, (2) Hare et al. (2001), (3) Huerta-Diaz et al. (1998), (4) Schubauer-Berigan and Ankley (1991), (5) Leonard et al. (1995), (6) Van den Berg et al. (1999), (7) Zhang et al. (1995), (8) Garban et al. (1996), (9) Leonard et al. (1996).

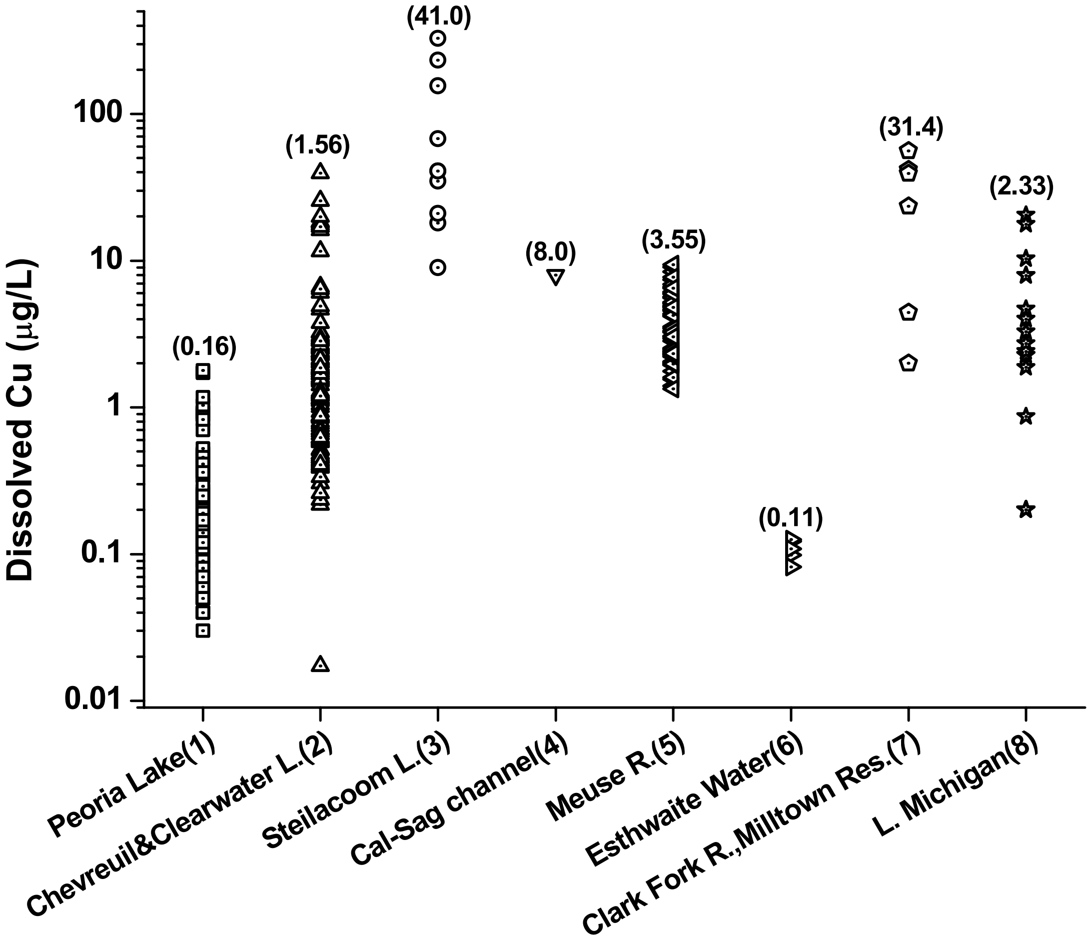

Figure 31. Comparison of dissolved Cu concentrations in Peoria Lake pore waters and other freshwater pore waters. Parentheses enclose median values for each location. Literature sources are as follows: (1)This study, (2) Huerta-Diaz et al. (1998), (3) Ankley et al. (1993), (4) Schubauer-Berigan and Ankley (1991), (5) Van den Berg et al. (1999), (6) Zhang et al. (1995), (7)Moore et al. (1988), (8) Leonard et al. (1996).

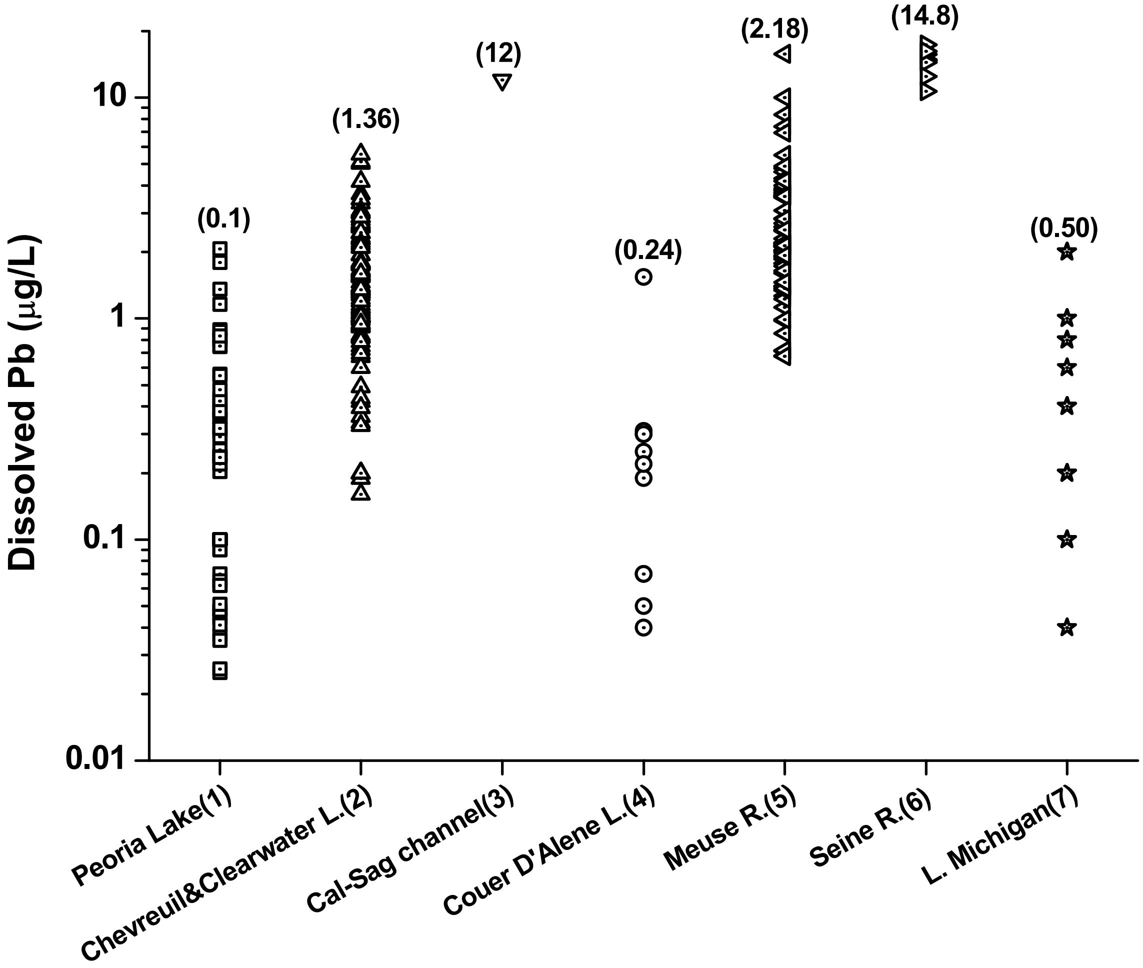

Figure 32. Comparison of dissolved Pb concentrations in Peoria Lake pore waters and other freshwater pore waters. Parentheses enclose median values for each location. Literature sources are as follows: (1) This study, (2) Huerta-Diaz et al. (1998), (3) Schubauer-Berigan and Ankley (1991), (4) Harrington et al. (1998), (5) Van den Berg et al. (1999), (6) Garban et al. (1996), (7) Leonard et al. (1996).

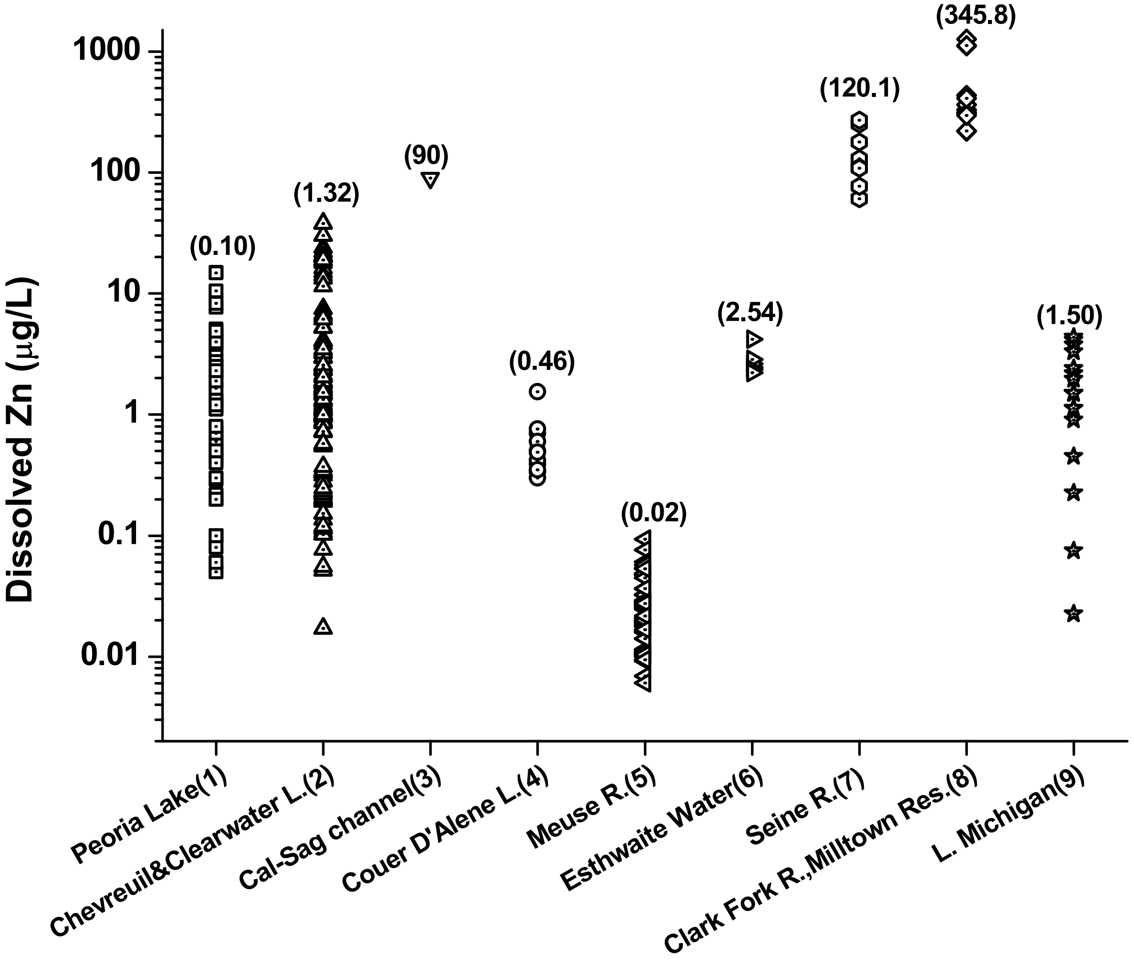

Figure 33. Comparison of dissolved Zn concentrations in Peoria Lake pore waters and other freshwater pore waters. Parentheses enclose median values for each location. Literature sources are as follows: (1) This study, (2) Huerta-Diaz et al. (1998), (3) Schubauer-Berigan and Ankley (1991), (4) Harrington et al. (1998), (5) Van den Berg et al. (1999), Zhang et al. (1995), (7) Garban et al. (1996), Moore et al. (1988), (8) Leonard et al. (1996).

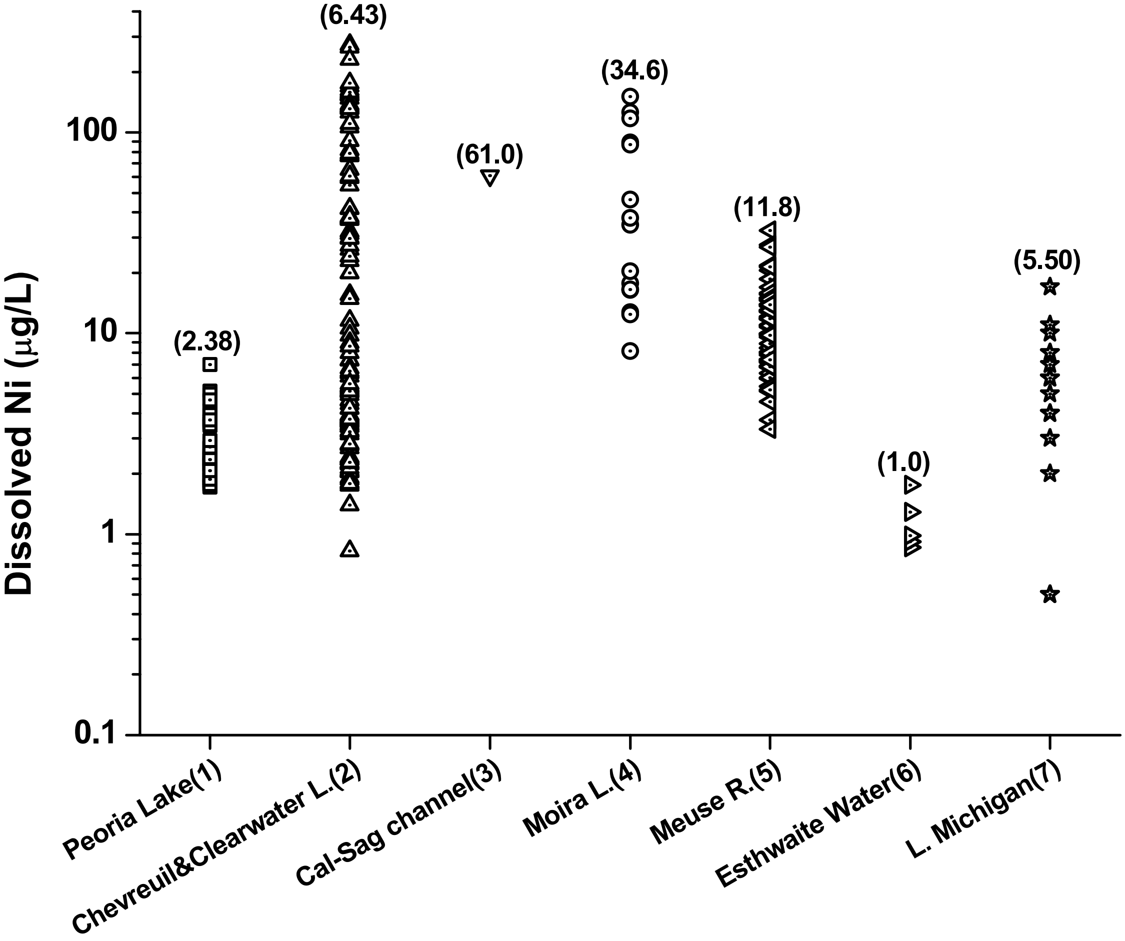

Figure 34. Comparison of dissolved Ni concentrations in Peoria Lake pore waters and other freshwater pore waters. Parentheses enclose median values for each location. Literature sources are as follows: (1) This study, (2) Huerta-Diaz et al. (1998), (3) Schubauer-Berigan and Ankley (1991), (4) Cornett et al. (1989), (5) Van den Berg et al. (1999), (6) Zhang et al. (1995), (7) Leonard et al. (1996).

Potential Toxicity of Metals in Peoria Lake Sediments

The dissolved concentrations of Cd, Cu, Pb, Ni, and Zn are too low to be acutely toxic by themselves. This can be demonstrated by comparing measured surface and pore water concentrations of these metals with the corresponding Criterion Continuous Concentrations (CCC) as defined by the U.S. EPA (U.S. EPA, 1999b). These concentrations increase as water hardness increases, and specific formulas incorporating the effect of water hardness are given in Appendices A and B of the U.S. EPA (1999b) document. Water hardness is normally dominated by dissolved Ca and Mg. Consequently, the mean surface water dissolved Ca concentration of about 60 mg/L represents a minimum water hardness value since mean pore water dissolved Ca concentrations are higher (Figures 7 and 8). With this minimum hardness concentration, the CCC for dissolved Cd, Cu, Pb, Ni and Zn are 3, 12.6, 3.9, 73.2, and 166.3 µg/L, respectively. The concentrations are well above measured surface and pore water concentrations of these metals. Therefore, measured dissolved concentrations are not likely to be toxic.

The Probable effect concentration (PEC) values for Cd, Ni, Cu, Pb, and Zn are 5, 49, 149, 128, and 459 µg/g, respectively (Figure 20). Based on this measure of potential metal toxicity (MacDonald et al., 2000), Cd and Ni are probably toxic at and below 15 cm average sediment depth in Peoria Lake sediments. Cahill (2001) also noted that Cd and Ni were often above PEC levels in Peoria Lake sediments. In any case, the actual toxicity of Cd, Ni, and other chemical species in Peoria Lake sediments would require further site specific tests, because a variety of physical, chemical and biological factors influence the bioavailability of chemicals in sediments (Table 1).

Estimating Dissolved Hydrogen Sulfide Concentrations

Hydrogen sulfide (H_2S) is toxic to many aquatic organisms. Although H_2S concentrations were not measured because of the limited volumes of pore water, they can be estimated from other measurements and by making certain assumptions.

AVS was found in all sections of all cores and in all cases AVS was greater than SEM (the sum of extracted Cd, Cu, Ni, Pb, and Zn). Therefore, some FeS was present and dissolved sulfide concentrations could be estimated by assuming equilibrium with FeS. Dissolution of FeS is described by equation (2).

$$FeS(s) + H^+ \rightleftarrows Fe^{2+} + HS^- \qquad (2)$$

At equilibrium the concentrations of the dissolved reactants and products in equation 2 are related by equation 3, where $^*K'_{FeS}$ is the conditional equilibrium constant (adjusted for ionic strength and temperature) and square brackets indicate concentrations.

$$^*K'_{FeS} = \frac{[Fe^{2+}][HS^-]}{[H^+]} \qquad (3)$$

In principle, the HS^- concentration could be calculated from the pH and Fe concentration by rearranging equation (3). However, there are different forms of FeS, all with different solubilities (Davison, 1991). For example, Huerta-Diaz et al. (1998) studied sediments from two sites each in two Canadian Lakes. At one site in one lake the ion activity product (IAP, the right side of equation 20) was close (± 0.5 log unit) to that of mackinawite throughout the sediment core. At the other site in the same lake, all IAP values were close to that of greigite. In the other lake, roughly one-half of the IAP values were between those of greigite and pyrrhotite, and the rest were below that of pyrrhotite.

Besides FeS dissolution (equation 2), complex formation reactions must also be considered. Ferrous iron (Fe^{2+}) can form soluble complexes with HS^-, OH^-, and CO_3^{2-} ions. As for sulfide, the dissolved carbonate was not determined because of the limited volume of pore water. However, calcite was found in the sediments by x-ray diffraction (Appendix E) and dissolved Ca concentrations were measured to improve the dissolved Ni measurements. Therefore, the bicarbonate concentrations could be estimated by assuming equilibrium with $CaCO_3$. Dissolution of $CaCO_3$ is described by equation (4).

$$CaCO_3(s) + H^+ \rightleftarrows Ca^{2+} + HCO_3^- \tag{4}$$

The concentrations of dissolved reactants and products in equation 4 at equilibrium are related by equation (5).

$$^{*}K'_{CaCO_3} = \frac{[Ca^{2+}][HCO_3^-]}{[H^+]} \tag{5}$$

As for HS^-, the HCO_3^- concentration can be calculated from the pH and Ca concentration by rearranging equation (5). The Fe^{2+} and Ca^{2+} ions form complexes with the HCO_3^- and OH^- ions and Fe^{2+} also forms complexes with the HS^- ion. Equilibrium calculations were performed using MINEQL+ (Schecher and McAvoy, 1994), which solves the large system of coupled linear and nonlinear equations. Equilibrium with one of the three FeS minerals (mackinawite, greigite, or pyrrhotite) as well as calcite ($CaCO_3$) was imposed and the pH and concentrations of Fe and Ca were used as input. The temperature and ionic strength were assumed to be 14ºC and 0.03mol/L. MINEQL+ calculates the concentration of unionized H_2S as part of its output.

Wang and Chapman (1999) compiled sulfide toxicity data for several fresh water organisms, including 96-hour LC_{50} (96h LC_{50}) and pH values. The 96h LC_{50} value is the total dissolved sulfide concentration at which 50% of the test organisms died within 96 hours. The dissolved H_2S concentrations in the studies cited by Wang and Chapman (1999) were calculated using MINEQL+.

Unionized H_2S concentrations were calculated for sites 165.5 and 177, the cores for which Fe concentrations were measured in pore waters (Figure 35). Figure 35 also shows the 96h LC_{50} H_2S values from the Wang and Chapman (1999) review, and the U.S. E.P.A. sediment quality criterion for H_2S (2 μg/L or 6.25×10^{-8} mol/L). The Peoria Lake values spanned a relatively narrow range. There were no significant differences between sites or between sampling dates. The values were in the range calculated for the 96h LC_{50} values. All of the estimated H_2S concentrations calculated assuming equilibrium with mackinawite were above the SQC. A few of the greigite H_2S concentrations were above or near the SQC. All of the pyrrhotite H_2S concentrations were well below the SQC. For each FeS mineral the calculated H_2S concentrations spanned a relatively narrow range of 0.5 to 0.7 log unit (a factor of 3-5). The estimated H_2S concentrations for October were somewhat higher than those for April because of the lower pH values. There were no significant differences between the two stations. Therefore, the Peoria Lake sediments may have been toxic to some organisms because of H_2S.

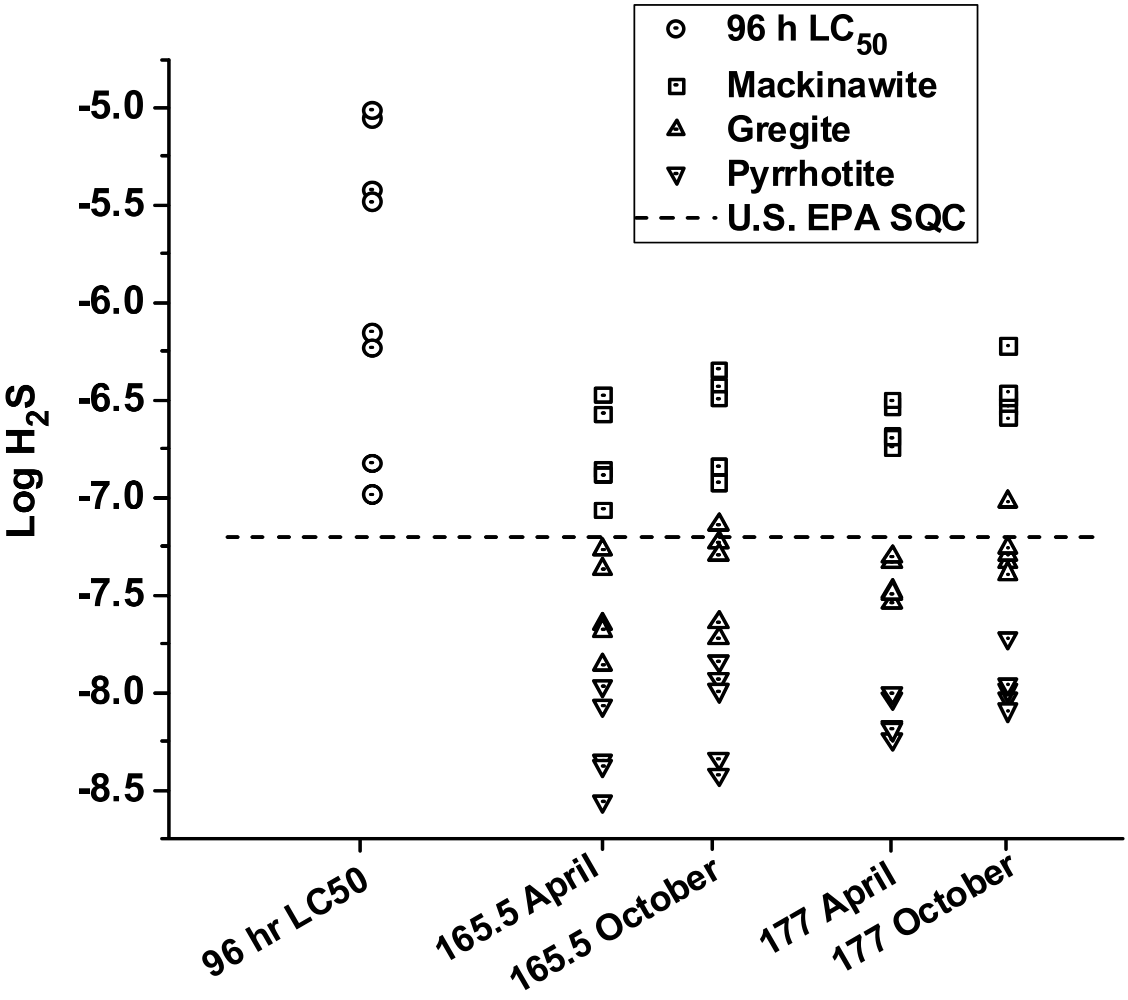

Figure 35. Comparison of H_2S concentrations estimated from pH and Fe concentrations in Peoria Lake sediment with 96-hour LC_{50} values from toxicity tests for several aquatic organisms.

CONCLUSIONS

The total extractable concentrations of Cd, Cu, Ni, Pb, and Zn in Peoria Lake sediments generally followed the pattern Zn>>Cu~Ni~Pb>>Cd. The concentrations of all five metals increased with depth in the top 18 cm and were essentially constant for 18-30 cm. The total Cd and Pb concentrations are comparable to those of freshwater sediments from other urban/industrial areas. The Cu, Ni, and Zn concentrations are at the low end of the published concentration ranges. The median Cd and Ni concentrations for sediments from 12-30 cm depth and the maximum Zn concentrations for the same depths exceeded the U. S. EPA probable effect levels. All total Cu and Pb concentrations and most Zn concentrations were below the probable effect levels for those metals.

Despite the high total sediment metal concentrations the dissolved concentrations of Cd, Cu, Ni, Pb, and Zn in sediment pore water were low. The concentrations were all less than 12 µg/L and most concentrations were less than 5 µg/L. Cadmium and Pb were undetectable in roughly half of the samples (Cd < 0.04 µg/L, Pb < 0.2 µg/L). Nickel had the highest concentration in most samples. Zinc had the highest concentration in a few samples. The dissolved Ni concentrations were higher in the October samples than in the April samples for all depths at all sites. For 8 of the 10 sites, the April Cu, Pb, and Zn concentrations were low but detectable in April but undetectable in October. These pore water trace metal concentrations were below toxic levels. The dissolved Fe concentrations increased with depth from approximately 1 mg/L in the top 6 cm to 20 mg/L for 24-30 cm. There were no significant differences between April and October Fe concentrations.

The trace metal concentrations in river water samples were similar to those of published studies in which ultra-clean sampling and analysis techniques were used. This gives credence to the results of the present work. The Ni concentrations in river water were similar to those in sediment pore water.

Ammonium was undetectable in river water, while the concentrations in sediment pore water were up to 35 mg/L as N. There was little or no difference between April and October NH_4-N concentrations for the top 12 cm, while for 18-30 cm the October concentrations were somewhat higher. The NH_4-N concentrations increased with depth and the concentration gradient may cause NH_4-N to diffuse out of the sediments. The median unionized NH_3 concentrations exceeded the chronic criterion concentration at all depths below 12 cm. Therefore, Peoria Lake sediments may be toxic to indigenous sediment biota such as fingernail clams because of their NH_4-N content.

Acid-volatile sulfide (AVS) was found in all sediment samples at concentrations of 10-40 µmol/g. These levels are at the high end of the range of values published for freshwater sediments. The molar sum of Cd, Cu, Ni, Pb, and Zn extracted with AVS (SEM) was less than AVS for all samples. The SEM:AVS ratio was less than 0.5 for over 90% of the samples. The excess of AVS over SEM is the likely cause of the low dissolved metal concentrations. The metals are probably present as relatively insoluble sulfides. Therefore, despite the high total metal concentrations, the metals in Peoria Lake sediments are not expected to be toxic. However, calculations indicate that the hydrogen sulfide concentrations in Peoria Lake pore water may exceed toxic levels.

The sediment temperatures were greater at all depths in October than in April, while the October pH values were less than the April values at all depths. The higher sediment temperatures in the spring and summer probably caused greater metabolic activity, including increased CO_2 production and solubilization/metabolism of organic N. Higher CO_2 concentrations would cause lower pH values. Increased N metabolism may explain the higher NH_4-N concentrations.

RECOMMENDATIONS FOR FURTHER STUDY

Questions worthy of additional study include conducting similar investigations in other reaches of the Illinois River or other rivers within the State, as well as before, during and after any dredging in Peoria Lake itself. The removal of two or more meters of sediment from areas of Peoria Lake would place previously deeply buried sediments near the sediment-water interface. Detailed studies of this new sediment-water interface environment should be an integral part of post-dredging research activities; the reestablishment of desired benthic organisms could be impaired if potentially toxic chemical species, such as ammonia, hydrogen sulfide, and metals, exist at elevated concentrations. These studies should also include a detailed characterization of potentially toxic dissolved and solid phase organic compounds, which were not part of the present investigation.

Detailed depth profiles of ammonia in Peoria Lake sediment with better than centimeter resolution could be conducted. The measurements could include dissolved NH_4-N in pore water, solid-phase NH_4^+, and total cation exchange capacity. Such measurements would enable transport modeling to see whether the sediments could be a significant source of N to the overlying water. Dissolved hydrogen sulfide could be measured in sediment pore water to see whether the levels are high enough to be toxic to benthic organisms. Acid-volatile sulfide concentrations could be determined in sediments from several locations along the length of the Illinois River. The AVS content of sediments near the mouth of the river (Grabowski et al., 2001) is much lower than was found in Peoria Lake. This suggests that sediment quality changes dramatically downstream from Peoria Lake.

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APPENDIX A: Data Tables and Figures

General Notes on Data Tables and Figures

The general top to bottom structure of the data tables that contain chemical concentration information is total blank values, followed by surface water values, and then sediment values. Dotted lines separate these sections. Station locations are designated by River Mile and direction (E for East, M for middle, and W for West) where appropriate. Surface water depths are given as -3 cm, which represents a depth 3 cm above the sediment water interface. This particular depth is for convenience and plotting purposes only since the actual depth of water coulum sampling varied between about 2 and 15 cm above the sediment surface. Sediment depths are given as positive values, increasing downward from the sediment-water interface. Blank corrected values are given in columns immediately to the right of the uncorrected values. Blank corrections were only applied if they were above method detection limits.

On April 18th, 2000 we took advantage of the opportunity to take water samples near Spindler Marina (approximately RM 165.5) during an active dredging project. Samples were collected right over a hole created by the dredge (designated by “165.5 ND”) within 20 minutes of creating the hole, and at 2 “background” sites located about 100 meters upstream of the hole (designated by 165.5 DB 1 and 165.5 DB 2) within a hour later. These samples were processed according to our usual procedures, and those data appear here as well as in other Tables that contain April data.

Table A-1. Sampling station coordinates.

Cahill (2001) Vibracore Locations

River Mile	Deg	Min	Sec	Decimal Degrees		Deg	Min	Sec	Decimal Degrees	
179	40	53	21.5	40.889306	N	89	29	24.5	89.490139	W
177	40	51	37.6	40.860444	N	89	29	58	89.499444	W
175	40	50	27.3	40.840917	N	89	31	1.4	89.517056	W
171W	40	47[a]	30.8	40.791889	N	89	33	59.6	89.566556	W
171M	40	47	29.9	40.791639	N	89	33	2.8	89.550778	W
171E	40	47	29.9	40.791639	N	89	32	30.4	89.541778	W
169	40	46	27.8	40.774389	N	89	33	3.4	89.550944	W
165.5	40	42	29.8	40.708278	N	89	32	29.8	89.541611	W
164E	40	41	29.9	40.691639	N	89	33	18.4	89.555111	W
164W	40	41	50.2	40.697278	N	89	33	30.7	89.558528	W

[a] Changed from 57 in Cahill (2001) due to transcription error

April 2000 Locations

River Mile	Core#	Date	Time	Deg	Min	[b]Dsec	Sec	Decimal Degrees		Deg	Min	Dsec	Sec	Decimal Degrees	
179	9	4/25	12:30PM	40	53	46	27.6	40.891000	N	89	29	40	24.0	89.490000	W
177	8	4/25	11:30AM	40	51	64	38.4	40.860667	N	89	29	95	57.0	89.499167	W
175	7	4/25	10AM	40	50	47	28.2	40.841167	N	89	31	14	8.4	89.519000	W
171W	4	4/18	1PM	40	47	50	30.0	40.791667	N	89	33	89	53.4	89.564833	W
171M	2	4/18	10:30AM	40	47	29	17.4	40.788167	N	89	33	8	4.8	89.551333	W
171E	3	4/18	12PM	40	47	29	17.4	40.788167	N	89	32	27	16.2	89.537833	W
169	1	4/17	3PM	40	45	46	27.6	40.757667	N	89	32	31	18.6	89.538500	W
165.5	10	4/25	2:30PM	40	42	81	48.6	40.713500	N	89	32	63	37.8	89.543833	W
164E	5	4/18	2:30PM	40	41	70	42.0	40.695000	N	89	33	3	1.8	89.550500	W
164W	6	4/18	3:30PM	40	41	84	50.4	40.697333	N	89	33	51	30.6	89.558500	W

October 2000 Locations

River Mile	Core#	Date	Time	Deg	Min	Dsec	Sec	Decimal Degrees		Deg	Min	Dsec	Sec	Decimal Degrees	
179	3	10/2	3:30PM	40	53	45	26.9	40.890817	N	89	29	45	26.8	89.490767	W
177	2	10/2	2:30PM	40	51	64	38.5	40.860700	N	89	29	95	56.7	89.499083	W
175	1	10/2	1:30PM	40	50	47	28.3	40.841183	N	89	31	14	8.6	89.519050	W
171W	4	10/3	10AM	40	47	50	29.8	40.791600	N	89	33	89	53.6	89.564883	W
171M	5	10/3	11AM	40	47	28	16.8	40.788000	N	89	33	7	4.2	89.551167	W
171E	6	10/3	12PM	40	47	29	17.2	40.788100	N	89	32	27	16.0	89.537783	W
169	7	10/3	1PM	40	45	46	27.5	40.757633	N	89	32	31	18.5	89.538467	W
165.5	8	10/11	10AM	40	42	81	48.7	40.713517	N	89	32	63	37.5	89.543750	W
164E	10	10/11	12PM	40	41	70	41.9	40.694967	N	89	33	2	1.4	89.550383	W
164W	9	10/11	11AM	40	41	84	50.4	40.697333	N	89	33	50	30.1	89.558367	W

[b] Dsec refers to decimal seconds as given by the GPS unit used.

Table A-2. pH and Temperature Data

River Mile	Depth (cm) April	Temp April	pH April	Buffer Check	Depth (cm) October	Temp October	pH October	Buffer Check	Depth (cm)	Interpolated pH April	Interpolated pH October
164E	-3	13.1	8.60		-3	11.7	8.32				
	7	12.2	7.39		7	12.4	7.49		3	7.87	7.82
	13	12.3	7.04	6.98	13	12.3	7.45	6.98	9	7.27	7.48
	19	11.8	7.06		19	13.5	7.09		15	7.05	7.33
	25	11.4	6.93		25	14.5	6.89		21	7.02	7.02
	31	11.4	7.03		31	15.4	6.78		27	6.96	6.85
					37	16.3	6.74				
164W											
	-3	13.0	8.56		-3	12.4	8.21				
	7	12.6	7.43		7	13.1	7.33		3	7.88	7.68
	13	12.4	7.28	6.99	13	13.3	7.17	7.01	9	7.38	7.28
	19	12.2	7.19		19	14.1	7.02		15	7.25	7.12
	25	12.1	7.09		25	14.9	6.91		21	7.16	6.98
	31	11.9	7.12		31	15.9	6.80		27	7.10	6.87
	37	11.9	7.07		37	17.0	6.79				
165.5											
	-3	14.6	7.82		-3	11.7	8.07				
	7	13.4	7.38		7	14.5	7.55		3	7.56	7.76
	13	13.2	7.27	7.03	13	15.2	7.24	7.03	9	7.34	7.45
	19	13.3	7.23		19	16.0	7.12		15	7.26	7.20
	25	13.2	7.14		25	16.7	7.02		21	7.20	7.09
	29	14.0	7.03		31	16.8	6.99		27	7.09	7.01
169											
	-3	13.6	8.50		-3	19.5	8.14				
	7	10.5	7.44		7		7.52		3	7.86	7.77
	11	11.6	7.42		13		7.25	6.97	9	7.43	7.43
	17	9.3	7.35		19		7.09		15	7.37	7.20
	23	8.9	7.17		25		6.91		21	7.23	7.03
	29	9.2	7.12		31		6.78		27	7.14	6.87
	33	10.5	7.04								
171E											
	-3	12.0	8.50		-3	19.5	8.23		3	7.75	7.61
	7	12.0	7.25		7		7.20		9	7.18	7.13
	11	12.2	7.10		13		7.00		15	6.93	6.95
	15	12.3	6.93		19		6.84		21		
	17	12.4	6.95						27		
171M											
	-3	12.9	8.48		-3	18.9	8.05				
	5	12.4	7.30		7		7.36		3	7.60	7.64
	10	12.3	7.25		13		7.23	6.90	9	7.26	7.32
	16	12.3	7.09		19		7.06		15	7.12	7.17
	22	12.1	7.02		25		6.92		21	7.03	7.01
	28	12.2	7.05		31		6.83		27	7.05	6.89
	32	12.2	7.03		37						
171W											
	-3	12.4	8.51		-3	18.7	8.05				
	5	12.5	7.42		7		7.32		3	7.69	7.61
	10	12.1	7.31	6.77	13		7.11	6.85	9	7.33	7.25
	16	12.3	7.18		19		6.95		15	7.20	7.06
	22	12.3	6.96		25		6.79		21	7.00	6.90
	28	12.3	6.86		31		6.71		27	6.88	6.76
	34	12.4	6.84								
	40	12.5	6.82								

Table A-2. pH and Temperature Data (Continued)

River Mile	Depth (cm) April	Temp April	pH April	Buffer Check	Depth (cm) October	Temp October	pH October	Buffer Check	Depth (cm)	Interpolated pH April	Interpolated pH October
175											
	-3	12.3	7.81		-3	19.0	7.91				
	7	12.4	7.39		7		7.15		3	7.56	7.45
	13	12.8	7.28		13		7.00		9	7.35	7.10
	19	13.0	7.02		19		6.84		15	7.19	6.95
	25	15.9	6.98		25		6.72		21	7.01	6.80
	31	14.8	6.86		31		6.74		27	6.94	6.73
	37				37						
177											
	-3	13.6	7.84		-3	20.2	8.07				
	3		7.56		7		7.36		3	7.56	7.64
	7	13.1	7.46		13		7.25		9	7.38	7.32
	13	13.3	7.23	6.97	19		7.01		15	7.19	7.17
	19	13.0	7.11		25		6.90		21	7.06	6.97
	25	12.7	6.96		31		6.85		27	6.94	6.88
	31	12.6	6.89		37		6.71				
179											
	-3	13.5	7.74		-3	19.6	8.08				
	7	13.1	7.41		7		7.13		3	7.54	7.51
	13	13.0	7.11		13		6.92		9	7.31	7.06
	19	13.3	7.00		19		6.83		15	7.07	6.89
	25	14.3	6.88		25		6.79		21	6.96	6.82
	29	14.0	6.86		31		6.71		27	6.87	6.76
	37				37		6.66				
					43		6.66				

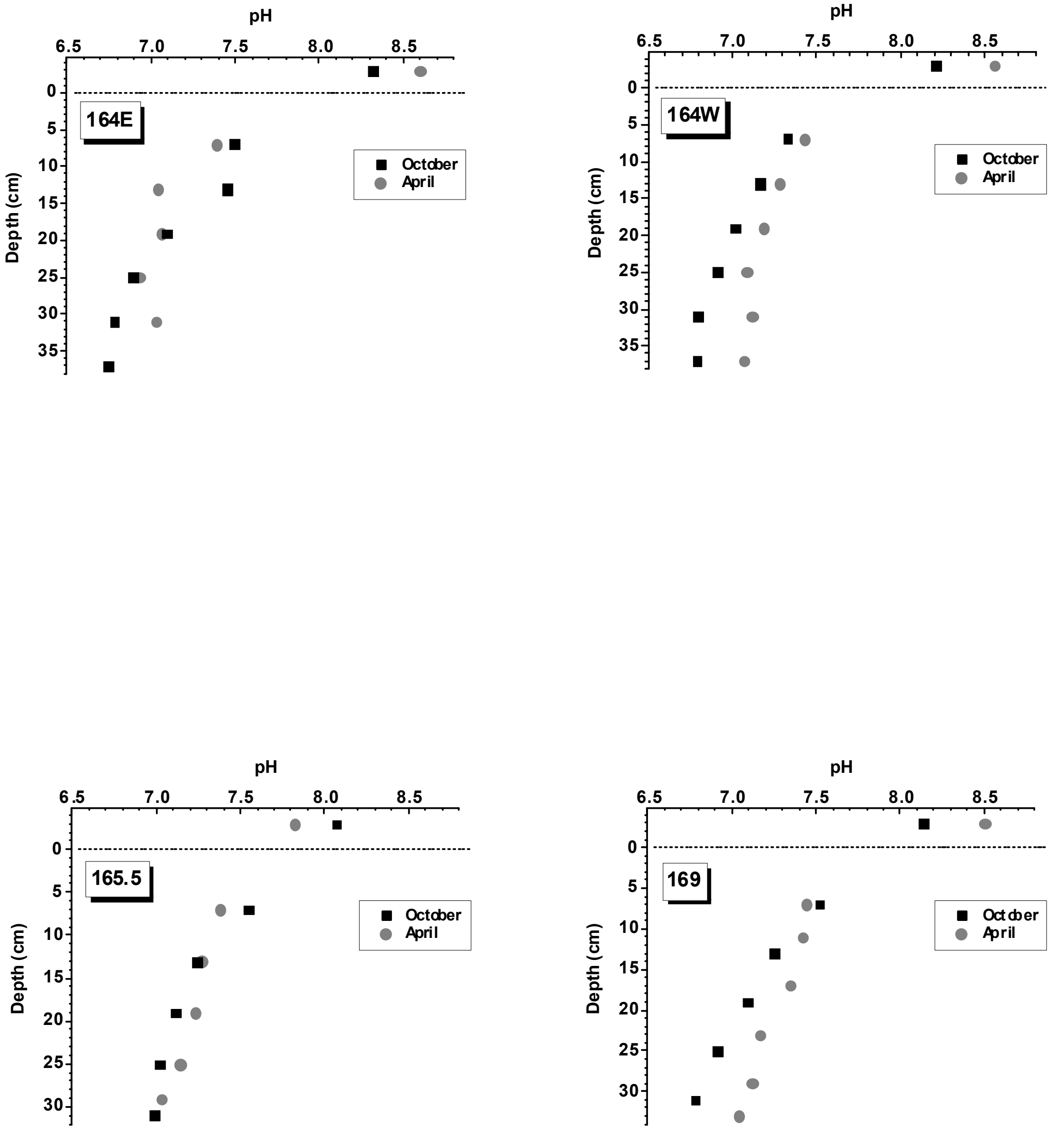

Figure A-1a. April and October pH values for stations 164 to 169.

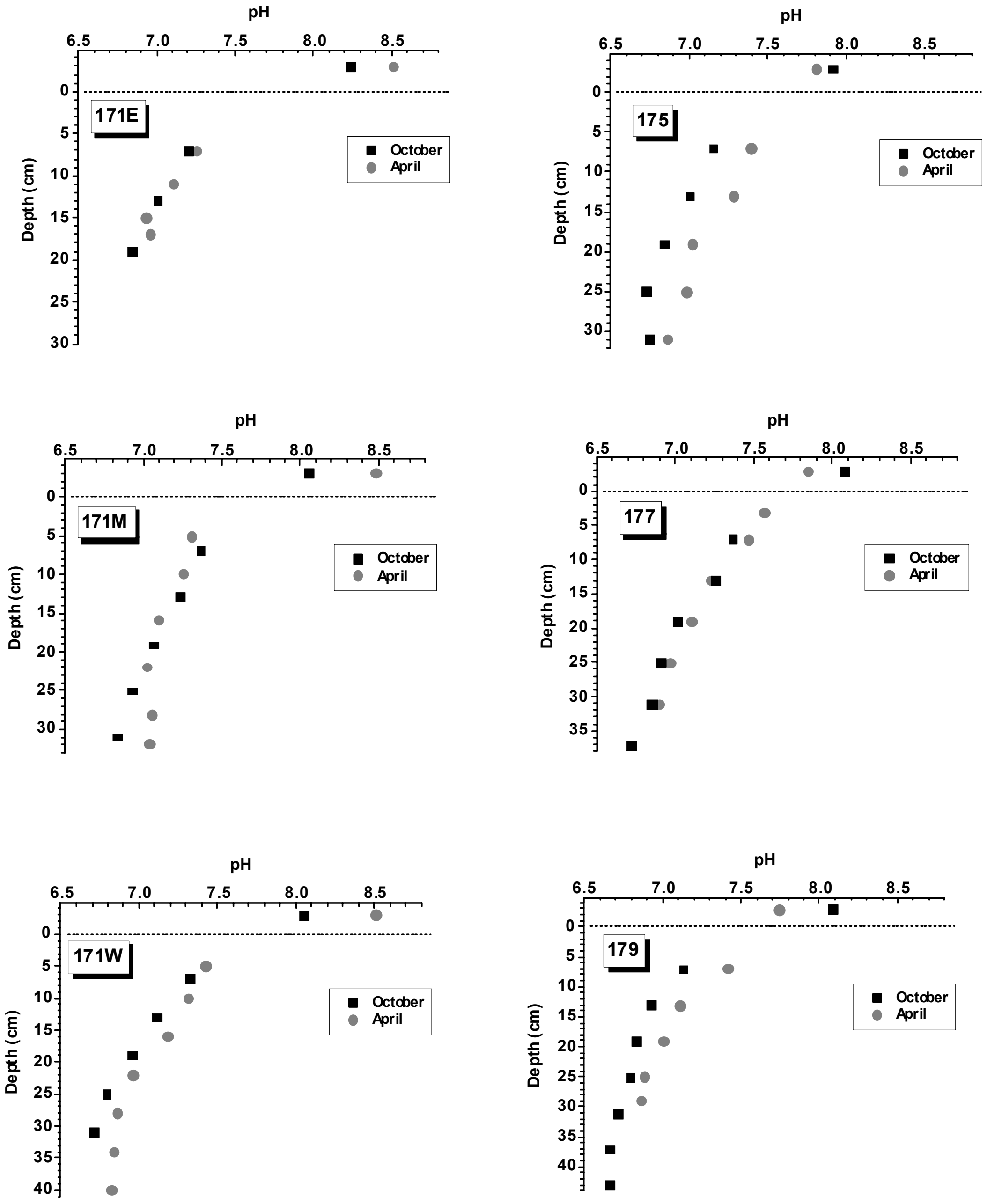

Figure A-1b. April and October pH values for stations 171 to 179.

Table A-3a. April dissolved ammonia data.

Sample ID	Date Sampled	Date Analyzed	Sample type or Section #	River Mile	Depth (cm)	NH_4-N mg/L
0A		05/02/00	Blank		-3	<0.07
5A	4/18/2000	05/02/00	Surface Water	164E	-3	0.08
6A	4/18/2000	05/02/00	Surface Water	164W	-3	<0.07
1RA	4/18/2000	05/02/00	Surface Water	165.5 (ND)	-3	0.21
2RA	4/18/2000	05/02/00	Surface Water	165.5 (ND)	-3	0.16
3RA	4/18/2000	05/02/00	Surface Water	165.5 (DB 1)	-3	<0.07
5RA	4/18/2000	05/02/00	Surface Water	165.5 (DB 2)	-3	<0.07
10A	4/25/2000	05/02/00	Surface Water	165.5	-3	0.26
1A	4/18/2000	05/02/00	Surface Water	169	-3	<0.07
3A	4/18/2000	05/02/00	Surface Water	171E	-3	<0.07
2A	4/18/2000	05/02/00	Surface Water	171M	-3	0.10
4A	4/18/2000	05/02/00	Surface Water	171W	-3	0.11
7A	4/25/2000	05/02/00	Surface Water	175	-3	0.31
8A	4/25/2000	05/02/00	Surface Water	177	-3	0.27
9A	4/25/2000	05/02/00	Surface Water	179	-3	0.28
35A		05/03/00	19	164E	3	0.38
38A		05/03/00	20	164E	9	2.02
39A		05/02/00	21	164E	15	4.65
40A		05/02/00	22	164E	21	8.52
41A		05/02/00	23	164E	27	9.92
42A		05/03/00	24	164W	3	1.40
43A		05/03/00	25	164W	9	3.76
20A		05/02/00	26	164W	15	4.98
21A		05/02/00	27	164W	21	8.12
22A		05/02/00	28	164W	27	10.52
46A		05/03/00	43	165.5	3	0.70
44A		05/03/00	44	165.5	9	3.13
60A		05/03/00	45	165.5	15	4.45
63A		05/03/00	46	165.5	21	7.20
55A		05/03/00	47	165.5	27	9.66
56A		05/03/00	47	165.5	27	9.72
13A		05/02/00	1	169	3	2.75
14A		05/02/00	2	169	9	1.37
15A		05/02/00	2	169	9	1.28
16A		05/03/00	3	169	15	4.07
17A		05/02/00	4	169	21	3.79
18A		05/02/00	4	169	21	3.77
19A		05/02/00	5	169	27	5.80

Table A-3a. April dissolved ammonia data cont'd.

Sample ID	Date Sampled	Date Analyzed	Sample type or Section #	River Mile	Depth (cm)	NH_4-N mg/L
28A		05/03/00	11	171E	3	1.00
29A		05/03/00	12	171E	9	2.77
30A		05/02/00	13	171E	15	3.03
33A		05/03/00	6	171M	3	1.73
23A		05/02/00	7	171M	9	3.69
24A		05/02/00	7	171M	9	3.75
25A		05/02/00	8	171M	15	10.05
27A		05/02/00	9	171M	21	12.96
26A		05/02/00	10	171M	27	13.89
31A		05/03/00	14	171W	3	1.29
32A		05/03/00	15	171W	9	2.87
36A		05/02/00	16	171W	15	3.81
37A		05/02/00	17	171W	21	7.85
34A		05/02/00	18	171W	27	11.97
52A		05/03/00	29	175	3	2.34
49A		05/03/00	31	175	15	3.57
50A		05/03/00	32	175	21	7.40
45A		05/02/00	33	175	27	9.87
47A		05/03/00	34	177	3	2.36
53A		05/22/00	35	177	9	4.87
57A		05/03/00	36	177	15	4.46
61A		05/03/00	37	177	21	7.62
62A		05/03/00	37	177	21	7.60
48A		05/03/00	38	177	27	9.87
51A		05/22/00	40	179	9	4.16
54A		05/03/00	41	179	15	8.34

Table A-3b. October dissolved ammonia data.

Sample ID	Date Sampled	Date Analyzed	Sample type or Section #	River Mile	Depth (cm)	NH_4-N mg/L
153A		10/25/00	DI-H20+acid Blk			<0.07
154A		10/25/00	Cameo filter Blk			<0.07
155A		10/25/00	Cameo filter Blk			<0.07
156A		10/25/00	PP filter Blk			<0.07
157A		10/25/00	capsule filter Blk			<0.07
158A		10/25/00	DI-H20 Blk			<0.07
178A	10/11/2000	10/25/00	Surface Water	164E	-3	<0.07
176A	10/11/2000	10/25/00	Surface Water	164W	-3	<0.07
177A	10/11/2000	10/25/00	Surface Water	164W	-3	<0.07
175A	10/11/2000	10/25/00	Surface Water	165.5	-3	<0.07
173A	10/3/2000	10/25/00	Surface Water	169	-3	<0.07
174A	10/3/2000	10/25/00	Surface Water	169	-3	<0.07
172A	10/3/2000	10/25/00	Surface Water	171E	-3	<0.07
171A	10/3/2000	10/25/00	Surface Water	171M	-3	0.10
170A	10/3/2000	10/25/00	Surface Water	171W	-3	<0.07
167A	10/2/2000	10/25/00	Surface Water	175	-3	<0.07
168A	10/2/2000	10/25/00	Surface Water	177	-3	<0.07
169A	10/2/2000	10/25/00	Surface Water	179	-3	<0.07
144A		10/25/00	94	164E	3	0.51
149A		10/25/00	95	164E	9	0.86
145A		10/25/00	96	164E	15	4.90
146A		10/25/00	96	164E	15	4.80
150A		10/25/00	97	164E	21	12.4
148A		10/25/00	98	164E	27	18.5
151A		10/25/00	89	164W	3	0.79
152A		10/25/00	89	164W	3	0.80
142A		10/25/00	90	164W	9	2.91
140A		10/25/00	91	164W	15	17.4
141A		10/25/00	92	164W	21	27.4
143A		10/25/00	93	164W	27	36.7
138A		10/25/00	84	165.5	3	0.56
135A		10/25/00	85	165.5	9	1.37
136A		10/25/00	86	165.5	15	5.04
137A		10/25/00	86	165.5	15	5.01
147A		10/25/00	87	165.5	21	12.9
139A		10/25/00	88	165.5	27	18.3
129A		10/25/00	79	169	3	0.48
130A		10/25/00	80	169	9	0.89
131A		10/25/00	80	169	9	0.92
132A		10/25/00	81	169	15	5.82
133A		10/25/00	82	169	21	14.1
134A		10/25/00	83	169	27	17.9

Table A-3b. October dissolved ammonia data cont'd.

Sample ID	Date Sampled	Date Analyzed	Sample type or Section #	River Mile	Depth (cm)	NH_4-N mg/L
126A		10/25/00	75	171E	3	0.46
127A		10/25/00	75	171E	3	0.50
128A		10/25/00	76	171E	9	1.14
124A		10/25/00	77	171E	15	3.02
125A		10/25/00	78	171E	21	4.91
115A		10/25/00	70	171M	3	0.99
116A		10/25/00	71	171M	9	1.70
122A		10/25/00	72	171M	15	6.35
121A		10/25/00	73	171M	21	12.8
123A		10/25/00	74	171M	27	14.6
117A		10/25/00	65	171W	3	1.11
118A		10/25/00	65	171W	3	1.16
119A		10/25/00	66	171W	9	1.21
120A		10/25/00	67	171W	15	6.57
113A		10/25/00	68	171W	21	15.8
114A		10/25/00	69	171W	27	24.2
103A		10/25/00	50	175	3	11.1
104A		10/25/00	50	175	3	10.2
101A		10/25/00	51	175	9	3.84
110A		10/25/00	52	175	15	7.86
105A		10/25/00	53	175	21	19.4
111A		10/25/00	54	175	27	26.8
106A		10/25/00	55	177	3	1.88
100A		10/25/00	56	177	9	3.45
107A		10/25/00	57	177	15	8.51
102A		10/25/00	58	177	21	13.8
108A		10/25/00	59	177	27	16.9
109A		10/25/00	60	179	3	2.96
112A		10/25/00	63	179	21	36.2

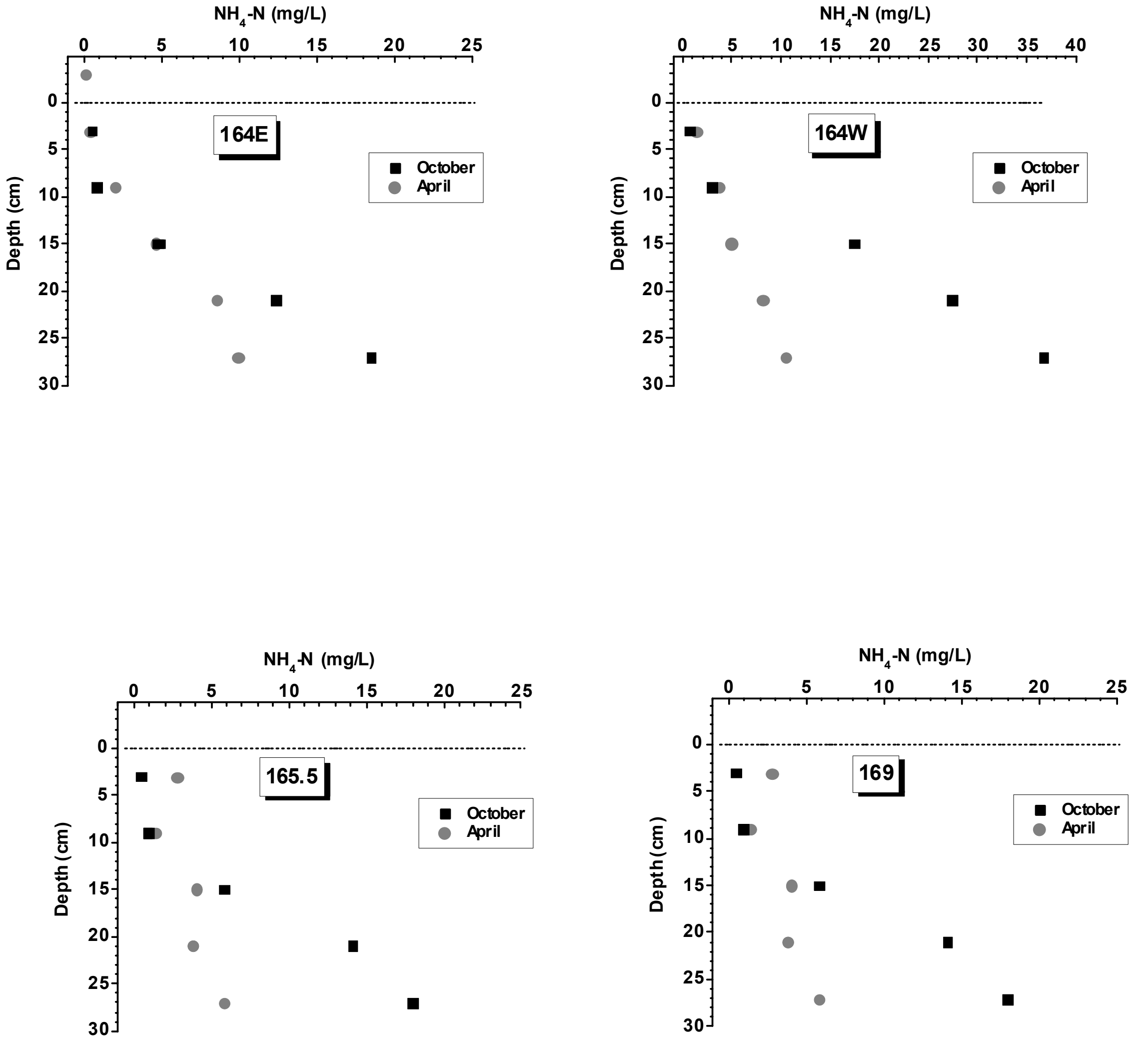

Figure A-2a. Ammonia-nitrogen data for stations 164 to 169.

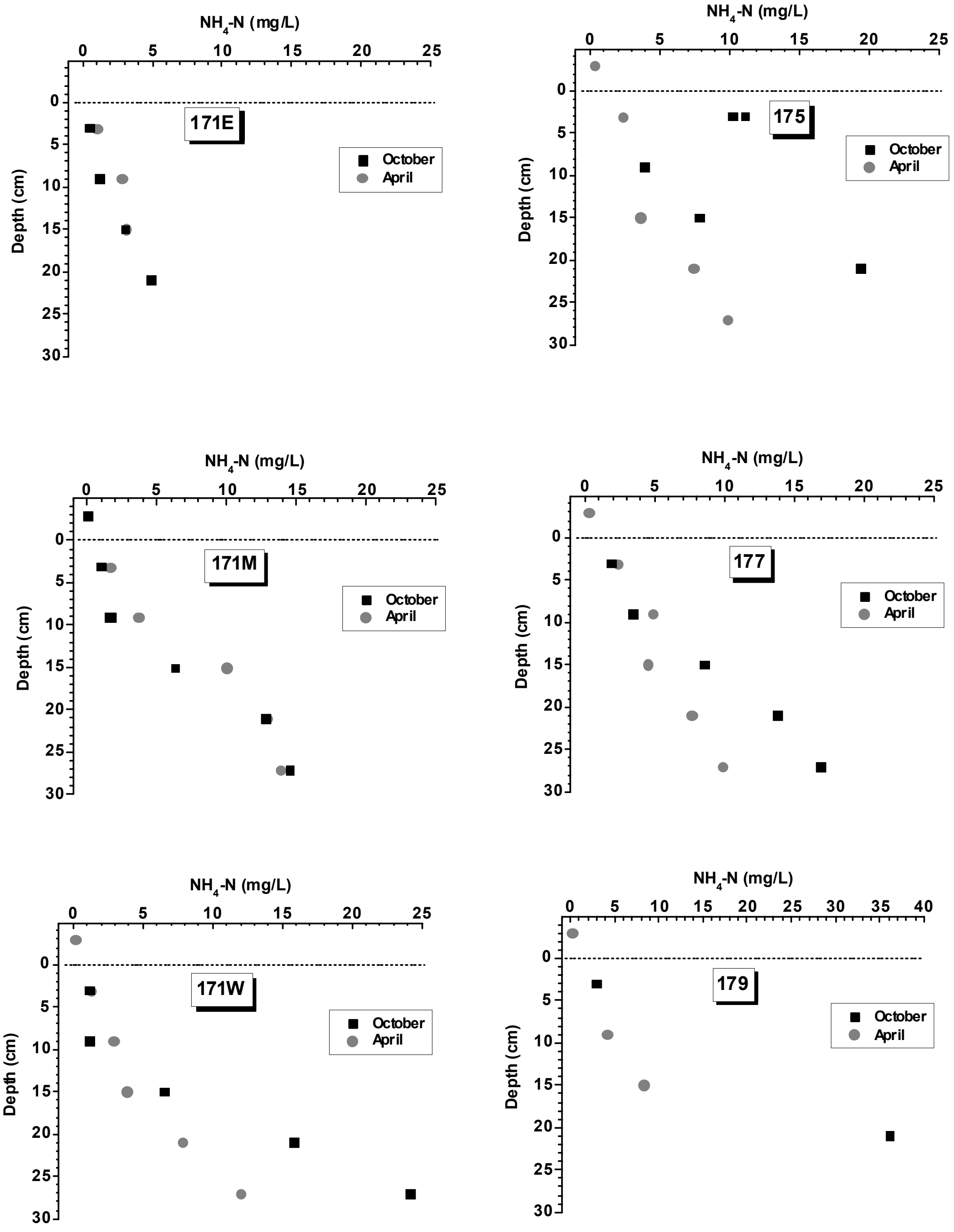

Figure A-2b. Ammonia-nitrogen data for stations 171 to 179.

Table A-4a. April dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data.

Identification		Sample Type	Depth	Calcium	Nickel,	Nickel	Nickel
Client	WMRC	or River Mile	(cm)	mg/L	ng/mL	Blk corr[b]	Ca corr[c]
0M	00-1651	Acid Blk			<0.2		
2M	00-1667	Nalgene filter Blk			<0.2		
11M	00-1668	Cameo filter Blk		<5	<0.2		
81M	00-1721	DI water Blk			<0.2		
IR	00-1652	165.5 (ND)	-3		4.81	4.81	
2R	00-1653	165.5 (ND)	-3	64.50	4.85	4.85	3.79
3R	00-1654	165.5 (DB 1)	-3	70.40	4.81	4.81	3.59
4R	00-1655	165.5 (DB 2)	-3		4.77	4.77	
6R	00-1656	165.5 (DB 2)	-3		4.79	4.79	
5M	00-1661	164E	-3	64.20	4.83	4.83	3.70
6M	00-1662	164E	-3	64.30	4.31	4.31	3.19
10M	00-1666	165.5	-3	56.90	3.73	3.73	2.72
1M	00-1657	169	-3	65.00	4.84	4.84	3.68
3M	00-1659	171E	-3	67.40	4.79	4.79	3.64
12M	00-1658	171M	-3	67.60	5.09	5.09	3.94
4M	00-1660	171W	-3	65.60	5.18	5.18	4.07
7M	00-1663	175	-3	51.40	2.92	2.92	2.02
8M	00-1664	177	-3	54.20	3.43	3.43	2.47
9M	00-1665	179	-3	55.30	3.60	3.60	2.65
40M	00-1690	164E	3	66.00	3.47	3.47	2.37
43M	00-1693	164E	9	72.80	2.48	2.48	1.25
44M	00-1694	164E	15	98.30	2.37	2.37	0.71
45M	00-1695	164E	21	140.00	2.39	2.39	<0.2
46M	00-1696	164E	27	150.00	1.83	1.83	<0.2
47M	00-1697	164W	3	70.70	3.64	3.64	2.38
48M	00-1698	164W	9	77.60	2.36	2.36	1.07
22M	00-1674	164W	15	85.50	2.22	2.22	0.73
23M	00-1675	164W	21	120.00	1.73	1.73	<0.2
24M	00-1676	164W	21	120.00	1.71	1.71	<0.2
26M	00-1677	164W	27	120.00	1.94	1.94	<0.2
53M	00-1702	165.5	3	64.50	3.69	3.69	2.59
49M	00-1699	165.5	9	66.10	2.47	2.47	1.36
50M	00-1700	165.5	9	150[a]	2.43	2.43	<0.2
76M	00-1717	165.5	15	88.30	1.94	1.94	0.38
79M	00-1719	165.5	21	101.60	2.28	2.28	0.55
80M	00-1720	165.5	21	105.40	2.25	2.25	0.39
70M	00-1714	165.5	27	125.70	1.83	1.83	<0.2
71M	00-1715	165.5	27	119.30	1.76	1.76	<0.2

[a] suspect value

[b] corrected for blank

[c] corrected for Ca interference

Table A-4a. April dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data cont'd.

Identification		Sample Type or River Mile	Depth (cm)	Copper, ng/mL	Copper Blk corr[b]	Zinc, ng/mL	Zinc Blk corr[b]	Cadmium, ng/mL	Cadmium Blk corr[b]	Lead ng/mL	Lead Blk corr[b]
Client	WMRC										
0M	00-1651	Acid BlK		0.31		1.15		<0.04		<0.2	
2M	00-1667	Nalgene filter Blk		0.53	0.33	0.98		<0.04	<0.04	<0.2	<0.2
11M	00-1668	Cameo filter Blk		<0.2		4.03		<0.04	<0.04	<0.2	<0.2
81M	00-1721	DI water Blk		0.98		1.50		<0.04	<0.04	<0.2	
IR	00-1652	165.5 (ND)	-3	1.68	1.48	4.21	3.23	0.08	0.08	0.24	0.24
2R	00-1653	165.5 (ND)	-3	1.72	1.52	4.45	3.47	0.09	0.09	0.37	0.37
3R	00-1654	165.5 (DB 1)	-3	1.69	1.49	4.41	3.43	0.08	0.08	0.22	0.22
4R	00-1655	165.5 (DB 2)	-3	1.70	1.50	4.03	3.05	0.08	0.08	0.22	0.22
6R	00-1656	165.5 (DB 2)	-3	1.73	1.53	6.83	5.85	0.08	0.08	0.29	0.29
5M	00-1661	164E	-3	2.28	2.08	4.72	3.74	0.09	0.09	0.23	0.23
6M	00-1662	164W	-3	2.03	1.83	4.55	3.57	0.07	0.07	<0.2	<0.2
10M	00-1666	165.5	-3	1.80	1.60	5.14	4.16	0.08	0.08	0.39	0.39
1M	00-1657	169	-3	2.03	1.83	4.44	3.47	0.09	0.09	0.20	0.20
3M	00-1659	171E	-3	1.89	1.69	3.47	2.49	0.10	0.10	<0.2	<0.2
12M	00-1658	171M	-3	1.73	1.53	4.30	3.32	0.07	0.07	<0.2	<0.2
4M	00-1660	171W	-3	1.64	1.44	4.74	3.76	0.07	0.07	<0.2	<0.2
7M	00-1663	175	-3	1.64	1.44	5.52	4.54	0.06	0.06	0.21	0.21
8M	00-1664	177	-3	1.50	1.30	4.07	3.09	0.10	0.10	0.20	0.20
9M	00-1665	179	-3	1.62	1.42	4.93	3.96	0.08	0.08	0.24	0.24
40M	00-1690	164E	3	0.54	0.34	2.21	1.24	<0.04	<0.04	0.36	0.36
43M	00-1693	164E	9	0.36	0.16	1.27	0.29	<0.04	<0.04	<0.2	<0.2
44M	00-1694	164E	15	0.66	0.46	0.90	<.2	<0.04	<0.04	<0.2	<0.2
45M	00-1695	164E	21	0.67	0.47	1.64	0.66	<0.04	<0.04	0.22	0.22
46M	00-1696	164E	27	0.34	0.14	1.03	0.06	<0.04	<0.04	<0.2	<0.2
47M	00-1697	164W	3	0.39	0.19	1.18	0.21	<0.04	<0.04	0.24	0.24
48M	00-1698	164W	9	0.24	0.04	0.51	<.2	<0.04	<0.04	<0.2	<0.2
22M	00-1674	164W	15	0.35	0.15	2.09	1.11	<0.04	<0.04	0.20	0.20
23M	00-1675	164W	21	0.39	0.19	0.86	<.2	<0.04	<0.04	<0.2	<0.2
24M	00-1676	164W	21	0.23	0.03	0.48	<.2	<0.04	<0.04	<0.2	<0.2
26M	00-1677	164W	27	0.26	0.06	0.55	<.2	<0.04	<0.04	<0.2	<0.2
53M	00-1702	165.5	3	1.09	0.89	7.43	3.40	<0.04	<0.04	0.82	0.82
49M	00-1699	165.5	9	1.92	1.72	6.28	2.25	0.05	0.05	1.79	1.79
50M	00-1700	165.5	9	1.09	0.89	6.23	2.20	<0.04	<0.04	0.87	0.87
76M	00-1717	165.5	15	0.56	0.36	7.84	3.80	<0.04	<0.04	0.35	0.35
79M	00-1719	165.5	21	<0.2	<0.2	18.91	14.88	<0.04	<0.04	<0.2	<0.2
80M	00-1720	165.5	21	0.41	0.21	14.52	10.48	<0.04	<0.04	<0.2	<0.2
70M	00-1714	165.5	27	0.33	0.13	8.46	4.43	<0.04	<0.04	0.24	0.24
71M	00-1715	165.5	27	0.32	0.12	5.92	1.89	<0.04	<0.04	<0.2	<0.2

[b] corrected for blank

Table A-4a. April dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data cont'd.

Identification		Sample Type	Depth	Calcium	Nickel,	Nickel	Nickel	
Client	WMRC	or River Mile	(cm)	mg/L	ng/mL	Blk corr[b]	Ca corr[c]	
13M	00-1669	169	3	78.80	3.57	3.57	2.25	
14M	00-1670	169	3	73.10	3.56	3.56	2.34	
16M	00-1671	169	15	69.50	2.19	2.19	1.01	
18M	00-1672	169	21	82.50	1.81	1.81	0.38	
20M	00-1673	169	27	99.00	1.76	1.66	0.10	
32M	00-1682	171E	3	73.20	4.15	4.15	2.94	
33M	00-1683	171E	9	68.30	2.51	2.51	1.33	
34M	00-1684	171E	15	80.20	5.16	5.16	3.82	
38M	00-1688	171M	3	73.80	4.06	4.06	2.83	
27M	00-1678	171M	9	76.10	2.11	2.11	0.79	
29M	00-1679	171M	15	120.00	2.84	2.84	<0.2	
31M	00-1681	171M	21	129.60	3.94	3.94	1.67	
30M	00-1680	171M	27	130.00	4.68	4.68	2.46	
35M	00-1685	171W	3	73[a]	1.88	1.88	0.63	?(est Ca)
36M	00-1686	171W	9	73.10	2.69	2.69	1.44	
37M	00-1687	171W	9	70.40	2.72	2.72	1.49	
41M	00-1691	171W	15	88.40	2.54	2.54	0.98	
42M	00-1692	171W	21	99.20	2.23	2.23	0.49	
39M	00-1689	171W	27	130.00	3.51	3.51	1.26	
65M	00-1711	175	3	80.20	6.99	6.99	5.62	
63M	00-1709	175	9	73.80	4.97	4.97	3.73	
59M	00-1705	175	15	130.00	1.76	1.76	<0.2	
60M	00-1706	175	21	77.10	2.20	2.20	0.87	
61M	00-1707	175	21	98.50	2.72	2.72	1.01	
51M	00-1701	175	27	110.00	2.72	2.72	0.81	
55M	00-1703	177	3	81.60	4.66	4.66	3.30	
68M	00-1712	177	9	75.20	2.35	2.35	1.11	
72M	00-1716	177	15	83.50	2.08	2.08	0.67	
78M	00-1718	177	21	105.40	2.09	2.09	0.28	
57M	00-1704	177	27	160.00	2.93	2.93	0.15	
62M	00-1708	179	9	88.60	1.98	1.98	0.48	
64M	00-1710	179	9	64.70	1.87	1.87	0.79	
69M	00-1713	179	15	99.00	2.07	2.07	0.40	

[a] estimated value

[b] corrected for blank

[c] corrected for Ca interference

Table A-4a. April dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data cont'd.

Identification		Sample Type	Depth	Copper,		Zinc,		Cadmium,		Lead	
Client	WMRC	or River Mile	(cm)	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]
13M	00-1669	169	3	0.60	0.40	2.63	1.65	<0.04	<0.04	0.44	0.44
14M	00-1670	169	3	0.42	0.22	2.12	1.14	<0.04	<0.04	<0.2	<0.2
16M	00-1671	169	15	0.90	0.70	1.50	0.52	0.08	0.08	0.75	0.75
18M	00-1672	169	21	0.42	0.22	1.06	0.08	<0.04	<0.04	0.24	0.24
20M	00-1673	169	27	0.27	0.07	0.40	-0.58	<0.04	<0.04	<0.2	<0.2
32M	00-1682	171E	3	0.65	0.45	2.28	1.30	0.05	0.05	<0.2	<0.2
33M	00-1683	171E	9	1.12	0.92	1.40	0.42	0.05	0.05	0.56	0.56
34M	00-1684	171E	15	0.63	0.43	2.23	1.26	<0.04	<0.04	0.25	0.25
38M	00-1688	171M	3	1.13	0.93	2.20	1.22	0.29	0.29	0.89	0.89
27M	00-1678	171M	9	1.93	1.73	2.29	1.31	0.08	0.08	2.07	2.07
29M	00-1679	171M	15	<0.2	<0.2	0.38	<.2	<0.04	<0.04	<0.2	<0.2
31M	00-1681	171M	21	0.35	0.15	0.71	<.2	<0.04	<0.04	<0.2	<0.2
30M	00-1680	171M	27	0.30	0.10	0.70	<.2	<0.04	<0.04	0.22	0.22
35M	00-1685	171W	3	0.64	0.44	0.72	<.2	<0.04	<0.04	0.24	0.24
36M	00-1686	171W	9	0.59	0.39	1.70	0.72	<0.04	<0.04	0.42	0.42
37M	00-1687	171W	9	<0.2	<0.2	0.43	<.2	<0.04	<0.04	<0.2	<0.2
41M	00-1691	171W	15	0.57	0.37	1.20	0.22	<0.04	<0.04	0.38	0.38
42M	00-1692	171W	21	0.54	0.34	0.92	<.2	<0.04	<0.04	0.42	0.42
39M	00-1689	171W	27	0.36	0.16	1.45	0.47	<0.04	<0.04	<0.2	<0.2
65M	00-1711	175	3	0.69	0.49	18.82	14.78	<0.04	<0.04	0.31	0.31
63M	00-1709	175	9	1.98	1.78	553.50	549.47	0.26	0.26	1.35	1.35
59M	00-1705	175	15	0.41	0.21	4.54	0.51	<0.04	<0.04	0.37	0.37
60M	00-1706	175	21	0.68	0.48	8.30	4.27	0.06	0.06	0.80	0.80
61M	00-1707	175	21	0.72	0.52	6.58	2.55	<0.04	<0.04	0.38	0.38
51M	00-1701	175	27	0.46	0.26	11.76	7.73	1.23	1.23	0.75	0.75
55M	00-1703	177	3	0.66	0.46	57.00	52.97	<0.04	<0.04	0.32	0.32
68M	00-1712	177	9	0.38	0.18	8.30	4.27	<0.04	<0.04	0.29	0.29
72M	00-1716	177	15	1.03	0.83	12.33	8.30	<0.04	<0.04	0.83	0.83
78M	00-1718	177	21	1.23	1.03	8.00	3.97	<0.04	<0.04	0.48	0.48
57M	00-1704	177	27	0.34	0.14	6.76	2.73	<0.04	<0.04	<0.20	<0.20
62M	00-1708	179	9	1.37	1.17	90.18	86.14	<0.04	<0.04	1.16	1.16
64M	00-1710	179	9	0.61	0.41	9.12	5.08	<0.04	<0.04	0.55	0.55
69M	00-1713	179	15	0.35	0.15	8.90	4.87	0.06	0.06	0.32	0.32

[b] corrected for blank

Table A-4b. October dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data.

Identification		Sample Type	Depth	Calcium	Nickel	Nickel	Nickel
Client	WMRC	or River Mile	(cm)	mg/L	ng/mL	blkcorr[b]	Ca corr[c]
156M	00-3048	BDI-unfiltered Blk 1		<5	<0.2		
157M	00-3049	PolyPropylene filter Blk 1		5.3	<0.2		
158M	00-3050	PolyPropylene filter Blk 2		<5	<0.2		
159M	00-3051	BDI-unfiltered Blk 2		<5	<0.2		
160M	00-3052	FilterCapsule Blk 1		<5	<0.2		
161M	00-3053	FilterCapsule Blk 2		<5	<0.2		
187M	00-3054	175W	-3	53.5	5.69	5.69	4.46
198M	00-3065	164E	-3	56.2	5.34	5.34	4.00
196M	00-3063	164W	-3	54	5.44	5.44	4.15
197M	00-3064	164W	-3	57.9	5.78	5.78	4.46
195M	00-3062	165.5	-3	55.1	5.35	5.35	4.13
193M	00-3060	169	-3	51.6	5.80	5.80	4.61
194M	00-3061	169	-3	58.9	5.79	5.79	4.44
192M	00-3059	171E	-3	55.8	5.63	5.63	4.31
191M	00-3058	171M	-3	55.6	5.73	5.73	4.42
190M	00-3057	171W	-3	55.7	5.75	5.75	4.41
188M	00-3055	177	-3	63.9	5.76	5.76	4.32
189M	00-3056	179	-3	49.9	5.62	5.62	4.45
146M	00-3039	164E	3	47.6	4.70	4.64	3.60
151M	00-3044	164E	9	56.2	4.36	4.30	3.10
147M	00-3040	164E	15	65.8	4.29	4.23	2.78
148M	00-3041	164E	15	74.6	4.29	4.23	2.58
152M	00-3045	164E	21	109.8	6.22	6.16	3.66
150M	00-3043	164E	27	130.2	7.29	7.23	4.29
153M	00-3046	164W	3	56	6.71	6.65	5.41
154M	00-3047	164W	3	56.5	6.72	6.66	5.40
144M	00-3037	164W	9	59.4	5.14	5.08	3.73
141M	00-3034	164W	15	150	7.22	7.16	3.81
142M	00-3035	164W	21	170	9.71	9.65	5.73
143M	00-3036	164W	21	170	9.00	8.94	5.10
145M	00-3038	164W	27	180	9.43	9.37	5.21
139M	00-3032	165.5	3	53.6	5.01	4.95	3.76
137M	00-3030	165.5	9	54.7	5.58	5.52	4.34
138M	00-3031	165.5	15	61.6	4.24	4.18	2.78
149M	00-3042	165.5	21	96.9	5.41	5.35	3.16
140M	00-3033	165.5	27	120.3	6.47	6.41	3.72

[b] corrected for blank

[c] corrected for Ca interference

Table A-4b. October dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data cont'd.

Identification		Sample Type	Depth	Copper	Copper	Zinc	Zinc	Cadmium	Cadmium	Lead	Lead
Client	WMRC	or River Mile	(cm)	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]
156M	00-3048	unfiltered acid Blk 1		<0.1		<0.2		<0.02		<0.05	
157M	00-3049	Polyproplylene filter Blk 1		<0.1		0.60		<0.02		<0.05	
158M	00-3050	Polyproplylene filter Blk 2		<0.1		1.30		<0.02		<0.05	
159M	00-3051	unfiltered acid Blk 2		0.14		0.60		<0.02		0.05	
160M	00-3052	FilterCapsule Blk 1		0.31		0.50		<0.02		<0.05	
161M	00-3053	FilterCapsule Blk 2		0.24		0.40		0.02		<0.05	
187M	00-3054	175W	-3	2.53	2.23	4.60	4.10	0.11	0.10	0.23	0.23
198M	00-3065	164E	-3	2.01	1.71	3.30	2.80	0.10	0.09	0.19	0.19
196M	00-3063	164W	-3	2.17	1.87	3.40	2.90	0.09	0.08	0.19	0.19
197M	00-3064	164W	-3	1.97	1.67	4.10	3.60	0.11	0.10	0.22	0.22
195M	00-3062	165.5	-3	1.90	1.60	3.50	3.00	0.11	0.10	0.22	0.22
193M	00-3060	169	-3	2.23	1.93	3.00	2.50	0.10	0.09	0.15	0.15
194M	00-3061	169	-3	2.09	1.79	3.00	2.50	0.10	0.09	0.20	0.20
192M	00-3059	171E	-3	2.05	1.75	3.70	3.20	0.10	0.09	0.15	0.15
191M	00-3058	171M	-3	1.69	1.39	3.60	3.10	0.11	0.10	0.23	0.23
190M	00-3057	171W	-3	2.00	1.70	4.30	3.80	0.13	0.12	0.20	0.20
188M	00-3055	177	-3	1.80	1.50	3.70	3.20	0.10	0.09	0.22	0.22
189M	00-3056	179	-3	1.80	1.50	4.60	4.10	0.09	0.08	0.21	0.21
146M	00-3039	164E	3	0.18	0.11	1.40	0.80	0.03	0.03	0.07	0.05
151M	00-3044	164E	9	0.26	0.19	0.30	<0.2	0.02	0.02	<0.05	<0.05
147M	00-3040	164E	15	0.13	0.06	0.60	<0.2	<0.02	<0.02	<0.05	<0.05
148M	00-3041	164E	15	0.14	0.07	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
152M	00-3045	164E	21	0.19	0.12	0.60	<0.2	<0.02	<0.02	<0.05	<0.05
150M	00-3043	164E	27	0.24	0.17	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
153M	00-3046	164W	3	0.24	0.17	1.30	0.70	0.03	0.03	0.06	0.04
154M	00-3047	164W	3	0.36	0.29	1.10	0.50	0.10	0.10	0.07	0.05
144M	00-3037	164W	9	0.15	0.08	0.20	<0.2	<0.02	<0.02	<0.05	<0.05
141M	00-3034	164W	15	0.23	0.16	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
142M	00-3035	164W	21	0.32	0.25	0.30	<0.2	<0.02	<0.02	0.05	0.03
143M	00-3036	164W	21	0.31	0.24	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
145M	00-3038	164W	27	0.32	0.25	0.20	<0.2	<0.02	<0.02	<0.05	<0.05
139M	00-3032	165.5	3	<0.1	<0.1	1.80	1.20	<0.02	<0.02	0.08	0.06
137M	00-3030	165.5	9	<0.1	<0.1	0.90	0.30	<0.02	<0.02	0.07	0.05
138M	00-3031	165.5	15	<0.1	<0.1	0.90	0.30	<0.02	<0.02	<0.05	<0.05
149M	00-3042	165.5	21	0.18	0.11	0.20	<0.2	<0.02	<0.02	<0.05	<0.05
140M	00-3033	165.5	27	<0.1	<0.1	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05

[b] corrected for blank

Table A-4b. October dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data cont'd.

Identification		Sample Type	Depth	Calcium	Nickel	Nickel	Nickel
Client	WMRC	or River Mile	(cm)	mg/L	ng/mL	Blk corr[b]	Ca corr[c]
132M	00-3025	169	3	54.2	5.99	5.93	4.75
133M	00-3026	169	9	57.6	4.59	4.53	3.27
134M	00-3027	169	15	69.9	4.25	4.19	2.68
135M	00-3028	169	21	110	5.37	5.31	2.88
136M	00-3029	169	27	130	6.54	6.48	3.46
129M	00-3022	171E	3	58.7	6.46	6.40	5.14
130M	00-3023	171E	3	56.1	6.43	6.37	5.10
131M	00-3024	171E	9	55.1	4.27	4.21	3.03
127M	00-3020	171E	15	61.7	3.48	3.42	2.07
128M	00-3021	171E	21	69.6	3.69	3.63	2.09
118M	00-3011	171M	3	63.6	8.68	8.62	7.23
119M	00-3012	171M	9	56.1	5.06	5.00	3.80
125M	00-3018	171M	15	64.7	4.30	4.24	2.80
124M	00-3017	171M	21	88.2	5.49	5.43	3.46
126M	00-3019	171M	27	100	6.11	6.05	3.73
120M	00-3013	171W	3	62.3	6.55	6.49	5.16
121M	00-3014	171W	9	58.6	5.16	5.10	3.85
122M	00-3015	171W	9	65.8	5.22	5.16	3.68
123M	00-3016	171W	15	94.1	5.53	5.47	3.33
115M	00-3008	171W	21	120	6.85	6.79	4.23
116M	00-3009	171W	21	110	6.50	6.44	3.86
117M	00-3010	171W	27	140	8.32	8.26	5.06
103M	00-2996	175	3	86.2	6.22	6.16	4.21
100M	00-2993	175	9	66.1	4.50	4.44	2.79
111M	00-3004	175	15	83.3	4.70	4.64	2.78
105M	00-2998	175	21	107.9	6.32	6.26	3.81
113M	00-3006	175	27	130	7.06	7.00	4.05
106M	00-2999	177	3	69.5	7.93	7.87	6.29
107M	00-3000	177	3	75.1	8.41	8.35	6.67
101M	00-2994	177	9	73.2	5.53	5.47	3.81
108M	00-3001	177	15	102.2	5.04	4.98	2.64
102M	00-2995	177	21	115.6	5.96	5.90	3.33
109M	00-3002	177	27	125	6.44	6.38	3.51
110M	00-3003	179	3	92.5	13.49	13.43	11.20
114M	00-3007	179	21	220	14.86	14.80	10.00

[b] corrected for blank

[c] corrected for Ca interference

Table A-4b. October dissolved metals (Ca, Ni, Cu, Zn, Cd, Pb) data cont'd.

Identification		Sample Type	Depth	Copper	Copper	Zinc	Zinc	Cadmium	Cadmium	Lead	Lead
Client	WMRC	or River Mile	(cm)	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]	ng/mL	Blk corr[b]
132M	00-3025	169	3	0.11	0.04	1	0.4	0.02	0.02	0.066	0.046
133M	00-3026	169	9	<0.1	<0.1	0.8	0.2	<0.02	<0.02	<0.05	<0.05
134M	00-3027	169	15	<0.1	<0.1	0.6	<0.2	0.03	0.03	<0.05	<0.05
135M	00-3028	169	21	<0.1	<0.1	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
136M	00-3029	169	27	<0.1	<0.1	0.5	<0.2	<0.02	<0.02	<0.05	<0.05
129M	00-3022	171E	3	0.34	0.27	3.1	2.5	0.1	0.1	0.11	0.09
130M	00-3023	171E	3	0.32	0.25	2.9	2.3	0.09	0.09	0.082	0.062
131M	00-3024	171E	9	<0.1	<0.1	1.2	0.6	<0.02	<0.02	<0.05	<0.05
127M	00-3020	171E	15	<0.1	<0.1	0.5	<0.2	<0.02	<0.02	0.055	0.035
128M	00-3021	171E	21	<0.1	<0.1	0.5	<0.2	<0.02	<0.02	<0.05	<0.05
118M	00-3011	171M	3	0.18	0.11	0.6	<0.2	0.03	0.03	<0.05	<0.05
119M	00-3012	171M	9	0.14	0.07	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
125M	00-3018	171M	15	<0.1	<0.1	0.6	<0.2	<0.02	<0.02	0.064	0.044
124M	00-3017	171M	21	<0.1	<0.1	0.8	0.2	<0.02	<0.02	0.057	0.037
126M	00-3019	171M	27	0.12	0.05	<0.2	<0.2	<0.02	<0.02	0.057	0.037
120M	00-3013	171W	3	0.29	0.22	0.7	0.1	0.02	0.02	<0.05	<0.05
121M	00-3014	171W	9	0.18	0.11	0.3	<0.2	<0.02	<0.02	<0.05	<0.05
122M	00-3015	171W	9	<0.1	<0.1	0.5	<0.2	<0.02	<0.02	0.085	0.065
123M	00-3016	171W	15	<0.1	<0.1	0.2	<0.2	<0.02	<0.02	<0.05	<0.05
115M	00-3008	171W	21	0.32	0.25	0.7	0.1	0.02	0.02	0.11	0.09
116M	00-3009	171W	21	0.19	0.12	0.2	<0.2	<0.02	<0.02	<0.05	<0.05
117M	00-3010	171W	27	0.24	0.17	<0.2	<0.2	0.04	0.04	0.045	0.025
103M	00-2996	175	3	0.16	0.09	0.6	<0.2	<0.02	<0.02	<0.05	<0.05
100M	00-2993	175	9	0.11	0.04	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
111M	00-3004	175	15	0.13	0.06	0.2	<0.2	<0.02	<0.02	<0.05	<0.05
105M	00-2998	175	21	0.19	0.12	0.2	<0.2	<0.02	<0.02	<0.05	<0.05
113M	00-3006	175	27	0.33	0.26	0.3	<0.2	<0.02	<0.02	0.09	0.07
106M	00-2999	177	3	0.2	0.13	0.7	0.1	0.02	0.02	<0.05	<0.05
107M	00-3000	177	3	0.19	0.12	0.4	<0.2	0.03	0.03	<0.05	<0.05
101M	00-2994	177	9	0.16	0.09	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
108M	00-3001	177	15	0.15	0.08	0.2	<0.2	<0.02	<0.02	<0.05	<0.05
102M	00-2995	177	21	0.19	0.12	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05
109M	00-3002	177	27	0.21	0.14	0.2	<0.2	<0.02	<0.02	<0.05	<0.05
110M	00-3003	179	3	0.24	0.17	0.4	<0.2	0.03	0.03	<0.05	<0.05
114M	00-3007	179	21	0.43	0.36	<0.2	<0.2	<0.02	<0.02	<0.05	<0.05

[b] corrected for blank

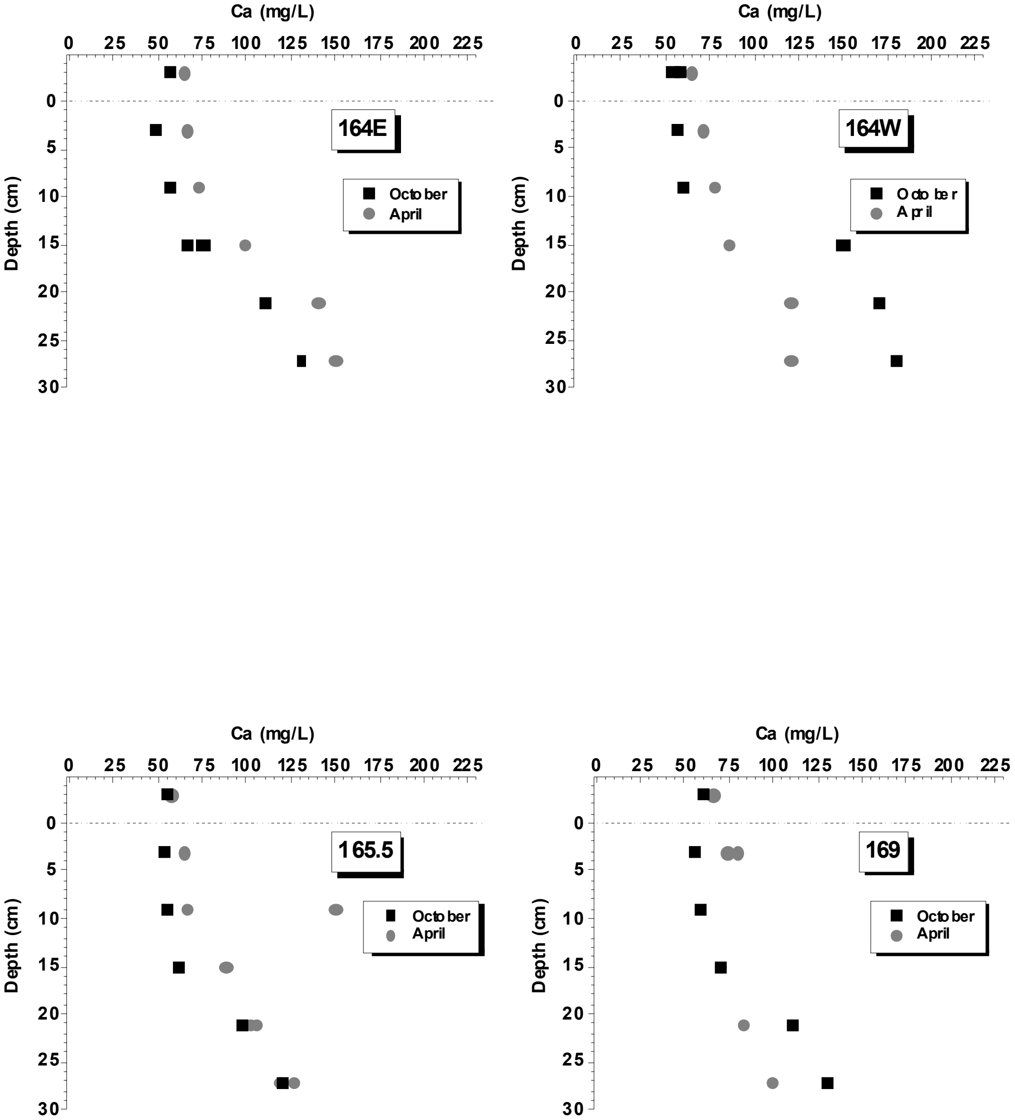

Figure A-3a. Dissolved calcium profiles for stations 164 to 169.

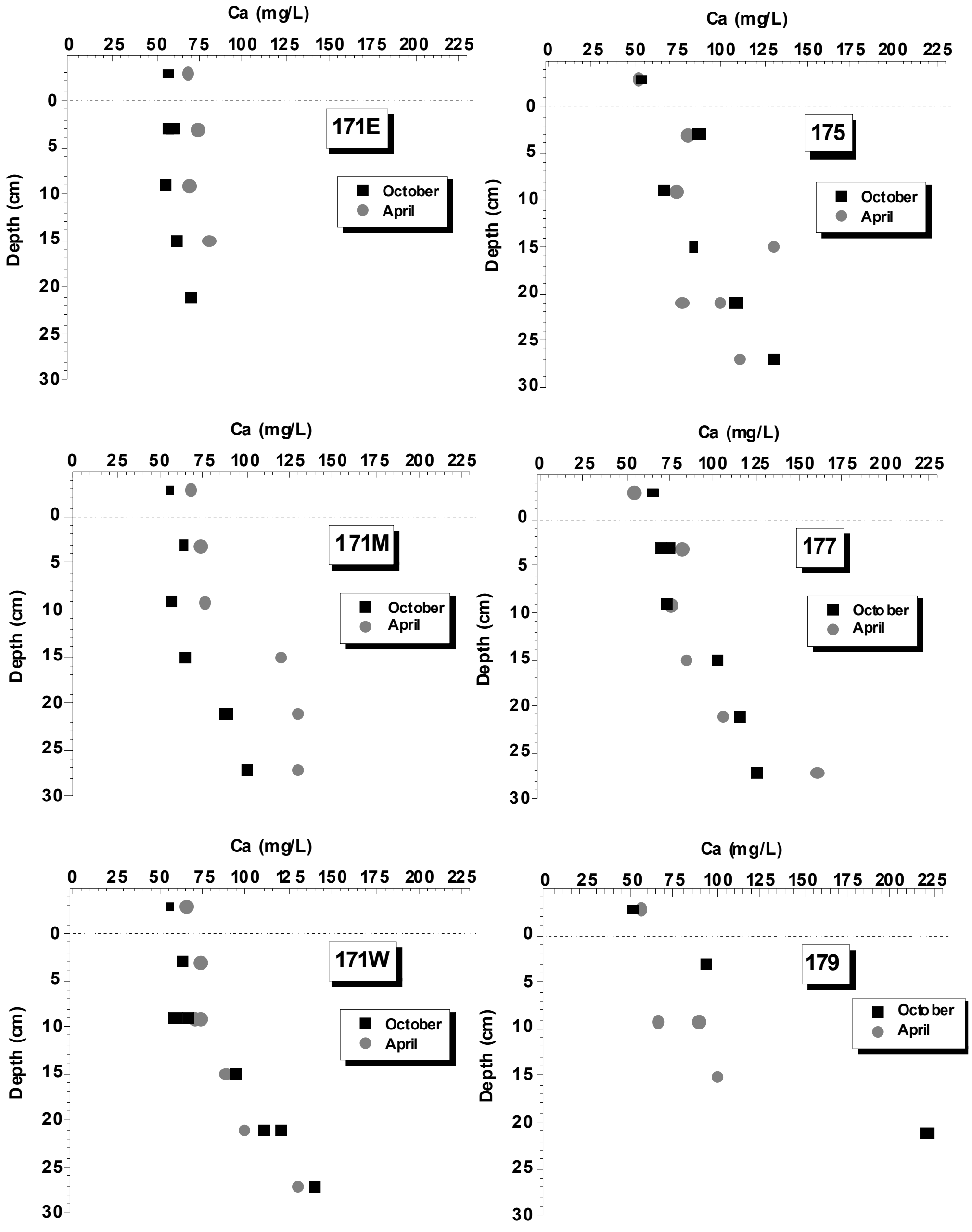

Figure A-3b. Dissolved calcium profiles for stations 171 to 179.

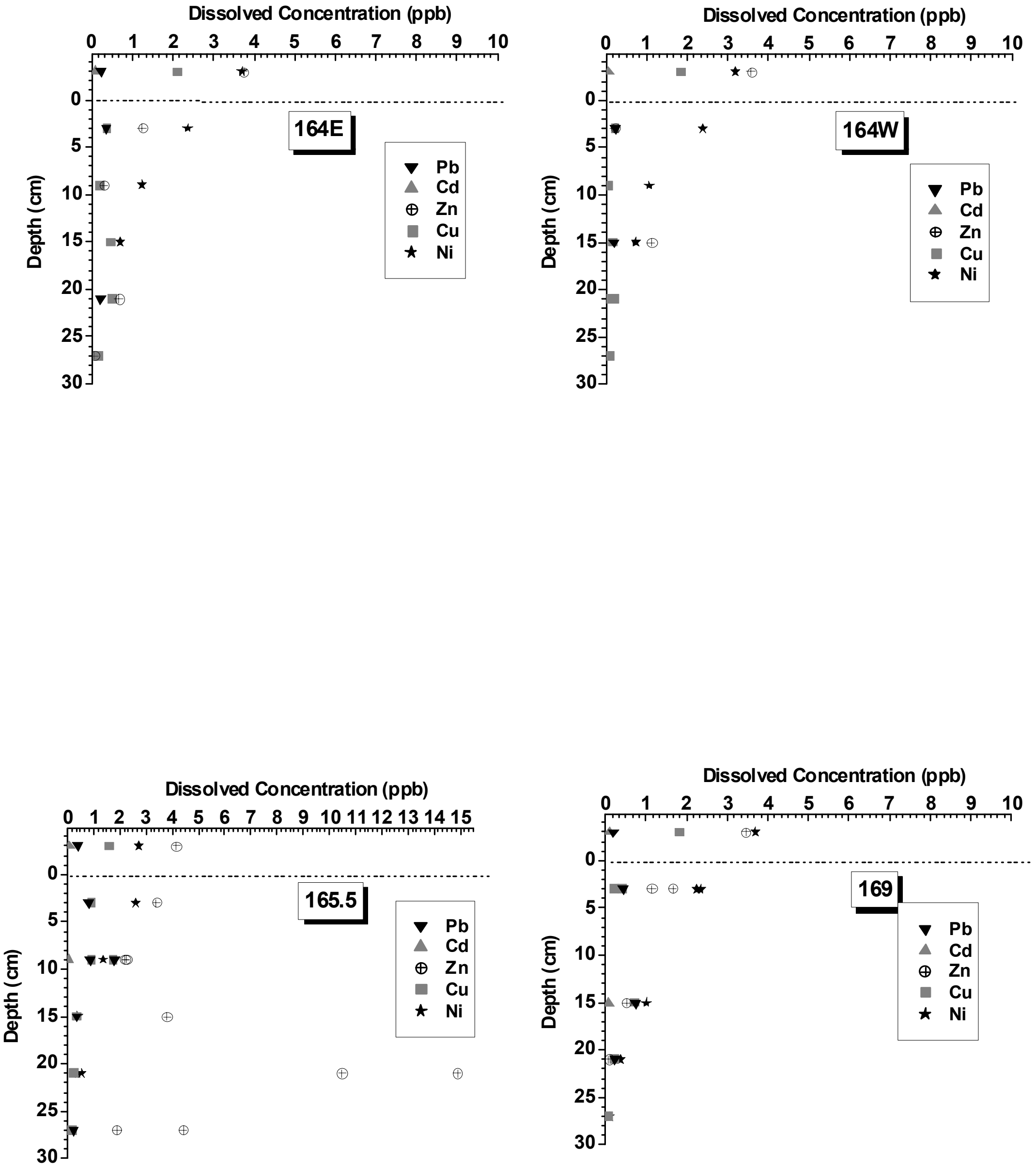

Figure A-4a. April dissolved metals data (Cd, Cu, Ni, Pb, Zn) for stations 164 to 169.

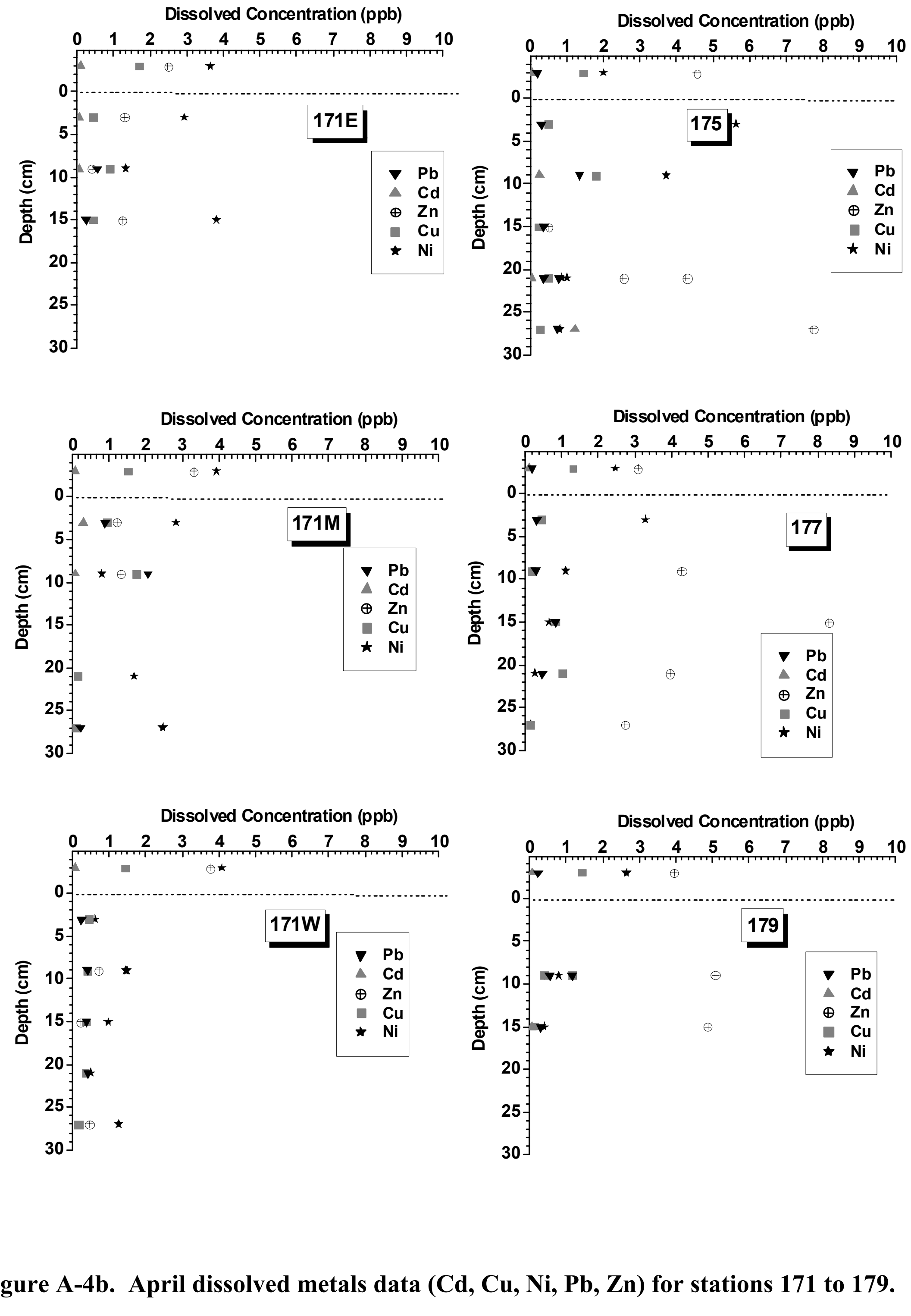

Figure A-4b. April dissolved metals data (Cd, Cu, Ni, Pb, Zn) for stations 171 to 179.

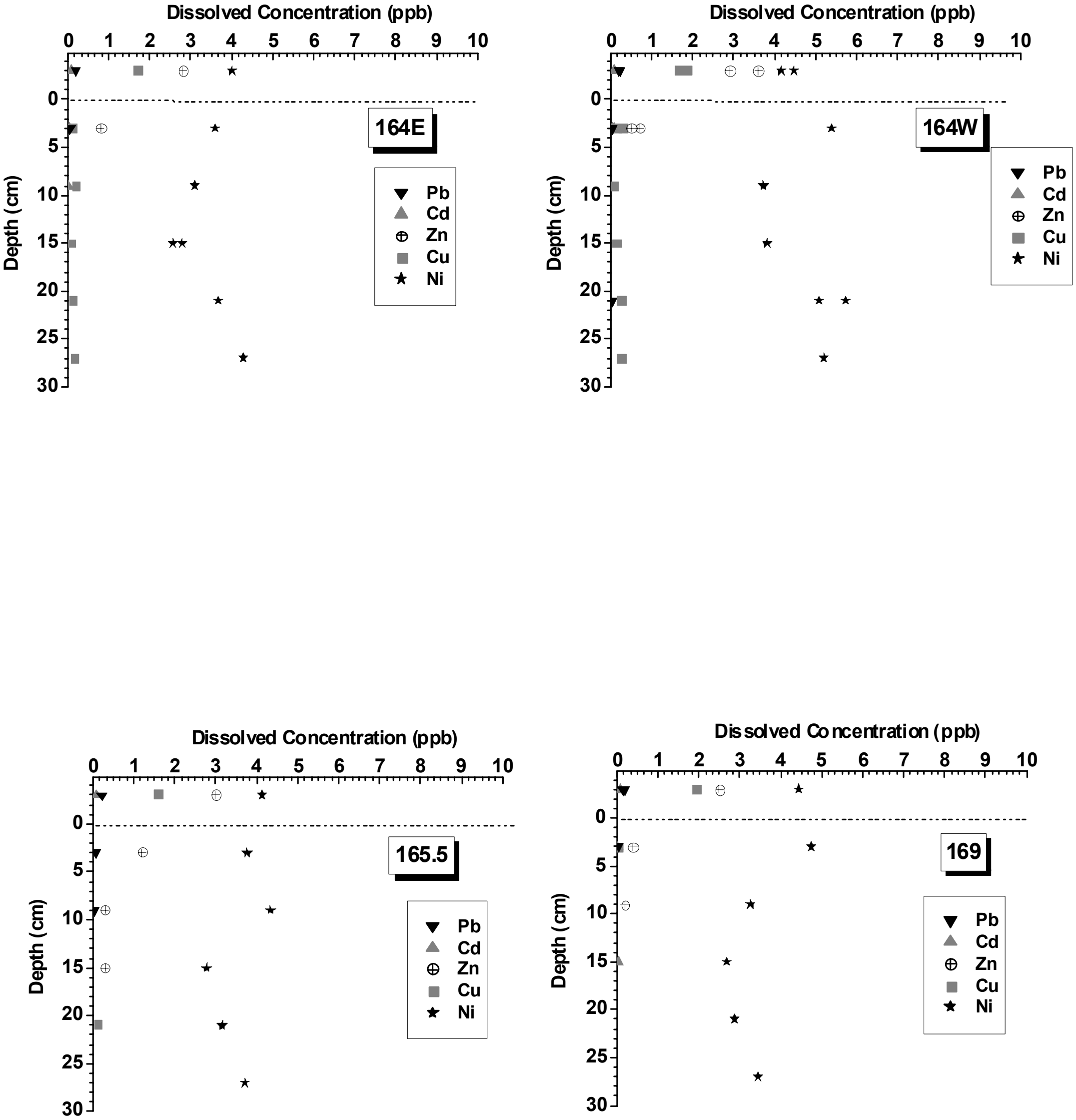

Figure A-4c. October dissolved metals data (Cd, Cu, Ni, Pb, Zn) for stations 164 to 169.

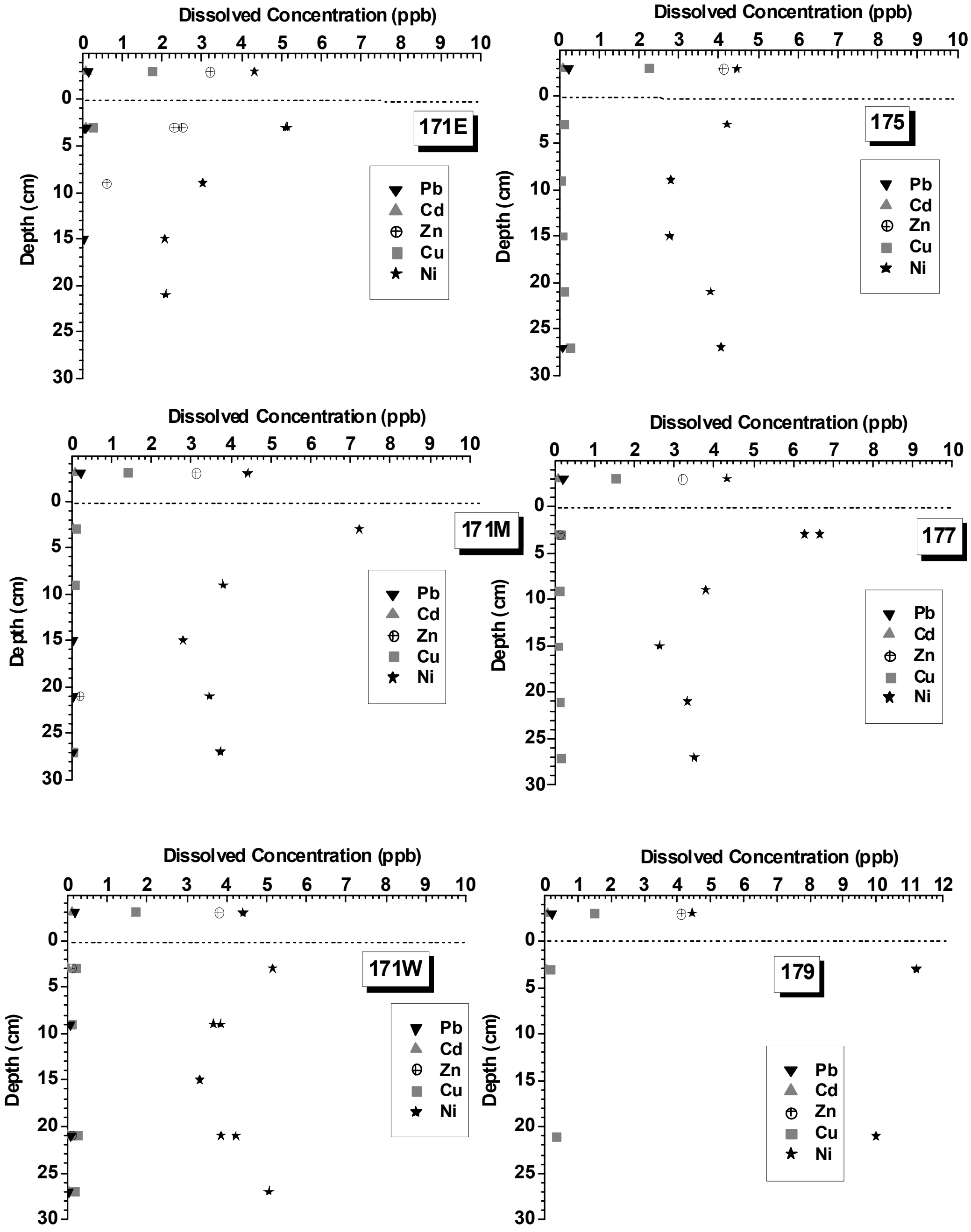

Figure A-4d. October dissolved metals data (Cd, Cu, Ni, Pb, Zn) for stations 171 to 179.

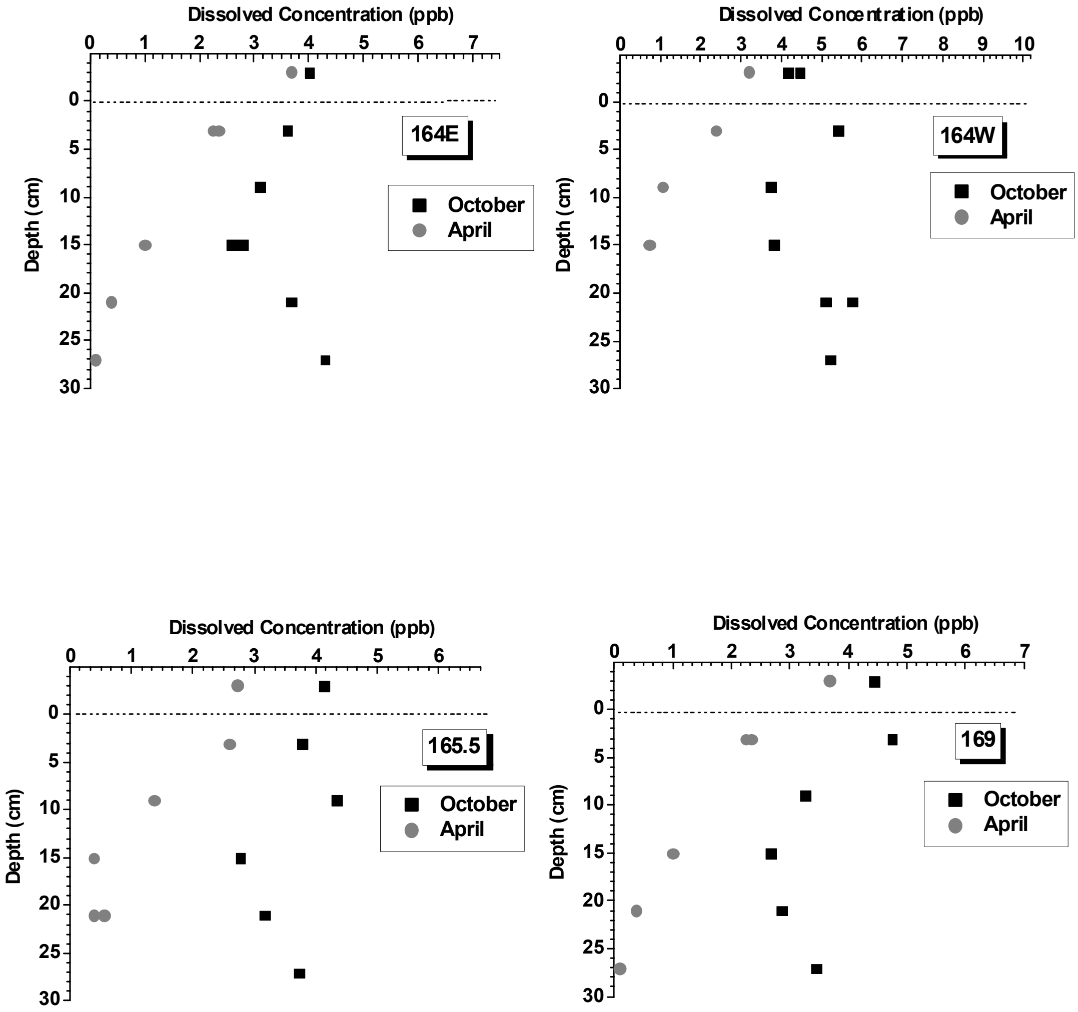

Figure A-4e. Dissolved nickel data for stations 164 to 169.

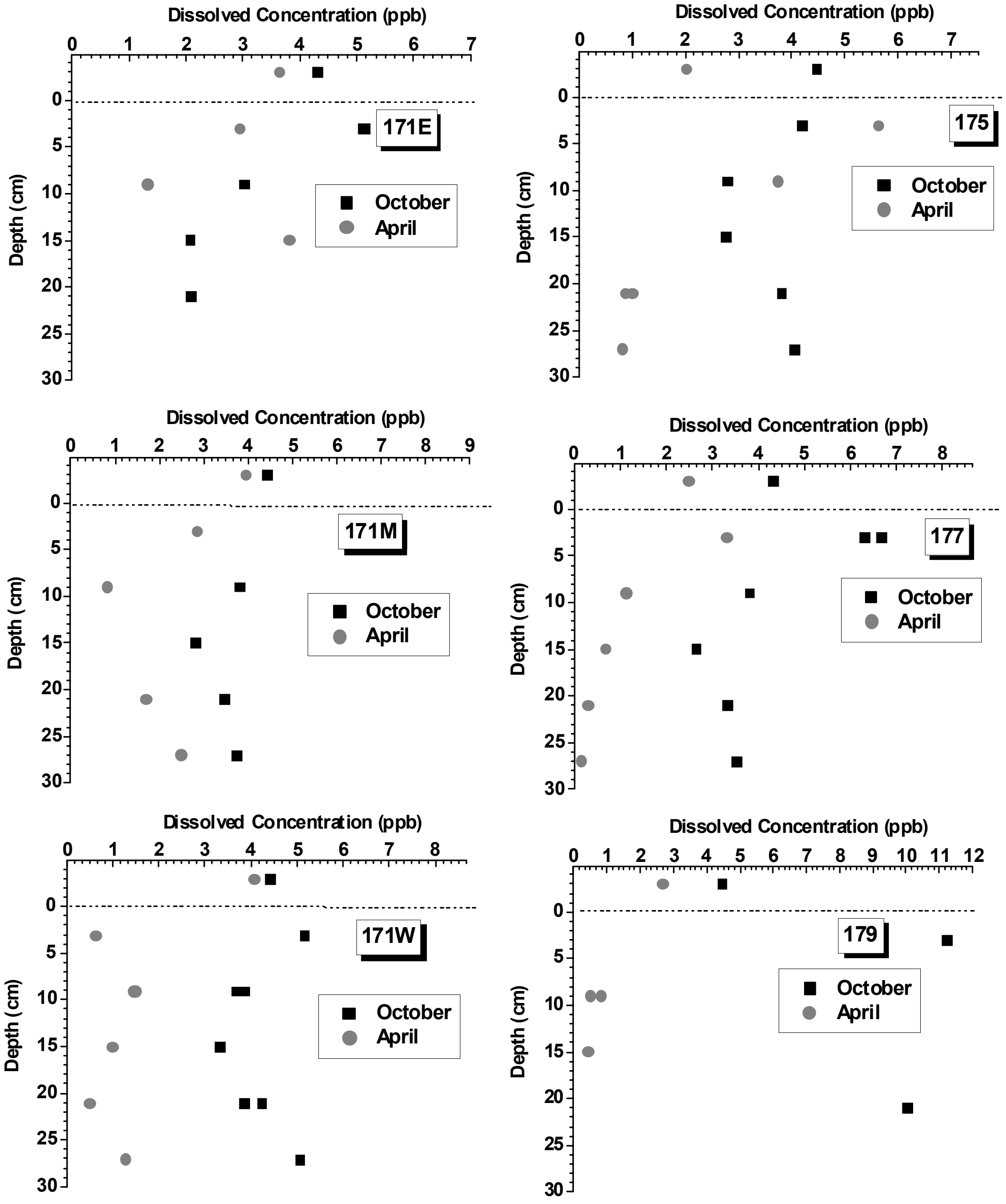

Figure A-4f. Dissolved nickel data for stations 171 to 179.

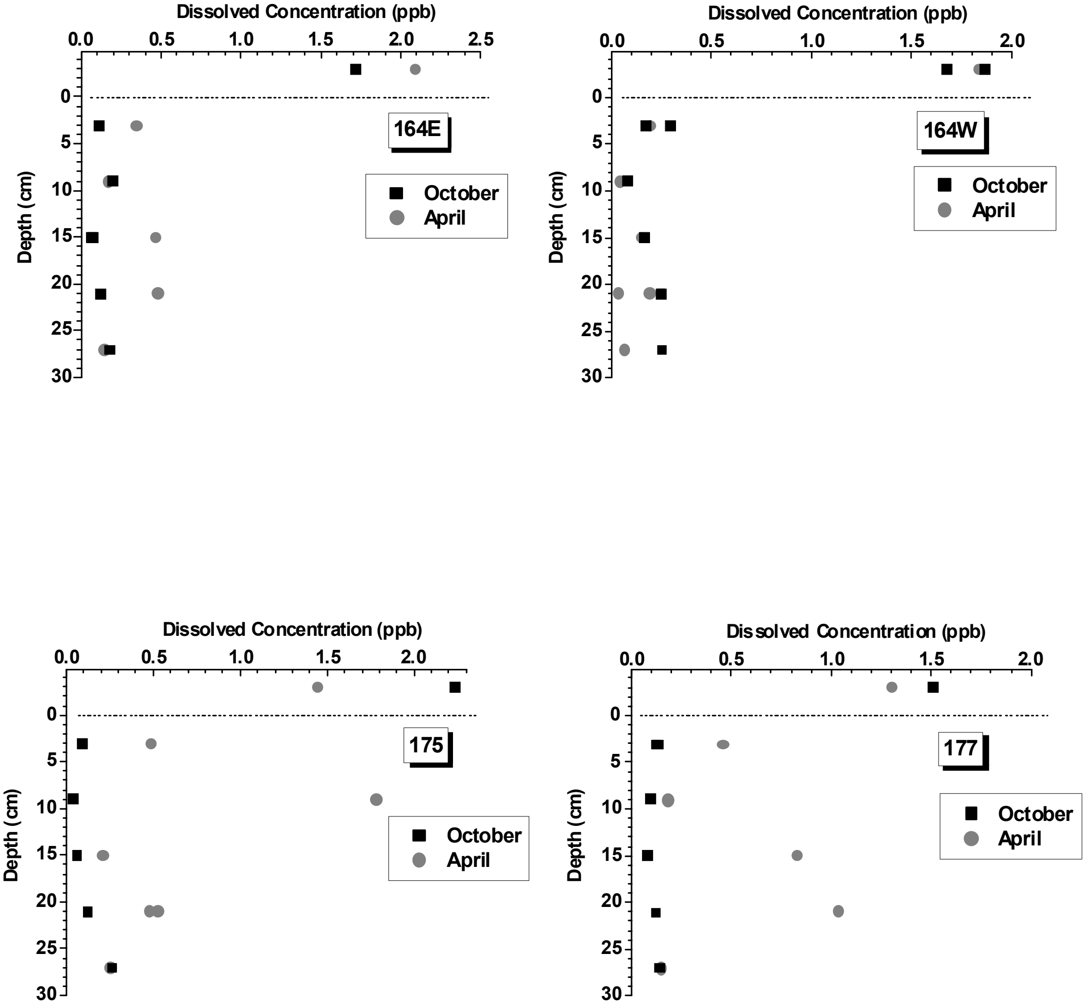

Figure A-4g. Dissolved copper data for stations 164E, 164W, 175, and 177.

Table A-5. Pore water dissolved iron data for stations 165.5 and 177.

Station	Date	Section	Average depth (cm)	Fe (mg/L)
165.5	April	43	3	1.13
		44	9	3.75
		45	15	9.25
		46	21	18.70
		47	27	19.50
165.5	October	84	3	1.00
		85	9	1.00
		86	15	4.25
		87	21	7.25
		88	27	20.50
177	April	34	3	0.81
		35	9	3.75
		36	15	9.25
		37	21	16.25
		38	27	18.25
177	October	55	3	0.69
		56	9	1.25
		57	15	7.50
		58	21	14.00
		59	27	17.75

Table A-6. October pore water dissolved ortho-phosphate and nitrate data for station 165.5.

SAMPLE ID	Date Analyzed	o-PO_4- P mg/L	Date Analyzed	NO_3- N mg/L	Section	River Mile	Depth
175A	10/26/00	0.28	10/27/00	1.80		165.5	-3
138A	10/26/00	1.26	10/27/00	<0.12	84	165.5	3
135A	10/26/00	1.41	10/27/00	<0.12	85	165.5	9
136A	10/26/00	1.28	10/27/00	<0.12	86	165.5	15
137A					86	165.5	15
147A	10/26/00	0.25	10/27/00	<0.12	87	165.5	21
139A	10/26/00	0.50	10/27/00	<0.12	88	165.5	27

Table A-7a. April SEM, AVS, and SEM/AVS data.

										AVS			
Depth (cm)	Ni(µmol/g)	Cu(µmol/g)	Zn(µmol/g)	Cd(µmol/g)	Pb(µmol/g)	Total(µmol/g)	Fe (mmol/g)	Mn (mmol/g)		Depth	(µmol/g)	Depth	SEM/AVS
164E													
3	0.27	0.39	1.90	0.0157	0.128	2.706	0.223	0.009		3	12.9	3	0.21
9	0.38	0.01	2.89	0.0244	0.214	3.517	0.248	0.010		9	46.0	9	0.08
9	0.39	0.01	2.87	0.0265	0.217	3.519	0.229	0.009		15	23.6	15	
21	1.05	0.02	6.40	0.0791	0.432	7.981	0.266	0.016		15	26.2	21	0.41
21	1.14	0.02	6.94	0.0882	0.500	8.689	0.294	0.016		21	19.3	27	0.15
27	0.75	0.02	4.39	0.0413	0.297	5.497	0.251	0.010		21	21.0		
										27	35.5		
164W										3	17.2	3	
9	0.31	0.06	3.53	0.0262	0.243	4.167	0.200	0.011		9	29.0	9	0.13
21	0.39	0.56	3.57	0.0272	0.231	4.785	0.270	0.010		9	36.5	15	
										21	26.2	21	0.18
										27	34.5	27	
165.5													
3	0.26	0.41	2.16	0.0152	0.153	2.997	0.200	0.008		3	11.2	3	0.27
9	0.33	0.43	2.49	0.0189	0.173	3.440	0.259	0.010		9	18.9	9	0.18
15	0.41	0.48	2.84	0.0232	0.193	3.943	0.231	0.008		15	31.8	15	0.12
21	0.51	0.48	2.71	0.0218	0.232	3.950	0.270	0.009		21	33.5	21	0.12
27	0.60	0.65	3.49	0.0331	0.283	5.055	0.257	0.008		27	19.5	27	0.26
169										3	29.2		
9	0.35	0.45	2.41	0.0199	0.174	3.395	0.231	0.009		3	22.1	3	
15	0.40	0.49	2.81	0.0224	0.203	3.920	0.245	0.009		9	14.7	9	0.23
21	0.35	0.47	2.42	0.0191	0.172	3.424	0.209	0.009		15	24.4	15	0.16
										21	56.4	21	0.06
										21	51.7	27	
										27	40.8		
171E													
3	0.22	0.20	0.63	0.0022	0.058	1.112	0.179	0.006		3	15.8	3	0.07
3	0.22	0.21	0.69	0.0021	0.061	1.180	0.179	0.006				9	0.12
9	0.24	0.22	0.68	0.0022	0.064	1.198	0.165	0.006		9	9.7	15	0.09
15	0.20	0.21	0.72	0.0037	0.066	1.198	0.221	0.006		15	13.3	21	
												27	
171M													
3	0.27	0.41	2.44	0.0182	0.163	3.295	0.214	0.009		3	12.9	3	0.26
9	0.66	0.82	5.83	0.0642	0.400	7.772	0.263	0.011		9	14.1	9	0.55
15	0.59	0.01	4.55	0.0482	0.327	5.528	0.199	0.009		15	24.8	15	0.22
21	0.83	0.04	6.97	0.0903	0.461	8.388	0.227	0.013		21	15.3	21	0.55
27	0.97	0.08	8.48	0.1139	0.544	10.186	0.282	0.016		27	27.6	27	0.43
										27	20.2		

Table A-7a. April SEM, AVS, and SEM/AVS data cont'd.

										AVS			
Depth (cm)	Ni(μmol/g)	Cu(μmol/g)	Zn(μmol/g)	Cd(μmol/g)	Pb(μmol/g)	Total(μmol/g)	Fe (mmol/g)	Mn (mmol/g)		Depth	(μmol/g)	Depth	SEM/AVS
171W													
3	0.243	0.378	2.212	0.018	0.155	3.005	0.190	0.009		3	9.2	3	0.27
9	0.290	0.445	2.679	0.021	0.170	3.605	0.217	0.009		3	13.3	9	0.25
15	0.416	0.518	3.235	0.028	0.202	4.399	0.251	0.008		9	13.9	15	0.18
21	0.503	0.598	3.565	0.035	0.231	4.931	0.237	0.008		9	15.4	21	0.24
										15	24.5	27	
										21	19.1		
										21	20.6		
										21	23.0		
										27	16.3		
175													
3	0.251	0.410	2.236	0.019	0.145	3.062	0.191	0.009		3	11.2	3	0.27
9	0.533	0.650	3.715	0.036	0.279	5.212	0.249	0.008		9	36.4	9	0.13
15	0.526	0.803	5.308	0.061	0.403	7.102	0.292	0.009		9	46.8	15	0.14
15	0.712	0.707	4.924	0.059	0.349	6.751	0.257	0.011		15	49.4	21	0.17
15	0.665	0.678	4.785	0.058	0.340	6.526	0.267	0.011				27	0.34
21	0.555	0.508	2.849	0.025	0.219	4.157	0.263	0.008		21	24.8		
27	0.656	0.819	5.677	0.067	0.393	7.612	0.303	0.012		27	21.8		
27	0.622	0.774	5.398	0.065	0.378	7.236	0.292	0.011					
177													
3	0.290	0.418	2.117	0.016	0.147	2.988	0.233	0.010		3	8.3	3	0.40
3	0.372	0.508	2.542	0.019	0.172	3.613	0.258	0.011		3	8.2	9	
15	0.281	0.370	2.061	0.016	0.144	2.872	0.191	0.007		9	25.5	15	0.14
21	0.588	0.605	3.140	0.026	0.230	4.588	0.301	0.010		15	20.6	21	0.23
27	0.690	0.728	4.063	0.043	0.308	5.831	0.279	0.009		21	19.7	27	0.29
										21	19.6		
										27	20.3		
179													
9	0.102	0.089	0.711	0.004	0.048	0.954	0.089	0.004		3	3.5	3	
9	0.081	0.064	0.541	0.003	0.035	0.725	0.086	0.004		9	6.3	9	0.13
												15	
												21	
												27	

Table A-7b. October SEM, AVS, and SEM/AVS data.

										AVS			
Depth (cm)	**Ni(µmol/g)**	**Cu(µmol/g)**	**Zn(µmol/g)**	**Cd (µmol/g)**	**Pb (µmol/g)**	**Total (µmol/g)**	**Fe (mmol/g)**	**Mn (mmol/g)**		**Depth**	**(µmol/g)**	**Depth**	**SEM/AVS**
165.5													
3	0.452	0.499	2.558	0.020	0.181	3.710	0.253	0.012		3	8.170	3	0.454
9	0.468	0.521	2.749	0.020	0.187	3.946	0.335	0.012		9	10.297	9	0.383
15	0.509	0.493	2.696	0.022	0.191	3.910	0.309	0.010		15	24.710	15	0.158
15	0.497	0.487	2.696	0.022	0.191	3.893	0.303	0.010		21	36.847	21	0.130
21	0.665	0.614	3.253	0.027	0.240	4.798	0.356	0.011		27	17.643	27	0.242
27	0.640	0.542	2.826	0.025	0.242	4.275	0.314	0.010					
169													
3	0.413	0.519	2.747	0.020	0.202	3.901	0.299	0.012		3	8.5	3	0.567
9	0.484	0.517	2.855	0.021	0.216	4.093	0.308	0.012		3	5.2	9	0.222
15	0.613	0.566	3.242	0.027	0.251	4.700	0.308	0.011		9	18.4	15	0.112
15	0.593	0.554	3.120	0.027	0.232	4.525	0.322	0.010		15	41.4	21	
27	0.903	0.775	4.749	0.054	0.384	6.865	0.325	0.013		27	19.0	27	0.361
171E													
3	0.346	0.295	1.240	0.006	0.104	1.991	0.263	0.010		3	5.5	3	0.385
9	0.304	0.241	0.742	0.003	0.067	1.357	0.261	0.009		3	4.8	9	0.156
15	0.337	0.241	0.680	0.003	0.063	1.324	0.292	0.015		9	8.7	15	0.181
15	0.345	0.245	0.718	0.003	0.066	1.376	0.292	0.015		15	7.5	21	0.324
21	0.344	0.276	0.763	0.003	0.070	1.456	0.238	0.011		21	4.5	27	
175													
3	0.623	0.801	4.740	0.049	0.335	6.548	0.389	0.015		3	18.7	3	0.359
3	0.646	0.874	4.952	0.053	0.335	6.860	0.414	0.015		9	39.0	9	
15	1.171	1.082	6.232	0.074	0.450	9.009	0.457	0.019		9	24.6	15	0.879
21	0.768	0.903	5.643	0.066	0.416	7.796	0.389	0.013		15	10.2	21	0.375
27	0.776	0.717	4.180	0.047	0.321	6.042	0.364	0.009		21	20.4	27	0.326
										21	21.2		
										27	18.5		
177													
3	0.429	0.487	2.426	0.019	0.170	3.530	0.312	0.012		3	11.6	3	0.304
9	0.382	0.436	2.305	0.017	0.164	3.304	0.282	0.011		9	13.8	9	0.239
15	0.433	0.461	2.481	0.018	0.170	3.562	0.303	0.011		15	16.8	15	0.212
21	0.475	0.467	2.571	0.022	0.190	3.725	0.288	0.009		21	16.8	21	0.239
21	0.579	0.540	2.954	0.025	0.207	4.306	0.301	0.010		27	14.6	27	0.335
27	0.705	0.651	3.269	0.029	0.250	4.903	0.333	0.010					
179													
3	0.162	0.186	1.076	0.007	0.080	1.511	0.122	0.006		3	2.4	3	0.640
3	0.159	0.186	1.076	0.007	0.078	1.505	0.130	0.006		9	4.3	9	0.248
9	0.120	0.104	0.784	0.005	0.061	1.074	0.107	0.005		21	3.1	15	0.506
21	0.170	0.154	1.148	0.007	0.075	1.555	0.146	0.007				21	
												27	

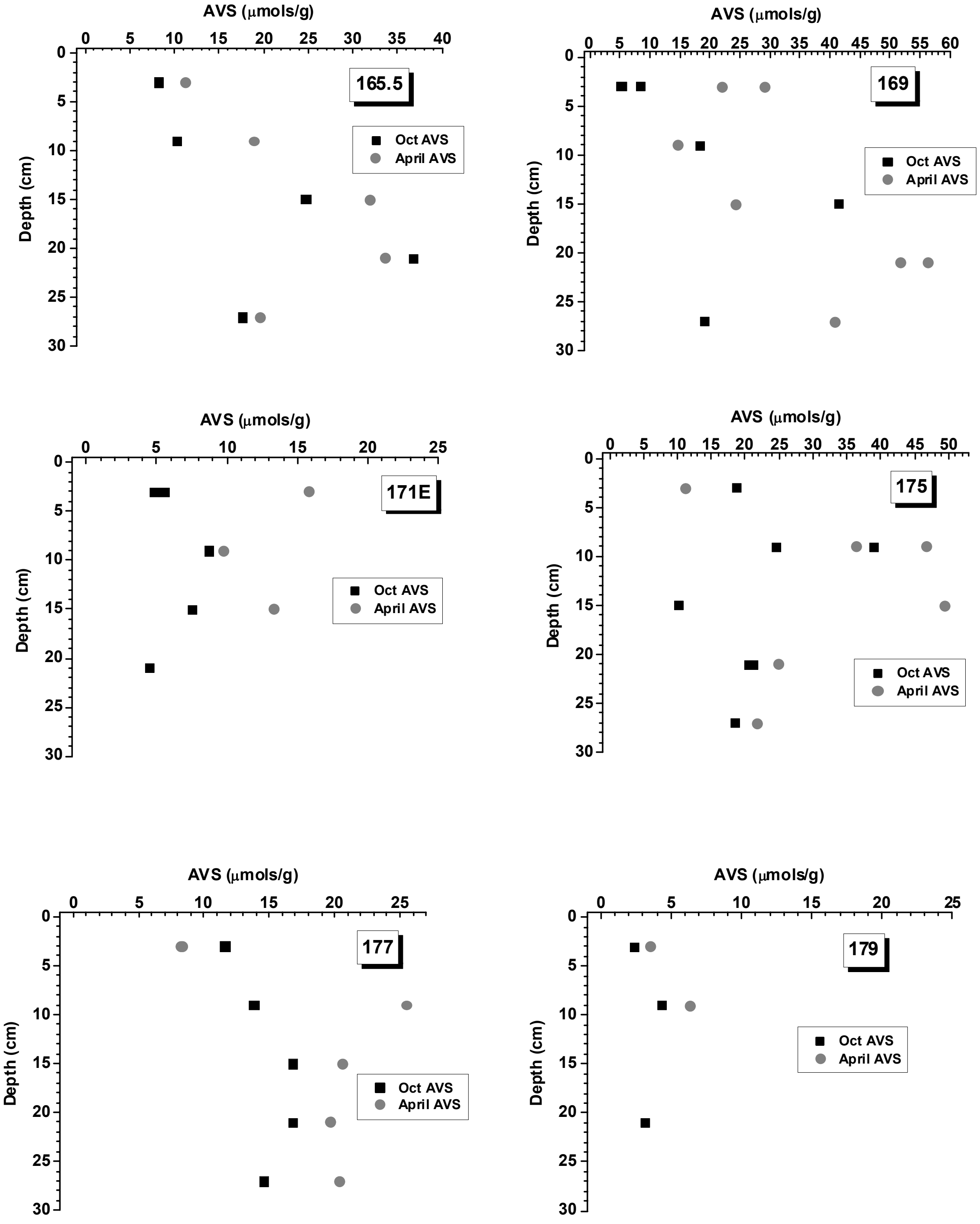

Figure A-5a. April and October Acid Volatile Sulfide profiles.

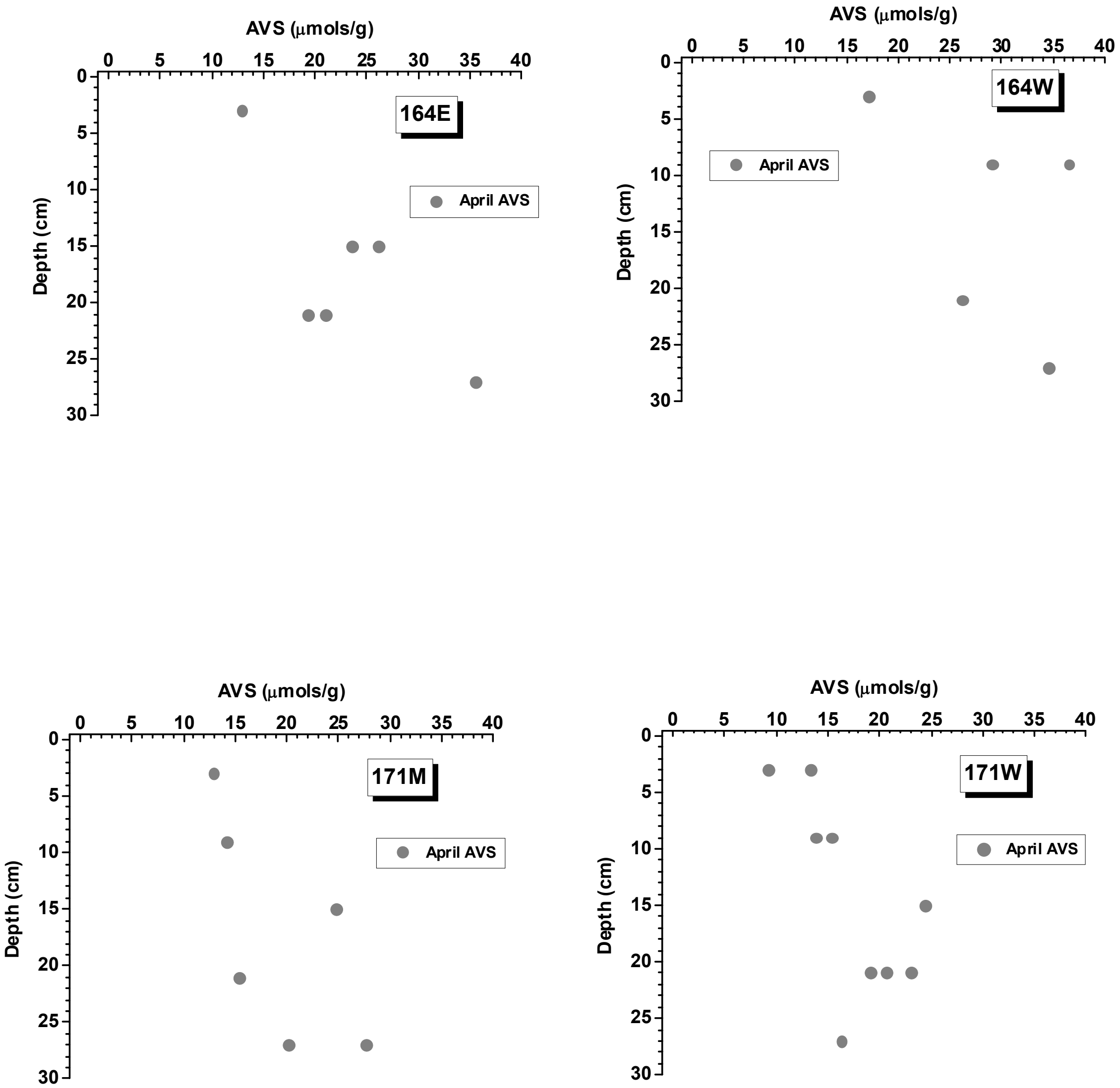

Figure A-5b. April Acid Volatile Sulfide profiles.

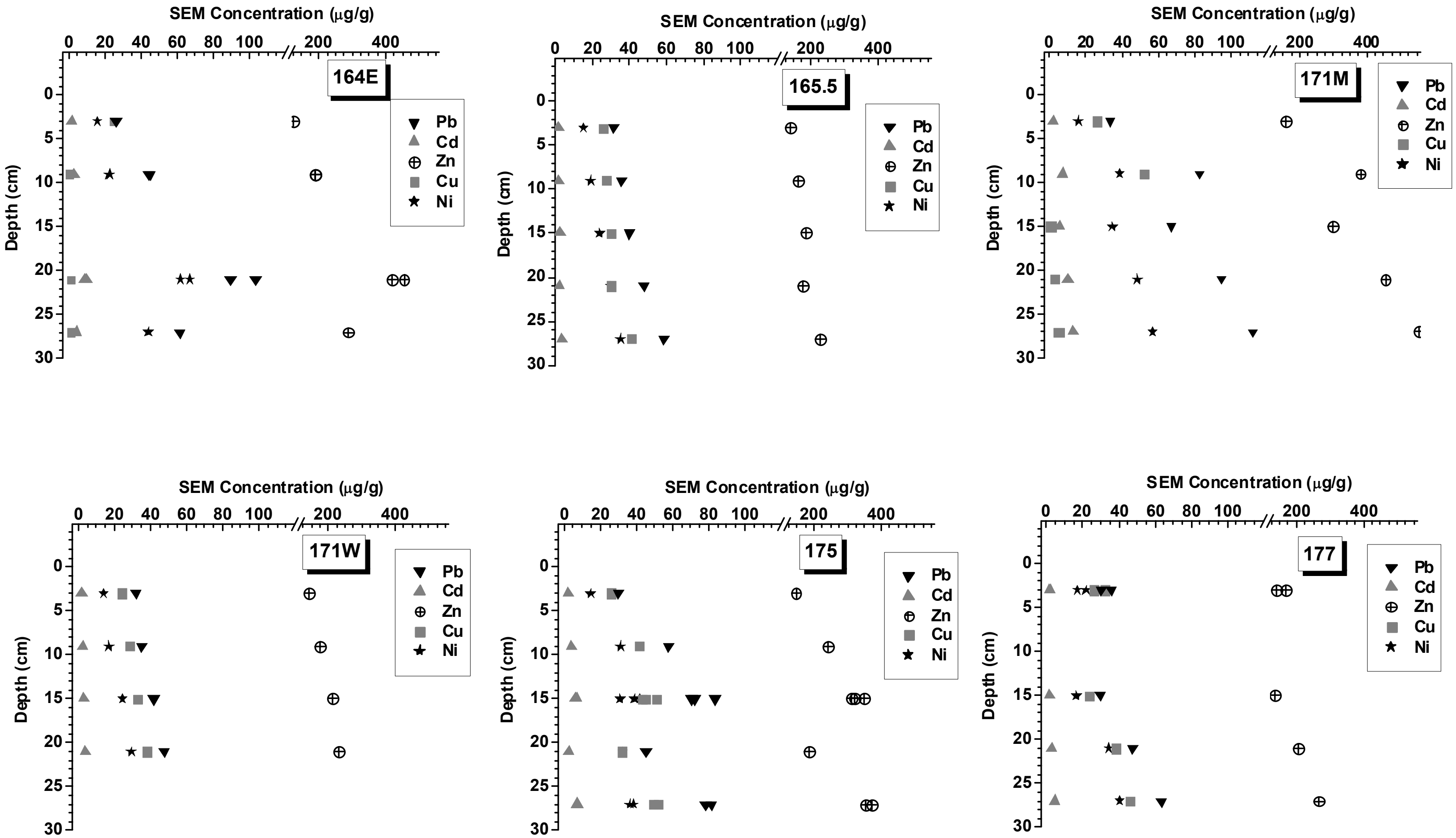

Figure A-6. April SEM profiles.

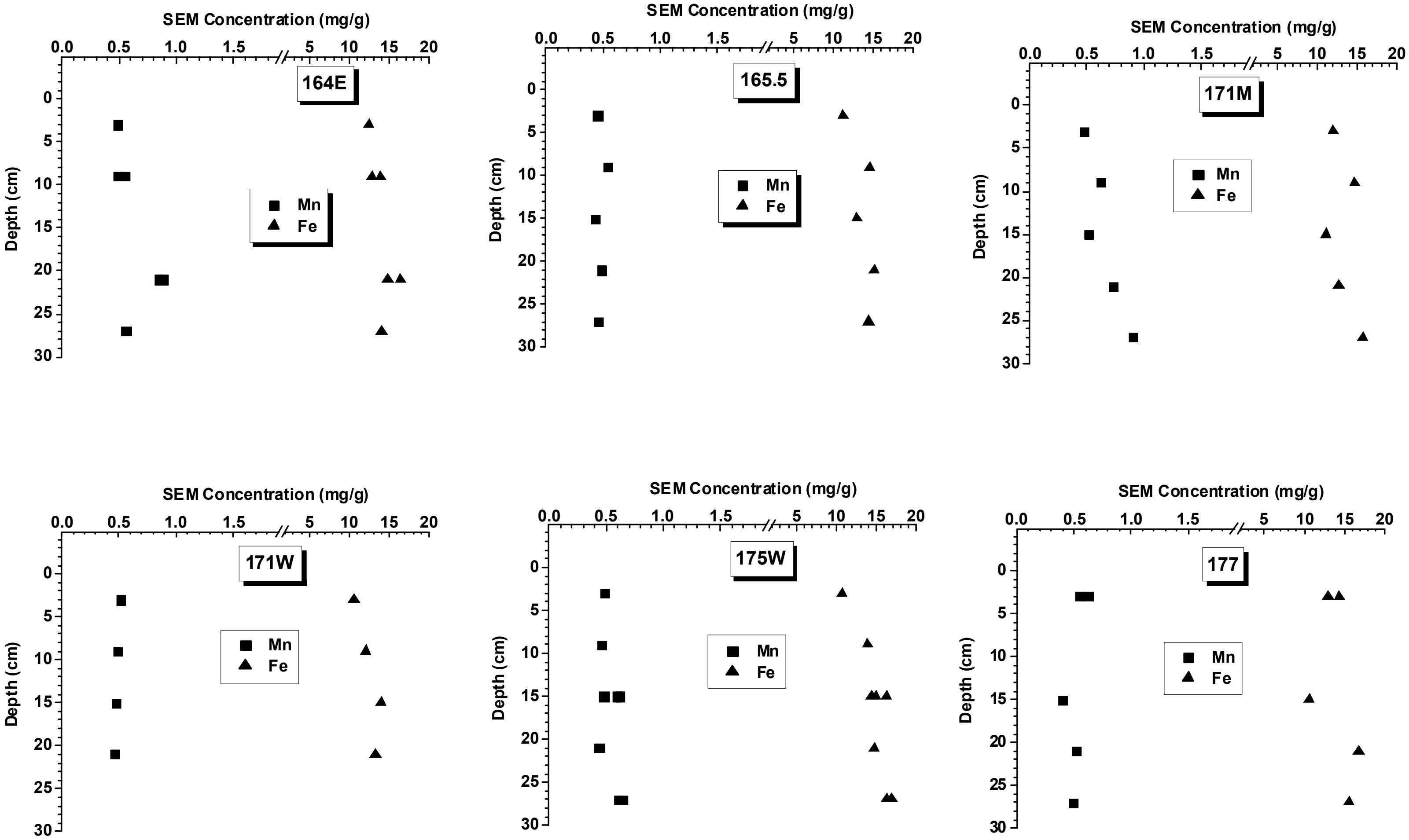

Figure A-7. April simultaneously extracted iron and manganese profiles.

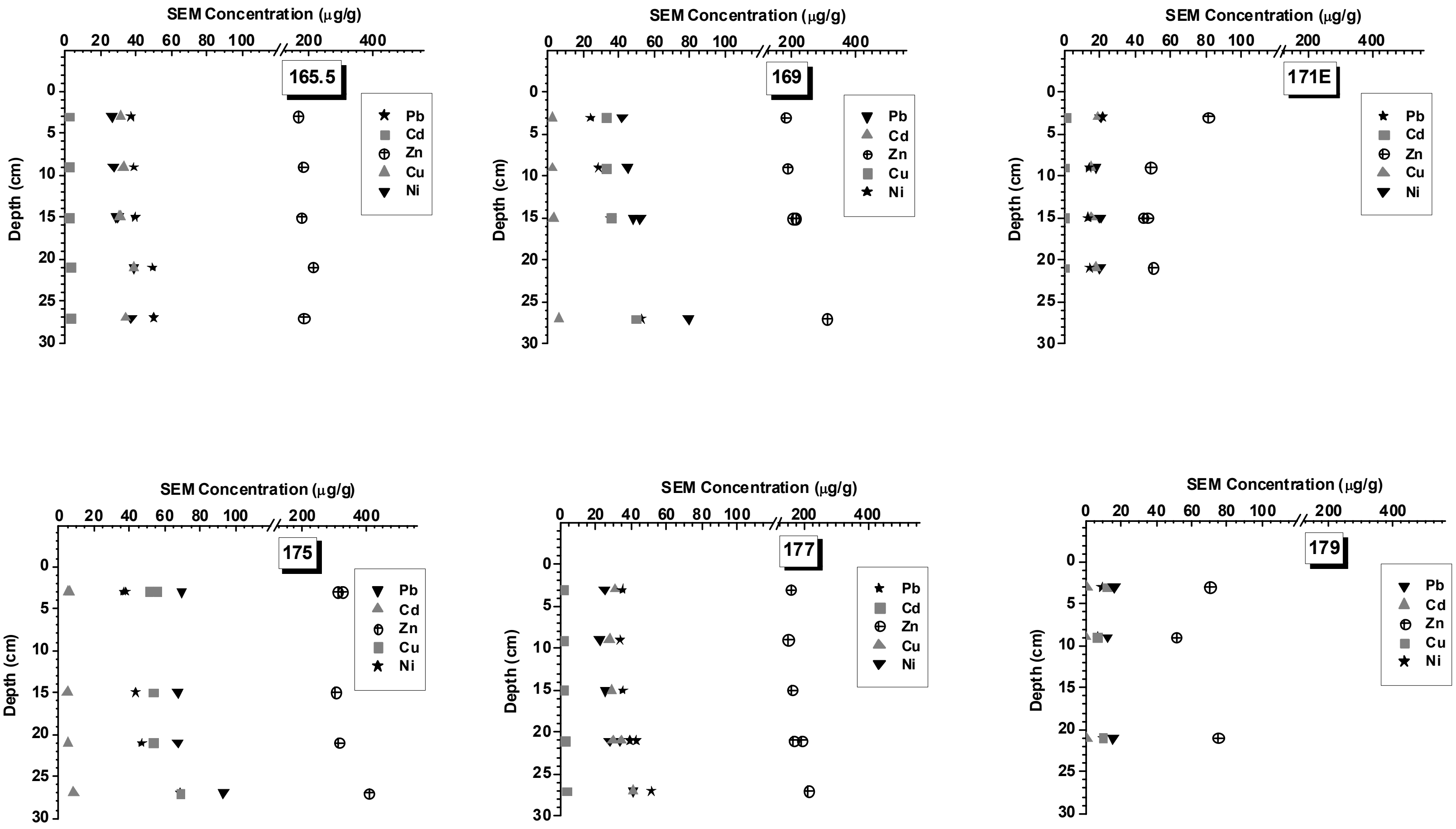

Figure A-8. October SEM profiles.

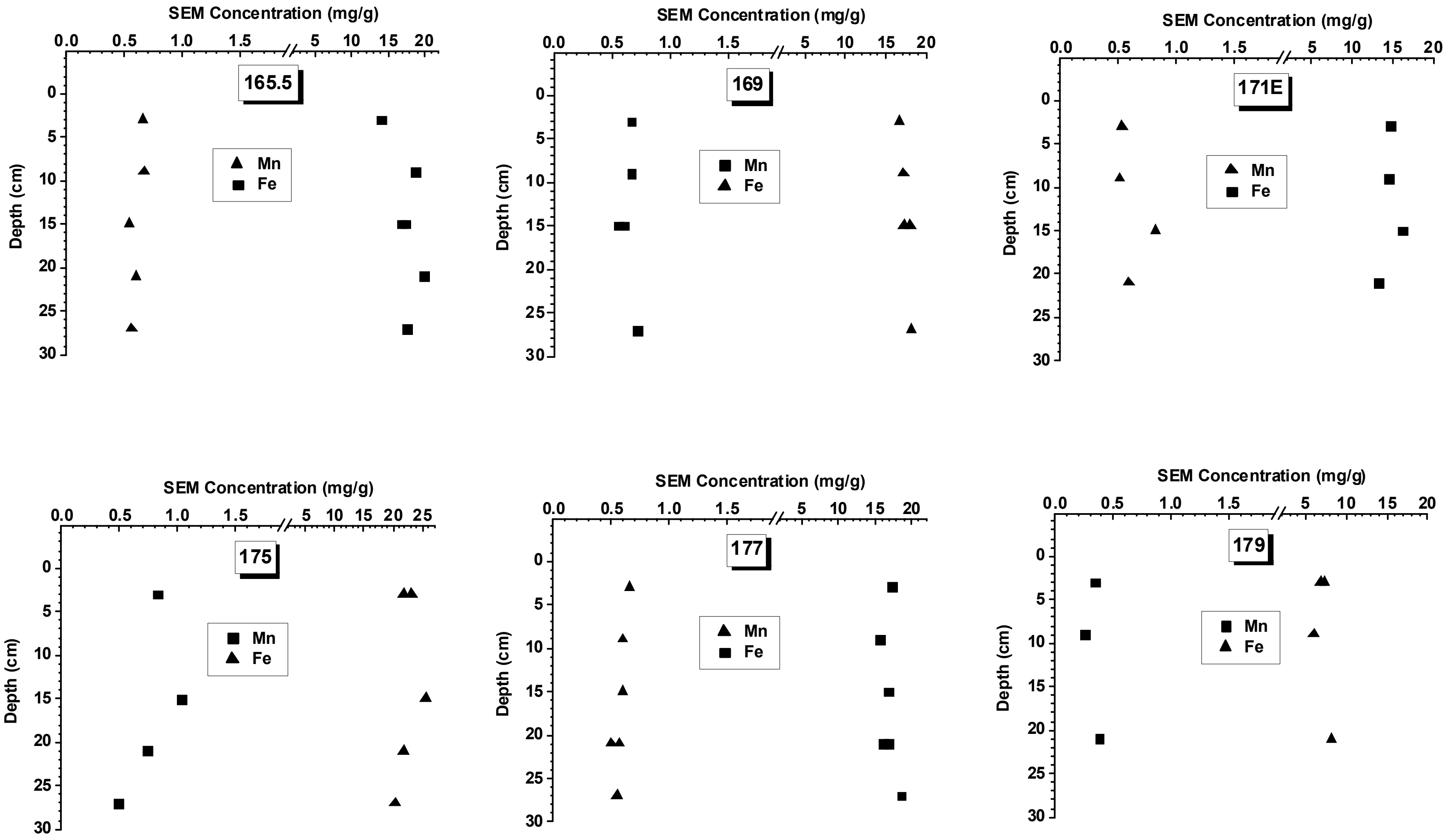

Figure A-9. October simultaneously extracted iron and manganese profiles.

Table A-8. Total recoverable metals data for April.

Depth (cm)	Ni (μg/g)[a]	ISGS[b]	Cu (μg/g)	ISGS	Zn (μg/g)	ISGS	Cd (μg/g)	ISGS	Pb (μg/g)	ISGS
164E										
3	42.4	46.0	50.6	69.0	250.2	249.0	2.8	<5	42.0	30.0
9	44.8		45.1		227.7		3.0		38.0	
15	69.4		69.1		393.3		7.5		71.0	
21	82.0		69.6		425.0		9.2		73.0	
27	60.4	67.0	41.6	70.0	292.7	323.0	3.9	<5	52.3	45.0
164W										
3	39.5	37.0	47.9	49.0	251.5	231.0	2.8	<5	44.4	30.0
9	39.0		49.0		261.0		2.9		41.0	
15	36.2		45.7		229.3		2.6		38.0	
21	39.8		48.4		250.6		3.0		42.0	
27	39.0	42.0	47.2	49.0	239.7	267.0	3.2	<5	40.0	30.0
165.5										
3	39.8	38.0	46.2	42.0	239.6	222.0	2.6	<5	43.0	40.0
9	34.6		36.9		195.4		2.4		34.4	
15	40.1		44.6		218.4		2.9		38.0	
21	43.3		43.3		202.7		2.8		41.0	
27	55.3	54.0	59.8	69.0	273.9	281.0	4.5	<5	51.0	40.0
169										
3	41.4	43.0	48.9	50.0	228.3	235.0	2.9	<5	42.0	30.0
9	35.2		43.7		200.7		2.4		37.0	
15	40.7		44.3		214.3		2.7		39.0	
21	51.8		48.9		237.2		3.4		45.0	
27	64.2	65.0	59.2	55.0	330.9	336.0	6.2	6.0	68.0	55.0

[a] analyzed by WMRC

[b] analyzed by the State Geological Survey

Table A-8. Total recoverable metals data for April cont'd.

Depth (cm)	Ni (µg/g)	ISGS	Cu (µg/g)	ISGS	Zn (µg/g)	ISGS	Cd (µg/g)	ISGS	Pb (µg/g)	ISGS
171E										
3	18.0	17.0	15.8	16.0	50.9	62.0	0.4	<5	11.0	<20
9	20.3		18.4		53.8		0.3		12.0	
15	21.8	28.0	19.5	22.0	55.7	84.0	0.2	<5	13.0	<20
171M										
3	36.3	33.0	46.3	39.0	234.6	215.0	3.1	5.0	38.0	30.0
9	61.6		71.4		372.4		6.4		74.0	
15	58.0		67.0		379.6		7.8		74.0	
21	64.7		79.6		455.0		9.9		86.0	
27	78.0	75.0	79.8	73.0	506.0	480.0	11.7	8.0	90.0	80.0
171W										
3	28.6	31.0	37.1	34.0	190.3	191.0	2.9		32.0	20.0
9	33.0		41.9		214.1		2.9		35.0	
15	42.8		51.2		261.6		4.1		44.0	
21	49.1		59.4		285.0		4.8		48.0	
27	60.0	61.0	65.1	65.0	361.2	365.0	6.4	5.0	64.0	60.0
175										
3	35.6	32.0	44.6	41.0	233.5	221.0	3.1	<5	43.5	<20
9	56.4		59.4		313.9		5.2		65.0	
15	65.7		72.8		430.0		9.0		90.1	
21	59.9		77.0		536.0		10.2		97.2	
27	52.7	51.0	68.2	63.0	414.0	423.0	8.0	7.0	79.2	80.0
177										
3	32.0	30.0	34.4	34.0	176.0	180.0	2.1	<5	32.4	<20
9	35.9		38.7		197.4		2.4		37.4	
15	35.0		40.2		191.0		2.9		33.0	
21	44.4		46.3		217.6		3.0		38.0	
27	58.8	61.0	57.7	58.0	323.9	331.0	5.9	5.0	69.7	60.0
179										
3	8.2	11.0	3.9	9.0	32.1	62.0	0.2	<5	6.5	<20
9	12.5		9.1		59.9		0.6		12.6	
15	24.7	28.0	27.4	29.0	134.4	165.0	1.6	<5	23.0	<20

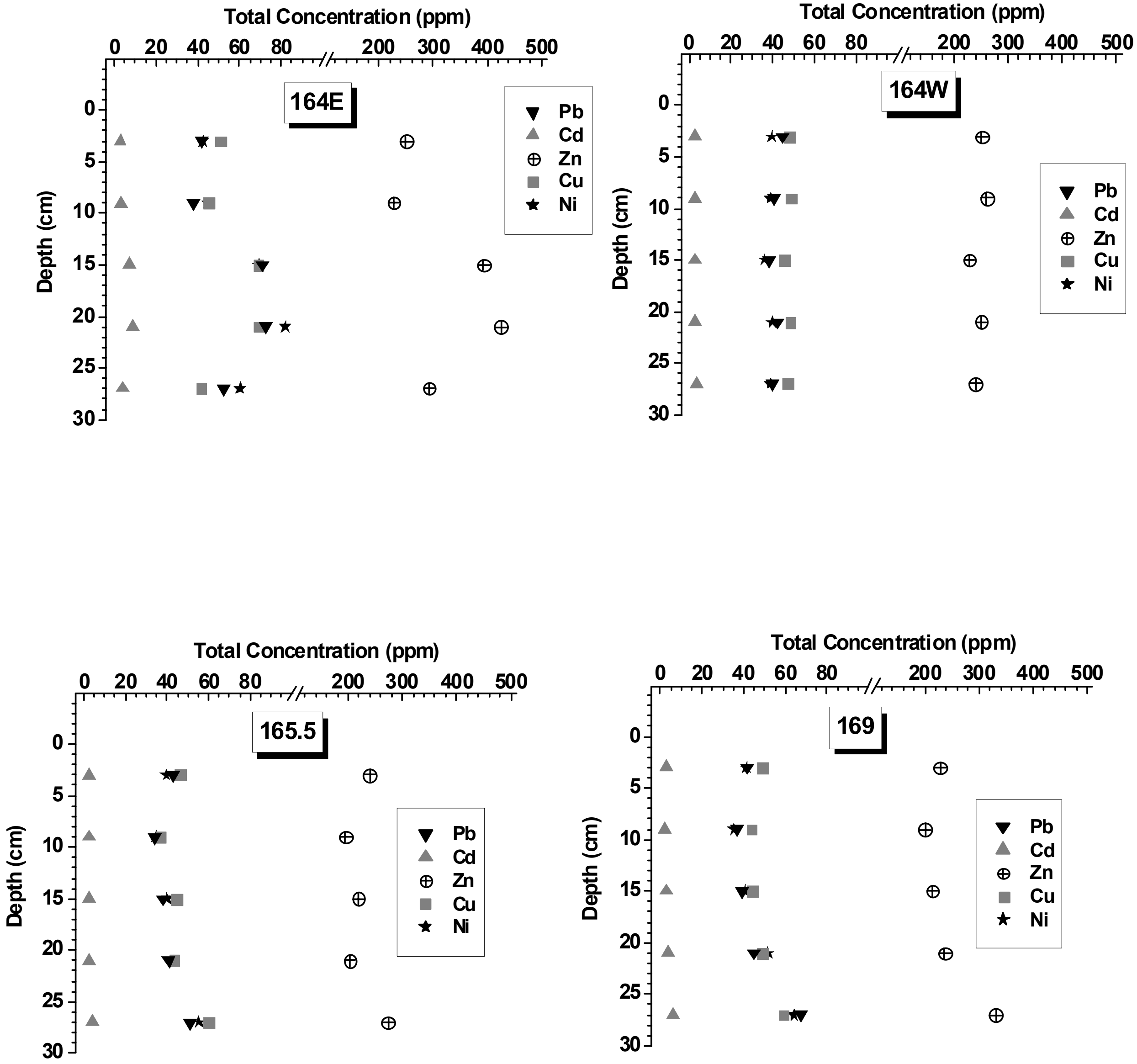

Figure A-10a. April total recoverable metals data for stations 164 to 169.

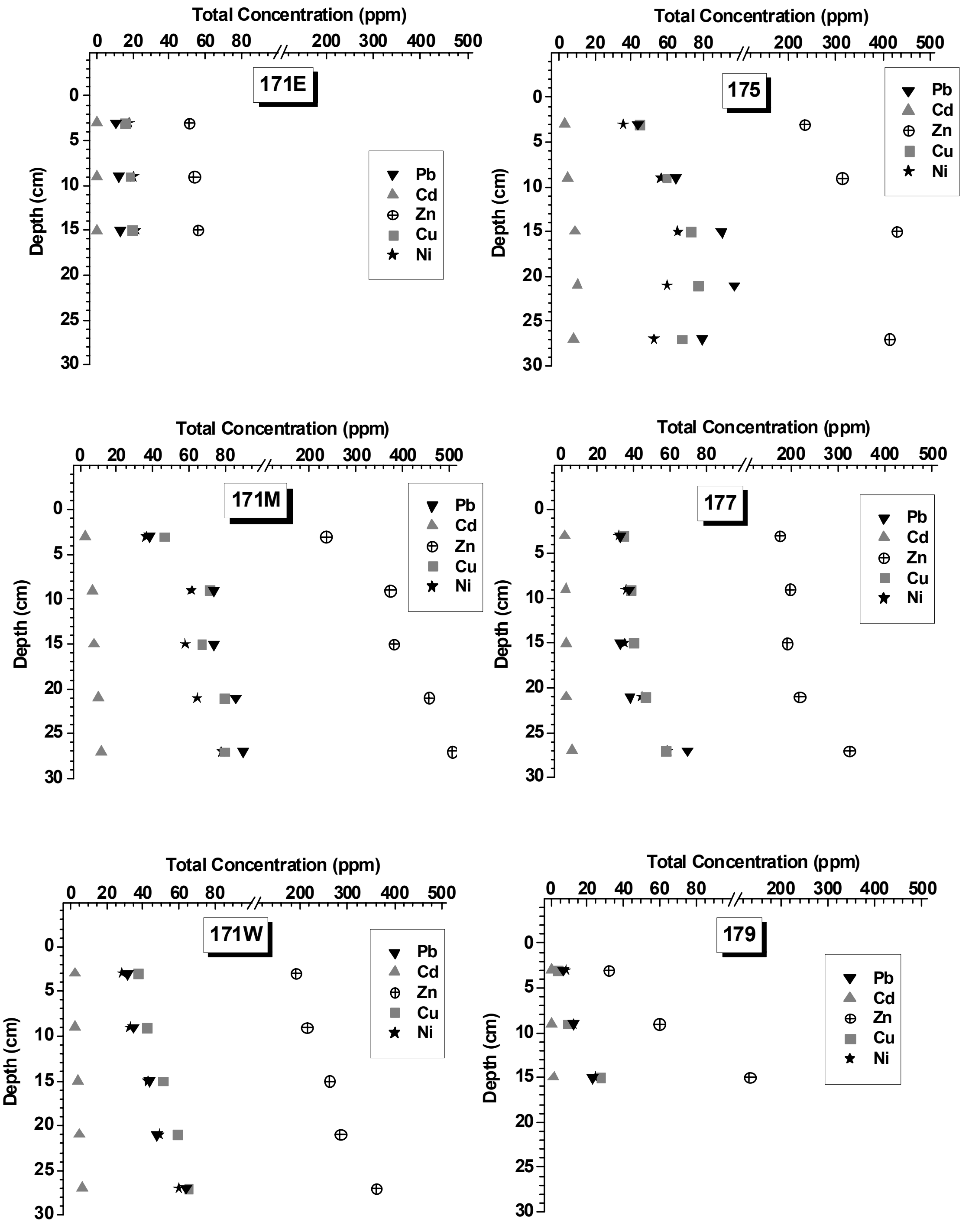

Figure A-10b. April total recoverable metals data for stations 171 to 179.

Table A-9. Illinois State Geological Survey chemical analysis results.

	Lab #	R21955	R21956	R21957	R21958	R21959	R21960	R21961	R21962	R21963	R21964	R21965	R21966	R21967	R21968	R21969	R21970	R21971	R21972	R21973	R21975
	ISWS ID	114	162	130	134	154	122	50	58	70	46	62	74	2	18	126	166	78	102	106	30
	River Mile	179	179	177	177	175	175	171E	171E	171M	171M	171W	171W	169	169	165	165	164E	164E	164W	164W
Depth Interval (cm)		0-6	12-18	0-6	24-30	0-6	24-30	0-6	12-18	0-6	24-30	0-6	24-30	0-6	24-30	0-6	24-30	0-6	24-30	0-6	24-30
Tot. C	%	2.3	3.62	3.67	3.42	3.78	3.4	1.92	2.39	3.9	3.8	3.75	3.7	4.13	3.71	3.78	3.49	3.79	4.74	3.95	3.73
Inc. C	%	1.55	1.84	1.7	1.23	1.57	0.83	0.95	0.79	1.55	1.12	1.76	0.9	1.4	1.12	1.25	1.23	1.32	1.3	1.24	1.31
Org. C	%	0.75	1.78	1.97	2.19	2.21	2.57	0.97	1.6	2.35	2.68	1.99	2.8	2.73	2.59	2.53	2.26	2.47	3.44	2.71	2.42
Total Recoverable Metal Concentrations																					
Si	mg/kg	182	170	200	216	204	176	139	231	226	267	323	252	120	179	251	248	251	302	280	319
Al	%	0.54	1.71	2.48	2.87	2.34	2.95	1.09	2.55	2.62	2.65	1.94	2.59	2.8	3.18	3.15	3.55	3.3	3.12	2.53	2.88
Fe	%	0.90	1.96	2.55	2.95	2.59	3.19	1.22	2.42	2.62	3.00	2.30	2.88	2.90	3.24	2.96	3.15	3.20	3.43	2.82	2.94
Ca	%	3.18	4.01	4.04	2.96	3.77	2.18	2.33	1.87	3.71	2.82	4.15	3.09	3.69	3.02	3.81	3.06	3.48	3.89	3.48	3.4
Mg	%	1.34	1.87	1.8	1.5	1.67	1.25	0.89	1.15	1.68	1.39	1.78	1.55	1.54	1.45	1.67	1.6	1.56	1.31	1.55	1.51
K	%	0.14	0.32	0.53	0.55	0.47	0.54	0.19	0.46	0.58	0.51	0.41	0.47	0.51	0.58	0.69	0.72	0.66	0.57	0.51	0.55
Na	%	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Ti	mg/kg	179	274	341	342	322	315	199	456	355	374	305	352	343	358	398	451	377	339	298	346
Mn	mg/kg	279	535	679	682	712	604	324	453	700	891	692	682	624	763	715	634	691	661	678	669
S	mg/kg	330	850	810	1415	980	1050	360	510	950	1420	950	1320	1610	1780	860	1170	1200	2450	1080	1430
As	mg/kg	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75
B	mg/kg	12	19	23	22	21	22	9	28	21	24	19	19	16	22	33	35	29	23	22	24
Be	mg/kg	0.4	0.8	1	1.2	1	1.2	0.6	0.9	1.1	1.2	1	1.2	1.2	1.3	1.2	1.3	1.4	1.5	1.2	1.2
Ba	mg/kg	43	109	140	184	145	189	72	154	154	203	128	177	166	205	179	198	184	201	152	166
Cd	mg/kg	<5	<5	<5	5	<5	7	<5	<5	5	8		5	<5	6	<5	<5	<5	<5	<5	<5
Co	mg/kg	3	8	11	13	13	10	14	7	11	15	10	14	12	15	13	14	14	16	12	13
Cr	mg/kg	7	26	32	65	36	71	12	21	37	87	31	65	53	68	43	58	44	52	37	44
Cu	mg/kg	9	29	34	58	41	63	16	22	39	73	34	65	50	55	42	69	69	70	49	49
La	mg/kg	9	17	21	23	20	26	13	24	21	23	20	24	21	24	24	24	21	23	22	22
Li	mg/kg	5	18	27	31	25	31	13	26	28	27	22	27	30	33	32	37	36	36	29	31
Mo	mg/kg	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Ni	mg/kg	11	28	30	61	32	51	17	28	33	75	31	61	43	65	38	54	46	67	37	42
Pb	mg/kg	<20	<20	<20	60	<20	80	<20	<20	30	80	20	60	30	55	40	40	30	45	30	30
Sb	mg/kg	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Sc	mg/kg	1	4	5	6	5	6	2	5	5	6	4	5	6	7	6	7	6	6	5	6
Se	mg/kg	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Sr	mg/kg	28	47	62	56	62	46	31	33	62	60	60	57	63	60	68	60	68	57	62	61
Tl	mg/kg	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
V	mg/kg	6	17	24	24	21	27	11	29	24	24	15	23	22	28	27	35	30	27	20	25
Zn	mg/kg	62	165	180	331	221	423	62	84	215	480	191	365	235	336	222	281	249	323	231	267

Table A- 10a. April dissolved organic carbon data.

Client ID#	WMRC ID# (00-)	Sediment Section	Sample Type or River Mile	Depth (cm)	DOC (ppm)	DOC Blk Corr
60C	1649		Filtered&acidified Blk		1.99	
5C	1596		164E	-3	6.90	4.92
6C	1597		164W	-3	7.64	5.66
10C	1601		165.5	-3	6.76	4.78
1C	1592		169	-3	7.14	5.15
3C	1594		171E	-3	6.40	4.42
2C	1593		171M	-3	6.71	4.73
4C	1595		171W	-3	7.31	5.32
7C	1598		175	-3	6.51	4.53
8C	1599		177	-3	5.96	3.98
9C	1600		179	-3	6.33	4.34
33C	1622	19	164E	3	11.3	9.35
36C	1625	20	164E	9	12.0	10.01
37C	1626	21	164E	15	16.2	14.25
38C	1627	22	164E	21	23.3	21.28
39C	1628	23	164E	27	27.0	25.06
40C	1629	24	164W	3	15.0	12.98
41C	1630	25	164W	9	15.0	13.03
18C	1607	26	164W	15	11.5	9.47
19C	1608	27	164W	21	13.6	11.58
20C	1609	28	164W	27	15.2	13.20
44C	1633	43	165.5	3	15.3	13.30
42C	1631	44	165.5	9	18.4	16.40
56C	1645	45	165.5	15	17.1	15.09
57C	1646	45	165.5	15	14.7	12.67
59C	1648	46	165.5	21	14.5	12.47
54C	1643	47	165.5	27	17.5	15.52
13C	1602	1	169	3	12.6	10.66
14C	1603	2	169	9	11.2	9.24
15C	1604	3	169	15	11.1	9.13
16C	1605	4	169	21	12.5	10.50
17C	1606	5	169	27	12.2	10.23

Table A- 10a. April dissolved organic carbon data con't.

Client ID#	WMRC ID# (00-)	Sediment Section	Sample Type or River Mile	Depth (cm)	DOC (ppm)	DOC Blk Corr
26C	1615	11	171E	3	14.1	12.16
27C	1616	12	171E	9	18.6	16.65
28C	1617	13	171E	15	16.1	14.11
31C	1620	6	171M	3	14.8	12.83
21C	1610	7	171M	9	12.7	10.74
22C	1611	7	171M	9	17.1	15.07
23C	1612	8	171M	15	23.7	21.67
25C	1614	9	171M	21	24.9	22.94
24C	1613	10	171M	27	24.0	22.03
29C	1618	14	171W	3	11.1	9.16
30C	1619	15	171W	9	11.8	9.85
34C	1623	16	171W	15	11.4	9.46
35C	1624	17	171W	21	16.0	14.03
32C	1621	18	171W	27	19.1	17.08
51C	1640	29	175	3	16.0	14.03
47C	1636	31	175	15	18.5	16.49
48C	1637	32	175	21	20.2	18.18
43C	1632	33	175	27	23.6	21.66
45C	1634	34	177	3	10.7	8.76
52C	1641	35	177	9	12.8	10.86
55C	1644	36	177	15	13.6	11.58
58C	1647	37	177	21	17.0	14.99
46C	1635	38	177	27	17.9	15.92
49C	1638	40	179	9	12.6	10.59
50C	1639	40	179	9	13.6	11.65
53C	1642	41	179	15	22.1	20.10

Table A-10 b. October dissolved organic carbon data.

WMRC ID# (00-)	Sediment Section	Sample Type or River Mile	Depth	DOC (ppm)	DOC Blk Corr	Notes
3116		Filtered&acidified Blk		<0.2		
3117		Filtered&acidified Blk		<0.2		
3118		Filtered&acidified Blk		<0.2		
3119		Filter Capsule Blk		0.184		
3130		164E	-3	3.77	3.57	
3128		164W	-3	3.70	3.50	
3129		164W	-3	5.13	4.93	
3127		165.5	-3	4.07	3.87	
3126		169	-3	3.82	3.62	
3125		171E	-3	4.07	3.87	
3124		171M	-3	4.99	4.79	
3123		171W	-3	5.47	5.27	
3120		175	-3	4.04	3.84	
3121		177	-3	3.68	3.48	
3122		179	-3	4.36	4.16	
3109	94	164E	3	6.33	6.33	
3113	95	164E	9	7.33	7.33	
3110	96	164E	15	9.58	9.58	
3114	97	164E	21	17.09	17.09	
3112	98	164E	27	21.77	21.77	
3115	89	164W	3	5.2*	5.20	
3107	90	164W	9	8.43	8.43	
3104	91	164W	15	15.64	15.64	
3105	91	164W	15	15.82	15.82	
3106	92	164W	21	18.31	18.31	
3108	93	164W	27	17.82	17.82	
3102	84	165.5	3	7.56	7.56	
3099	85	165.5	9	9.48	9.48	
3100	86	165.5	15	11.42	11.42	
3101	86	165.5	15	11.51	11.51	
3111	87	165.5	21	12.02	12.02	
3103	88	165.5	27	14.61	14.61	
3093	79	169	3	7.04	7.04	
3094	80	169	9	7.00	7.00	
3095	80	169	9	6.50	6.50	
3096	81	169	15	9.39	9.39	
3097	82	169	21	12.13	12.13	
3098	83	169	27	15.89	15.89	

Table A-10 b. October dissolved organic carbon data cont'd.

WMRC ID# (00-)	Sediment Section	Sample Type or River Mile	Depth	DOC (ppm)	DOC Blk Corr	Notes
3091	75	171E	3	13.67	13.67	
3092	76	171E	9	11.34	11.34	only ~7 mL sample
3089	77	171E	15	13.09	13.09	only ~8 mL sample
3090	78	171E	21	13.83	13.83	
3080	70	171M	3	9.08	9.08	
3081	71	171M	9	9.11	9.11	
3087	72	171M	15	13.81	13.81	
3086	73	171M	21	18.48	18.48	
3088	74	171M	27	19.49	19.49	
3082	65	171W	3	9.74	9.74	
3083	66	171W	9	8.82	8.82	
3084	66	171W	9	10.46	10.46	
3085	67	171W	15	11.44	11.44	
3078	68	171W	21	13.80	13.80	
3079	69	171W	27	15.87	15.87	
3069	50	175	3	12.30	12.30	
3066	51	175	9	9.08	9.08	
3076	52	175	15	12.86	12.86	
3070	53	175	21	20.97	20.97	
3077	54	175	27	19.73	19.73	
3071	55	177	3	8.21	8.21	Cameo filter (0.2micron)
3072	55	177	3	8.44	8.44	Glass fiber (1.0 micron)
3067	56	177	9	9.77	9.77	
3073	57	177	15	12.70	12.70	
3068	58	177	21	13.56	13.56	
3074	59	177	27	17.27	17.27	
3075	60	179	3	14.01	14.01	only ~7 mL sample

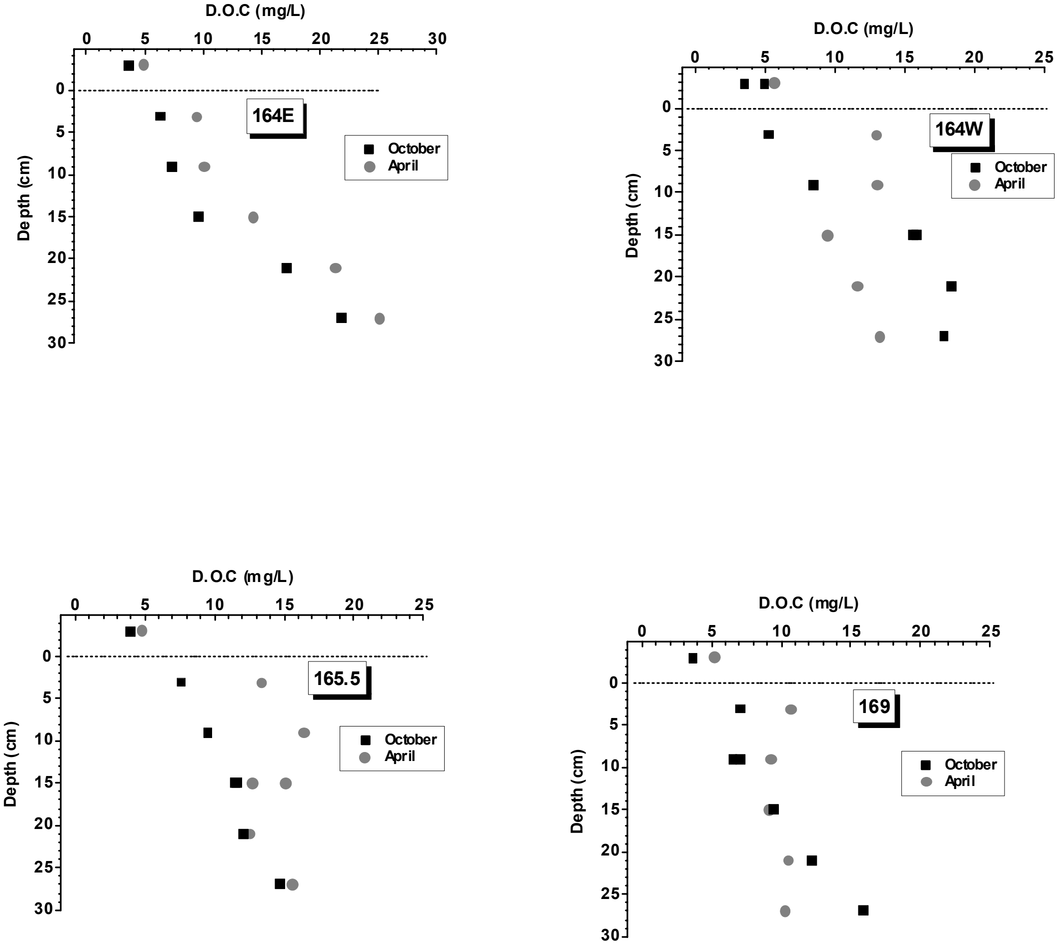

Figure A-11a. April and October dissolved organic carbon data for stations 164 to 169.

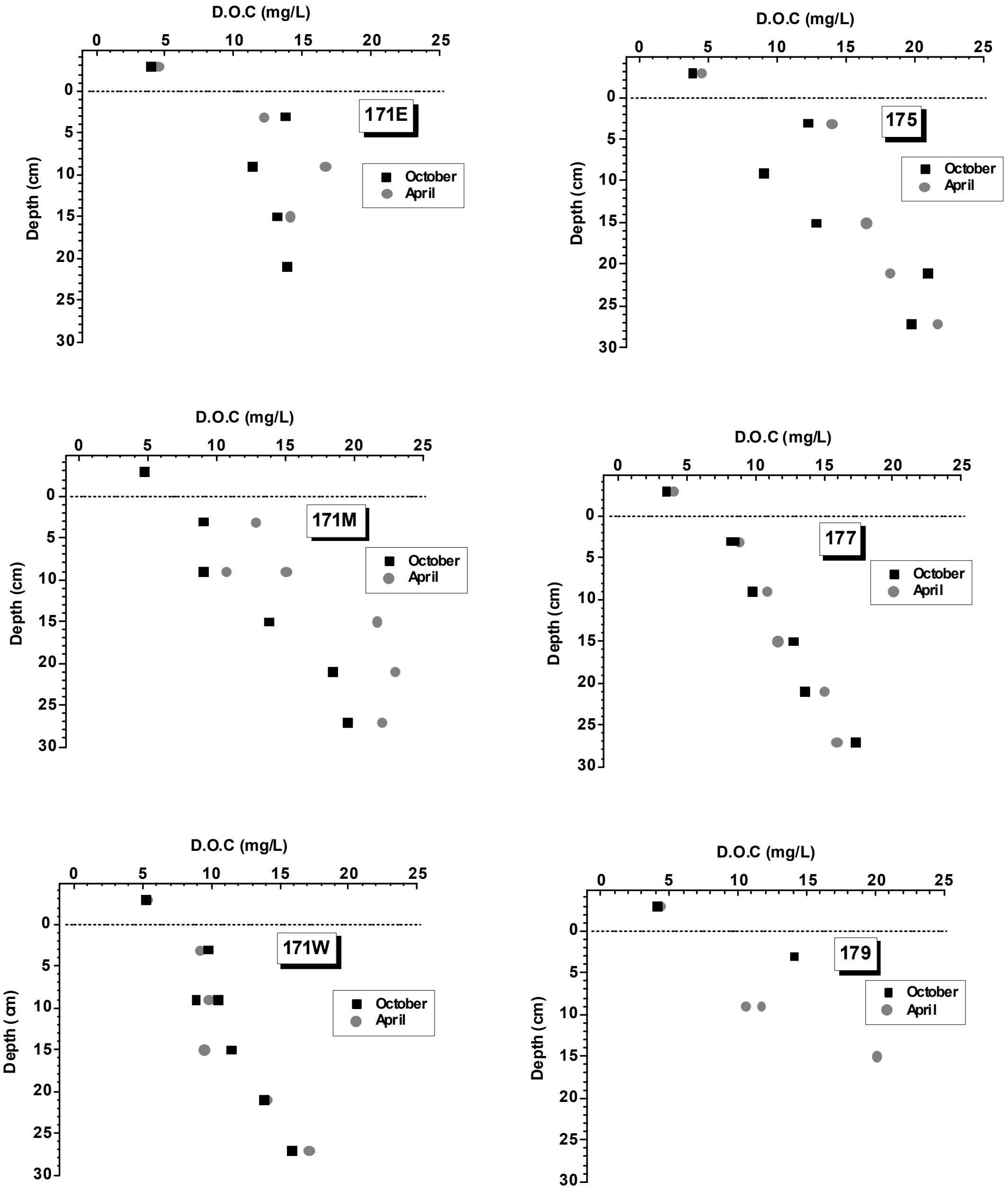

Figure A-11b. April and October dissolved organic carbon data for stations 171 to 179.

Table A-11. April total organic carbon data.

Client ID#	WMRC ID# (00-)	Sediment Section	Sample Type or River Mile	Depth (cm)	T.O.C[a] (%)	ISGS[b] (%)
77	1906	19	164E	3	3.11	2.47
89	1909	20	164E	9	2.74	
93	1910	21	164E	15	2.41	
97	1911	22	164E	21	2.55	
101	1912	23	164E	27	3.55	3.44
105	1913	24	164W	3	2.96	2.71
109	1914	25	164W	9	3.00	
21	1892	26	164W	15	3.08	
25	1893	27	164W	21	3.05	
29	1894	28	164W	27	2.99	2.42
125	1918	43	165.5	3	3.43	2.53
117	1916	44	165.5	9	3.06	
173	1930	45	165.5	15	2.90	
181	1932	46	165.5	21	2.94	
165	1928	47	165.5	27	2.60	2.26
1	1887	1	169	3	3.44	2.73
5	1888	2	169	9	3.61	
9	1889	3	169	15	3.23	
13	1890	4	169	21	3.13	
17	1891	5	169	27	3.32	2.59
49	1899	11	171E	3	1.23	0.97
53	1900	12	171E	9	1.47	
57	1901	13	171E	15	1.61	1.6
69	1904	6	171M	3	3.29	2.35
33	1895	7	171M	9	3.12	
37	1896	8	171M	15	3.06	
41	1897	9	171M	21	3.12	
45	1898	10	171M	27	3.12	2.68
61	1902	14	171W	3	3.24	1.99
65	1903	15	171W	9	3.07	
81	1907	16	171W	15	2.82	
85	1908	17	171W	21	2.94	
73	1905	18	171W	27	2.84	2.8
153	1925	29	175	3	2.95	2.21
145	1923	30	175	9	2.98	
137	1921	31	175	15	2.51	
141	1922	32	175	21	2.68	
121	1917	33	175	27	2.51	2.57
129	1919	34	177	3	2.97	1.97
157	1926	35	177	9	2.75	
169	1929	36	177	15	2.63	
177	1931	37	177	21	2.54	
133	1920	38	177	27	2.76	2.19
113	1915	39	179	3	0.73	0.75
149	1924	40	179	9	0.80	
161	1927	41	179	15	1.95	1.78

[a] analyzed by WRMC

[b] analyzed by the State Geological Survey

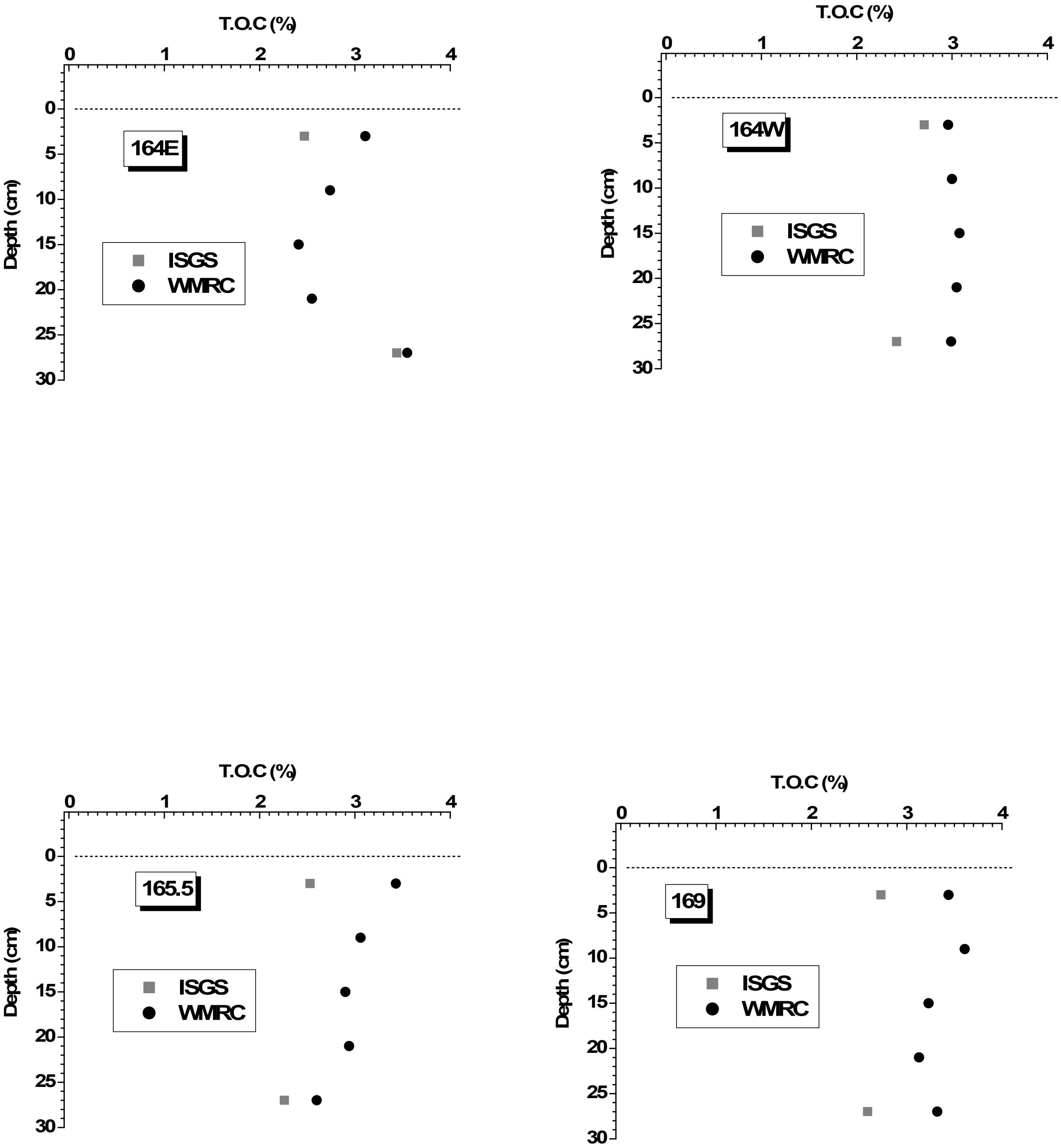

Figure A-12a. April total organic carbon data for stations 164 to 169.

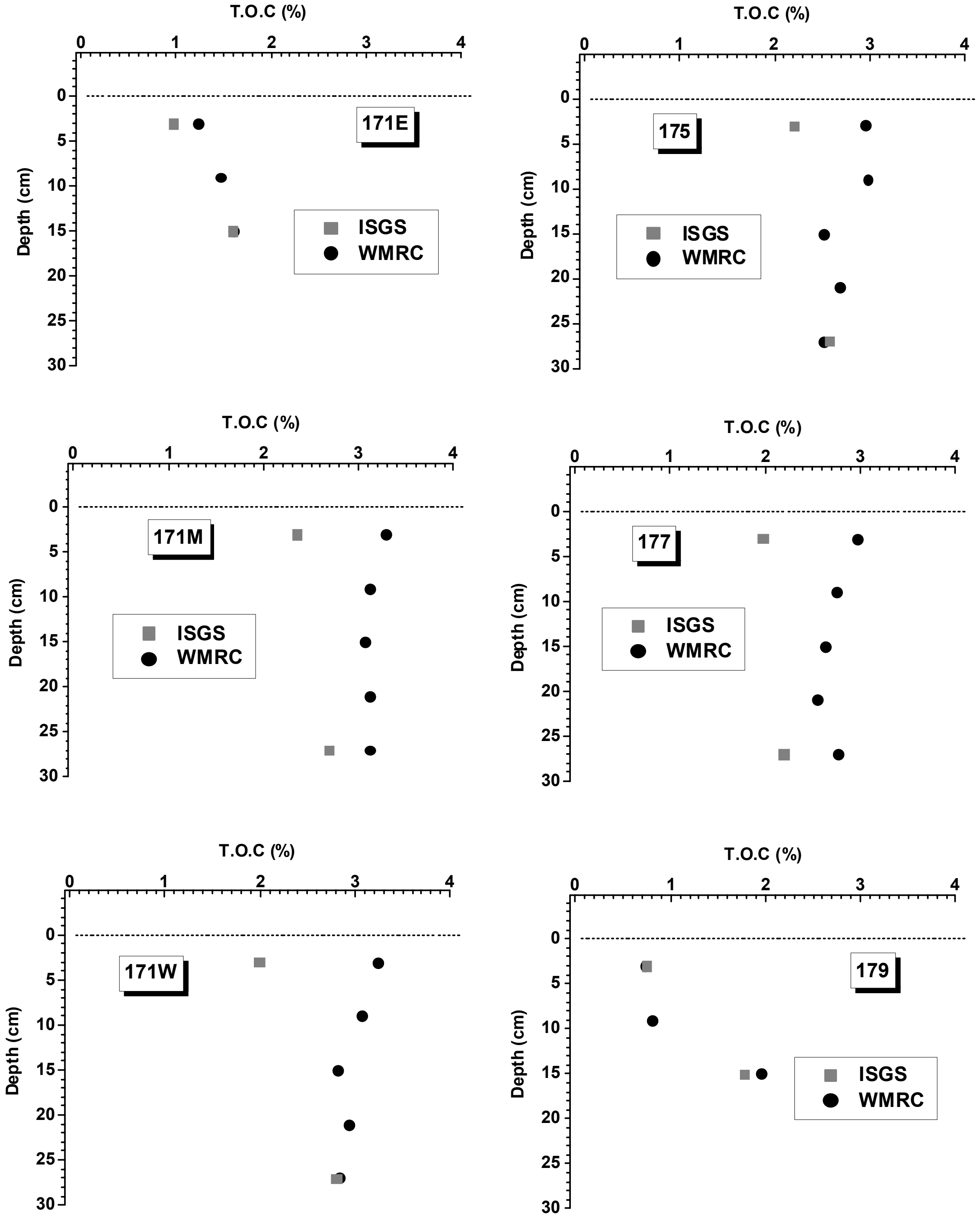

Figure A-12b. April total organic carbon data for stations 171 to 179.

APPENDIX B: QA/QC Tables

Table B-1. Sample containers, filtrate volumes collected, and preservatives added.

Measurement	Container Material	Capacity (mL)	Approx. Filtrate Volume (mL)	Preservative
Metals, River water	HDPE	125	100	0.2% HNO_3
Ammonia, River water	HDPE	125	100	0.2% H_2SO_4
Organic carbon, river water	Glass	20	10	0.5% H_2SO_4
Metals, Pore water	HDPE	30	12	0.2% HNO_3
Ammonia, Pore water	HDPE	30	10	0.2% H_2SO_4
Organic carbon, Pore water	Glass	20	10	0.5% H_2SO_4
Acid-volatile sulfide	Glass	60	NA	None

Table B-2. General metals data quality objectives.

Table of Data Quality Objectives		
Sample Matrix	Pore Waters	Sediments
Reference Analysis Method	EPA SW-846 Method 6020	EPA SW-846 Method 6020
Reference Preparation Method	EPA SW-846 Method 3005	EPA SW-846 Method 3052 and SW-846 Method 3050 for AVS extracted metals
Reporting Units	ng/mL	mg/kg
Quantitation Limits	1 ng/mL	0.2 mg/kg and 1 mg/kg (for AVS metals)
Precision	RPDs < 20 %	RPDs < 40 %
Accuracy	Aqueous SRMs within established control limits	Solid SRMs where available within established control limits
Completeness	95%	95 %

Table B-3. QA/QC data for April dissolved metals.

Quality Control Data Summary for April

Client: Mike Machesky
RSA: 0500-07
Sample Type: Pore Waters and River Waters

Instrument: VE Elemental Inductively Coupled Plasma/MS
Date Received: May 17, 2000
Date Completed: July 18, 2000

QC	WMRC	Analyte				
Parameter	**Identification**	**Nickel**	**Copper**	**Zinc**	**Cadmium**	**Lead**
Precision of Duplicates (RPDs)						
Analytical Duplicate: 2R	00-1653	5%	4%	1%	0%	NR(1)
Analytical Duplicate: 9M	00-1665	11%	1%	1%	0%	0%
Analytical Duplicate: 11M	00-1668	NR(1)	NR(1)	2%	-	-
Analytical Duplicate: 32M	00-1682	-	6%	8%	12%	7%
Analytical Duplicate: 36M	00-1686	-	20%	2%	12%	17%
Analytical Duplicate: 40M	00-1690	1%	3%	8%	-	-
Analytical Duplicate: 46M	001696	4%	8%	16%	13%	5%
Analytical Duplicate: 53M	00-1702	-	4%	16%	0%	2%
Analytical Duplicate: 55M	00-1703	5%	13%	-	17%	NR(1)
Analytical Duplicate: 59M	00-1705	-	14%	19%	-	-
Analytical Duplicate: 62M	00-1708	-	-	1%	-	-
Analytical Duplicate: 68M	00-1712	-	11%	3%	-	NR(1)
Analytical Duplicate: 69M	00-1713	23%	4%	8%	NR(1)	NR(1)
Analytical Duplicate: 71M	00-1715	-	3%	7%	0%	13%
Analytical Duplicate: 76M	00-1717	-	22%	11%	0%	4%

0.5% HNO3 Reagent Blank(ng/mL)	<0.1	<0.1	<0.1	<0.02	<0.1
Method Detection Limit(ng/mL)	0.2	0.2	0.2	0.04	0.2

NR: Not Reported due to: (1) RPD of duplicates less than detection limit

QC	WMRC	Analyte				
Parameter	**Identification**	**Nickel**	**Copper**	**Zinc**	**Cadmium**	**Lead**
Accuracy Parameters						
Analytical Spike Recoveries						
Recovery: 1R	00-1652	94%	95%	95%	100%	95%
Recovery: 7M	00-1663	96%	97%	99%	-	-
Recovery: 8M	00-1664	-	-	-	101%	103%
Recovery: 9M	00-1665	-	-	-	96%	92%
Recovery: 11M	00-1668	85%	85%	81%	-	-
Recovery: 33M	00-1683	76%	77%	104%	-	-
Recovery: 34M	00-1684	90%	87%	106%	100%	96%
Recovery: 43M	00-1693	91%	97%	-	100%	98%
Recovery:53M	00-1702	88%	75%	-	97%	90%
Recovery: 53M	00-1702	-	97%	92%	-	-
Recovery: 59M	00-1705	-	-	-	96%	91%
Recovery: 59M	00-1705	-	-	78%	-	-
Recovery: 65M	00-1711	68%	-	-	76%	76%
Recovery: 70M	00-1714	-		63%	-	-
Recovery: 71M	00-1715	-	71%	-	-	-
Recovery: 78M	00-1718	-	88%	-	99%	100%
Recovery: 81M	00-1721	96%	113%	-	100%	106%

Table B-4. QA/QC data for October dissolved metals.

Dissolved Metals Quality Control Summary for October Samples

Client: **Mike Machesky**
RSA: **1100-05**
Sample Type: **Pore Waters and River Water**

Instrument: Inductively Coupled Plasma/MS
Date Received: **Nov. 1, 2000**
Date Completed: **Feb. 14, 2001**

Quality Control Parameter	WMRC Identification	Analyte				
		Nickel	Copper	Zinc	Cadmium	Lead
Precision of Duplicates (RPDs)						
110M	00-3003	0%	NR(1)	8%	-	-
115M	00-3008	-	-	3%	NR(1)	13%
118M	00-3011	-	-	11%	-	-
129M	00-3022	-	-	-	33%	6%
137M	00-3030	5%	NR(1)	-	-	-
145M	00-3038	-	-	-	5%	0%
161M	00-3053	NR(1)	NR(1)	-	-	-
192M	00-3059	-	15%	-	-	-
0.5% HNO3 Reagent Blank(ng/mL)		<0.1	<0.1	<0.2	<0.02	<0.05
Method Detection Limit(ng/mL)		0.2	0.1	0.2	0.02	0.05

Quality Control Parameter	WMRC Identification	Analyte				
		Nickel	Copper	Zinc	Cadmium	Lead
Accuracy Parameters						
Analytical Spike Recoveries						
116M	00-3009	103%	-	-	-	-
132M	00-3025	-	-	-	78%	79%
134M	00-3027	-	-	-	80%	76%
141M	00-3034	103%	95%	-	-	-
143M	00-3036	-	-	-	107%	117%
147M	00-3040		81%	-	-	-
158M	00-3050	-	-	109%	-	-
187M	00-3054		81%	92%	-	-
187M	00-3061	-	-	-	102%	96%
-	-	-	-	-	-	-

NR: Not Reported due to: (1) difference between duplicates is less than detection limit

Table B-5. April SEM QA/QC results summary.

Table 2: Quality Control Summary

Client:	**Mike Machesky**	**Instrument:**	**Inductively Coupled Plasma/MS**
RSA:	**0201-02**	**Date Received:**	**February 8, 2001**
Sample Type:	**Soil Extracts in 1M HCl**	**Date Completed:**	**March 23, 2001**

Quality Control Parameter	**WMRC Identification**	**Analyte**				
		Nickel	**Copper**	**Zinc**	**Cadmium**	**Lead**
Precision of Duplicates (RPDs)						
SEM-3	01-1030	11%	NR(1)	4%	0%	7%
SEM-31	01-1046	1%	2%	0%	0%	1%
SEM-47	01-1055	8%	8%	7%	1%	7%
SEM-61	01-1064	2%	1%	3%	2%	3%
Accuracy Parameters						
Analytical Spike Recoveries						
SEM-1	01-1029	92%	93%	94%	99%	94%
SEM-13	01-1035	92%	96%	97%	90%	90%
SEM-23	01-1041	99%	94%	93%	100%	98%
0.5% HNO3 Reagent Blank (mg/L)		<0.0003	<0.0003	<0.0003	<0.00003	<0.0003
Method Detection Limit (mg/L)		0.0015	0.0015	0.0015	0.00015	0.0015

NR: Not Reported due to: (1) results are less than lowest standard

Table B-6 . October SEM QA/QC results summary.

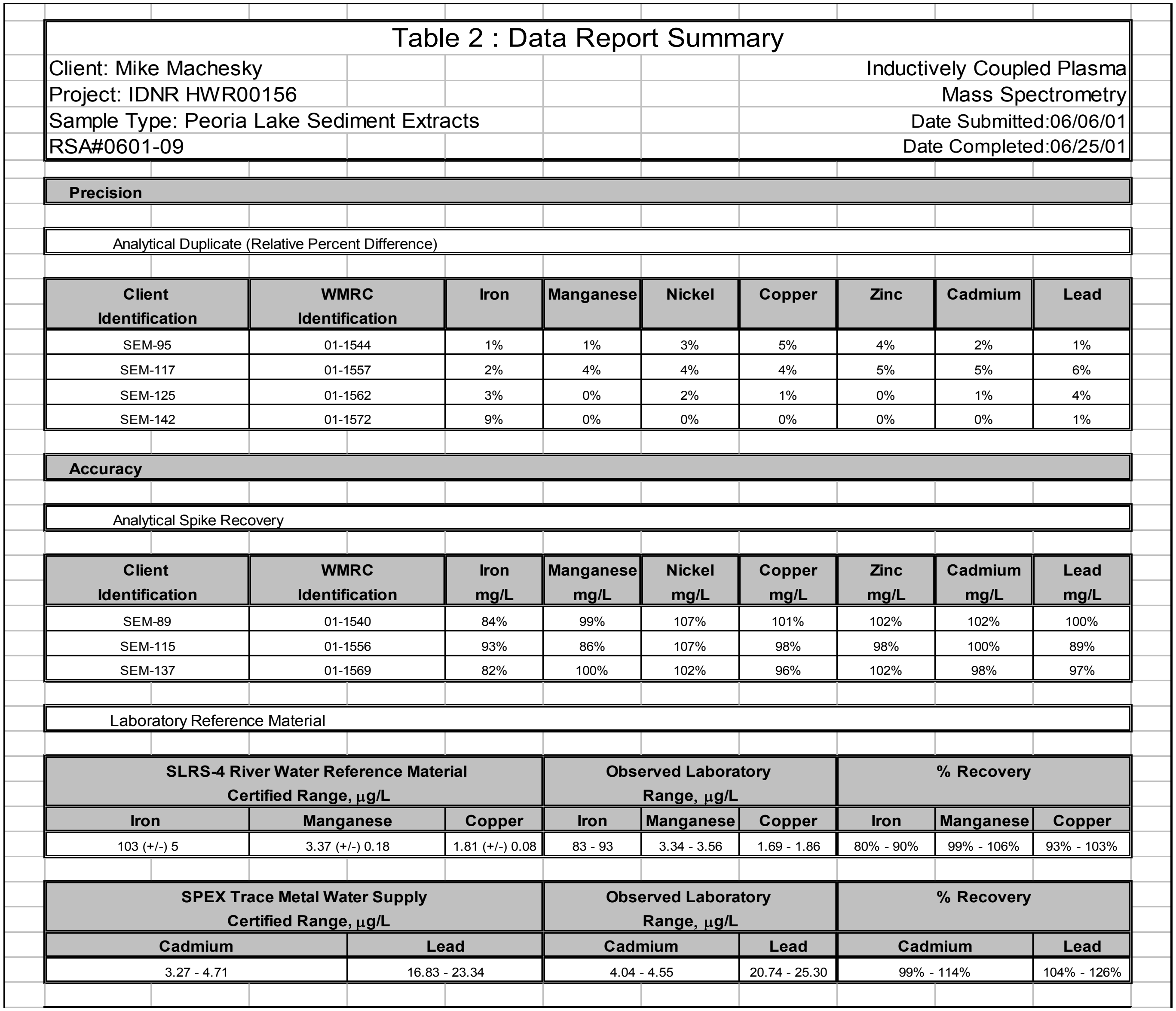

Table 2 : Data Report Summary

Client: Mike Machesky	Inductively Coupled Plasma
Project: IDNR HWR00156	Mass Spectrometry
Sample Type: Peoria Lake Sediment Extracts	Date Submitted:06/06/01
RSA#0601-09	Date Completed:06/25/01

Precision

Analytical Duplicate (Relative Percent Difference)

Client Identification	WMRC Identification	Iron	Manganese	Nickel	Copper	Zinc	Cadmium	Lead
SEM-95	01-1544	1%	1%	3%	5%	4%	2%	1%
SEM-117	01-1557	2%	4%	4%	4%	5%	5%	6%
SEM-125	01-1562	3%	0%	2%	1%	0%	1%	4%
SEM-142	01-1572	9%	0%	0%	0%	0%	0%	1%

Accuracy

Analytical Spike Recovery

Client Identification	WMRC Identification	Iron mg/L	Manganese mg/L	Nickel mg/L	Copper mg/L	Zinc mg/L	Cadmium mg/L	Lead mg/L
SEM-89	01-1540	84%	99%	107%	101%	102%	102%	100%
SEM-115	01-1556	93%	86%	107%	98%	98%	100%	89%
SEM-137	01-1569	82%	100%	102%	96%	102%	98%	97%

Laboratory Reference Material

SLRS-4 River Water Reference Material Certified Range, µg/L			Observed Laboratory Range, µg/L			% Recovery		
Iron	Manganese	Copper	Iron	Manganese	Copper	Iron	Manganese	Copper
103 (+/-) 5	3.37 (+/-) 0.18	1.81 (+/-) 0.08	83 - 93	3.34 - 3.56	1.69 - 1.86	80% - 90%	99% - 106%	93% - 103%

SPEX Trace Metal Water Supply Certified Range, µg/L		Observed Laboratory Range, µg/L		% Recovery	
Cadmium	Lead	Cadmium	Lead	Cadmium	Lead
3.27 - 4.71	16.83 - 23.34	4.04 - 4.55	20.74 - 25.30	99% - 114%	104% - 126%

Table B- 7. April total recoverable metals QA/QC results.

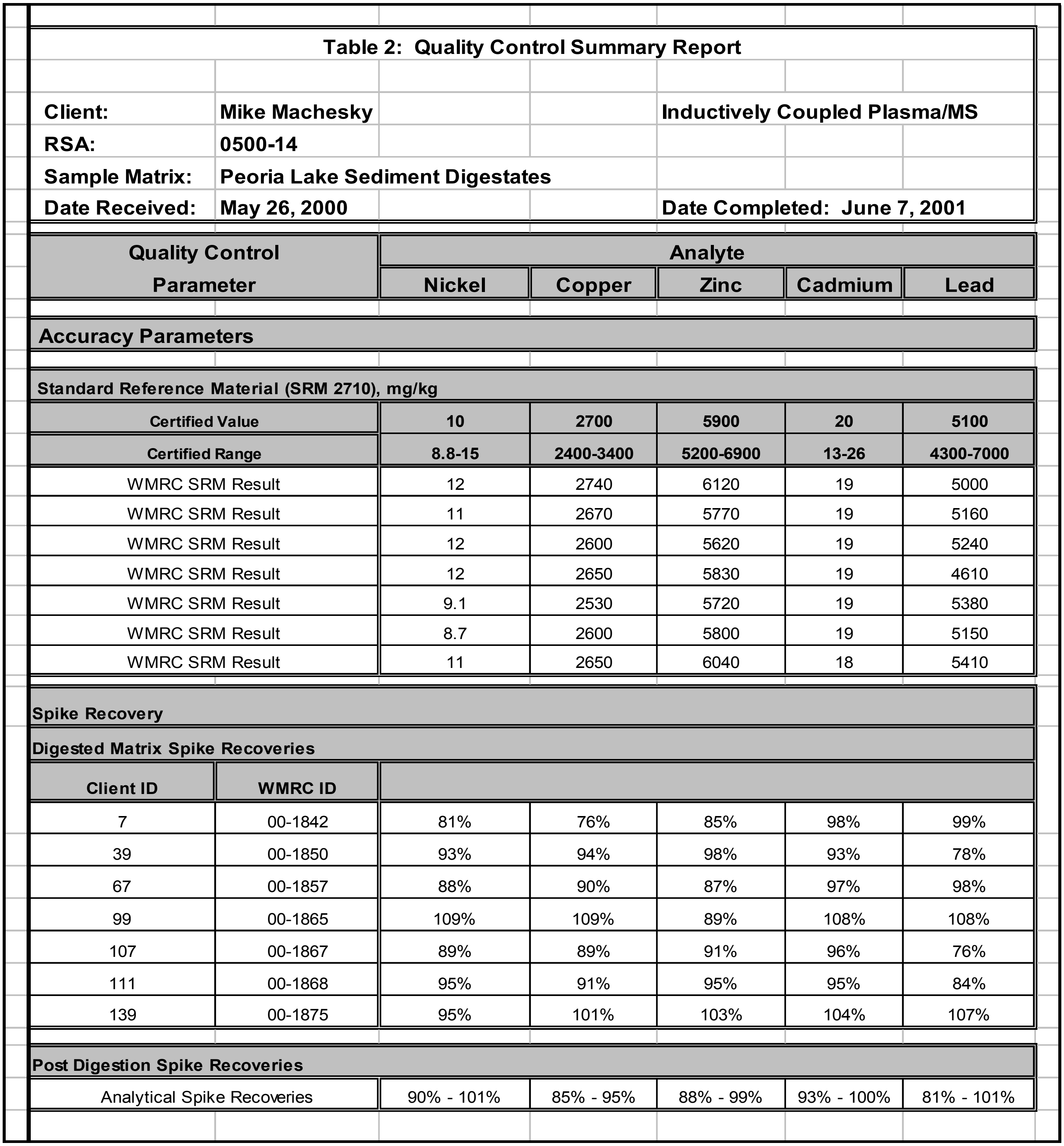

Table 2: Quality Control Summary Report

Client: **Mike Machesky** **Inductively Coupled Plasma/MS**
RSA: **0500-14**
Sample Matrix: **Peoria Lake Sediment Digestates**
Date Received: **May 26, 2000** **Date Completed: June 7, 2001**

Quality Control Parameter		Analyte				
		Nickel	Copper	Zinc	Cadmium	Lead
Accuracy Parameters						
Standard Reference Material (SRM 2710), mg/kg						
Certified Value		**10**	**2700**	**5900**	**20**	**5100**
Certified Range		**8.8-15**	**2400-3400**	**5200-6900**	**13-26**	**4300-7000**
WMRC SRM Result		12	2740	6120	19	5000
WMRC SRM Result		11	2670	5770	19	5160
WMRC SRM Result		12	2600	5620	19	5240
WMRC SRM Result		12	2650	5830	19	4610
WMRC SRM Result		9.1	2530	5720	19	5380
WMRC SRM Result		8.7	2600	5800	19	5150
WMRC SRM Result		11	2650	6040	18	5410
Spike Recovery						
Digested Matrix Spike Recoveries						
Client ID	**WMRC ID**					
7	00-1842	81%	76%	85%	98%	99%
39	00-1850	93%	94%	98%	93%	78%
67	00-1857	88%	90%	87%	97%	98%
99	00-1865	109%	109%	89%	108%	108%
107	00-1867	89%	89%	91%	96%	76%
111	00-1868	95%	91%	95%	95%	84%
139	00-1875	95%	101%	103%	104%	107%
Post Digestion Spike Recoveries						
Analytical Spike Recoveries		90% - 101%	85% - 95%	88% - 99%	93% - 100%	81% - 101%

Table B-7 continued. April Total recoverable metals QA/QC results.

Table 2: Quality Control Summary Report, continued

Client:	**Mike Machesky**	**Inductively Coupled Plasma/MS**
RSA:	**0500-14**	
Sample Matrix:	**Peoria Lake Sediment Digestates**	
Date Received:	**May 26, 2000**	**Date Completed: June 7, 2001**

Quality Control Parameter		Analyte				
		Nickel	Copper	Zinc	Cadmium	Lead
Precision Parameters						
Relative Percent Difference of Digested Duplicates						
Client ID	**WMRC ID**					
3	00-1841	3%	0%	2%	4%	2%
35	00-1849	0%	1%	1%	0%	2%
63	00-1856	4%	3%	3%	8%	2%
95	00-1864	0%	1%	0%	2%	1%
103	00-1866	6%	4%	6%	7%	7%
111	00-1868	3%	1%	0%	2%	0%
135	00-1874	1%	1%	2%	2%	3%
Detection Limits						
Method Detection Limit		4	4	4	0.1	4
Digested Reagent Blank, mg/kg		0.2	2	0.6	<0.02	0.5
Digested Reagent Blank, mg/kg		<0.2	0.5	<0.2	<0.02	0.2
Digested Reagent Blank, mg/kg		<0.2	0.3	<0.2	<0.02	<0.2
Digested Reagent Blank, mg/kg		<0.2	0.3	<0.2	<0.02	<0.2
Digested Reagent Blank, mg/kg		<0.2	<0.2	<0.2	<0.02	0.2
Digested Reagent Blank, mg/kg		<0.2	<0.2	<0.2	<0.02	0.2
Digested Reagent Blank, mg/kg		<0.2	0.2	<0.2	<0.02	0.5

Table B-8. QA/QC data for April dissolved organic carbon.

QA/QC Report

Client Sample ID	WMRC ID# (00-)	DOC (ppm)	RPD / RSD (%)
41C	1630	14.61	5.3
Duplicate		15.41	
13C	1602	13.23	7.9
Duplicate		12.05	
45C	1634	10.71	0.6
Duplicate		10.77	
19C	1608	13.31	3.7
Duplicate		13.81	
7C	1598	6.50	0.3
Duplicate		6.52	
			RSD (%)
26ppm Check Standard		27.42	3.6
		28.35	
		26.52	
		25.93	
		26.39	

Table B-9. QA/QC data for October dissolved organic carbon.

QA/QC Report

Client Sample ID 1100-06	WMRC ID# (00-)	DOC (ppm)	RPD (%)
101C	3067	9.27	10.0
Duplicate		10.28	
110C	3076	12.86	8.6
Duplicate		14.02	
119C	3084	10.02	8.0
Duplicate		10.89	
128C	3093	7.21	5.0
Duplicate		6.86	
133C	3098	15.81	1.0
Duplicate		15.97	
170C	3130	3.65	6.0
Duplicate		3.89	
26ppm Check Standard		25.40	2.5
		26.22	
		26.55	
		26.51	
		25.18	

Table B- 10. April total organic carbon QA/QC results.

Client Sample ID **0500-15**	WMRC ID# (00-)	TOC (%)	RPD (%)
1	1887	3.48	2.6
Duplicate		3.39	
37	1896	3.04	1.0
Duplicate		3.07	
77	1906	3.15	2.9
Duplicate		3.06	
117	1916	3.11	3.3
Duplicate		3.01	
157	1926	2.70	3.3
Duplicate		2.79	
181	1932	2.82	7.8
Duplicate		3.05	
12% CaCO3 Std		11.86	0.5
		11.82	
		11.97	
		11.91	
		11.89	

APPENDIX C: A Study of the Positive Bias Interference of Calcium^{44} Oxide^{16} on Nickel^{60} in Pore Waters Measured by ICP-MS

Dr. Mike Machesky
Illinois State Water Survey
2204 Griffith Dr.
Champaign, IL 61820
MC-674

Dear Dr. Machesky,

The Illinois Waste Management and Research Center has completed analyses of your pore water samples for nickel and calcium. Corrected nickel results, determined by calculation, and original calcium results, determined by Atomic Absorption, are provided in the attached report (Table 3 for sample data). As you will discover in the attached report, your suspicion was correct that $Ca^{44}O^{16}$ might interfere with (and yield a positive bias on) the ICP-MS determination of nickel at mass 60. Your samples for calcium were assigned Request for Sample Analysis (RSA) #0801-07 and a copy of that request is attached.

The pore water samples were originally assigned to RSA's #0500-07 and #1100-05 and the original nickel results were reported for those RSAs. When the samples were reassigned to RSA #0801-07 for calcium, a number of the original samples were missing and were not assigned. The missing samples are:

Your ID	WMRC Lab ID	Your ID	WMRC Lab ID
0M	00-1651	81M	00-1721
1R	00-1652	104M	00-2997
4R	00-1655	112M	00-3005
11M	00-1668		

No calcium data is available for these samples such that we were unable to determine a corrected nickel concentration. However, an average calcium could be assumed and could be used to correct original nickel values reported for these samples using the correlation in the attached report.

Quality control parameters associated with Calcium analyses included analytical duplicates and analytical spikes. Analytical spikes were acceptable and ranged from 95%-100% and duplicate samples were reproducible, yielding relative percent differences from 0%-6%. Based on quality control parameters, it is estimated that Calcium results have a maximum error of no more than +/- 10%.

Remaining sample portions may be picked up at the Center at your earliest convenience over the next three weeks. After that time, samples will be disposed of at the Center. If you have any questions or concerns regarding the data, please do not hesitate to contact Dr. Talbott at 333-7276 (jtalbott@wmrc.uiuc.edu) or myself at 333-8798 (jscott@wmrc.uiuc.edu).

Sincerely,

John Scott
Preparations Chemist

A Study of the Positive Bias Interference of Calcium^{44} Oxide^{16} on Nickel^{60} in Pore Waters Measured by ICP-MS

By John Scott and Jonathan Talbott, PhD
Illinois Waste Management and Research Center

Summary

Calcium in 100 ppm range in pore waters was determined to cause a positive bias on nickel results in the low ppb range measured at mass 60 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The error is on the order of 1 to 4 ng/mL (ppb) and depends upon the concentration of calcium present in the samples and upon the oxide conditions of the instrument at the time of analysis. The correlation is

Ni correct (μg/L) = Ni measured (μg/L) – k'[Ca (mg/L)]

where k' is the slope of the correlation between Ni (μg/L) and Ca (mg/L) corrected for the oxide level of the ICP at the time of analysis. The corrected slope is on the order of 0.020 (μg/L Ni/mg/L Ca) at 5 % instrument oxides.

Corrected nickel results and calcium data for the pore waters are presented in Table 3.

Introduction/Background

Pore waters are similar to ground waters in that they contain calcium in the 20-200 ppm (mg/L) range. Nickel may be present at the low ppb (μg/L) range. The calcium isotope at mass 44 is only 2.06 % of the element's natural abundance yet this concentration is still about 3 orders of magnitude greater than the nickel found in these samples. The calcium concentration is sufficient to interfere with and yield a positive bias on nickel when measured by ICP-MS at mass 60 if the molecular oxide ($Ca^{44}O^{16}$) is formed.

The ICP-MS instrument is typically set up to run with formation of molecular oxides (as in $Ca^{44}O^{16}$) minimized. Oxide formation, MO^+, as a percent of the metal ion, M^+, is checked daily using Cerium and ranges instrumentally from 2 to 6 % of the M^+. Cerium is used for this check because it has one of largest bond strengths between a metal and the first oxygen and therefore is one of the most easily formed monoxides (may also be that the monoxide is the most difficult to destroy in the torch). Other metals should yield less oxide formation.

Experimental Analysis

Contrived samples

Contrived laboratory samples were used to confirm the positive bias of $Ca^{44}O^{16}$ on Ni^{60} in the range of concentrations observed in pore waters. Two types of contrived samples were analyzed in this manner, samples containing only calcium at 160 part-per-million (ppm) and samples containing 160 ppm calcium and nickel at 2 parts-per-billion (ppb). In the case of 160 ppm calcium only (no nickel spiked into the sample), the observed nickel

Table 1:Contrived Laboratory Sample Results at Varies Oxide Levels for Conformation of Calcium Oxide Intererence at Nickel (amu 60)

Sample	Low Oxides (0.7%) Observed Nickel (μg/L)	Medium Oxides (2.9%) Observed Nickel (μg/L)	Medium Oxides (4.5%) Observed Nickel (μg/L)	High Oxides (6.5%) Observed Nickel (μg/L)
160 μg/L Calcium Only	2.0	3.7	4.1	3.1
160 μg/L Calcium/ 2 μg/L Nickel	3.7	5.3	5.6	4.7

result varied from 2 ppb to just greater than 4 ppb depending upon the oxide level in which the instrument was operated (Table 1). With 160 ppm Calcium and 2 ppb nickel, the observed nickel result varied from 3.7 to 5.6 ppb of nickel, again depending upon the oxide level in which the ICP was operated. Thus in both cases, a positive bias in the measured nickel concentration was observed over that actually present in solution (Table 1).

The bias in these contrived samples is on the order of 2 to 4 ppb of Ni for 160 ppm of calcium. This ratio is on the order of 1 in 100,000. Nickel impurity levels in the NIST traceable calcium standard used to prepared these solutions are < 20 ppb nickel in the 10,000 ppm calcium stock standard (Spex certificate of analysis). Thus the stock standard is less than 2 in 1,000,000, a factor of 5 less than the bias effect observed.

Calcium Spiked Pore Waters

Calcium spiked pore waters were also used to confirm and quantify the bias effect. Four different pore waters were spiked at several levels of calcium similar to levels observed in the pore waters and Ni^{60} was measured. This approach is similar to the Method of Standard Additions (MSA) except that the interferent rather than the analyte of interest is spiked. The MSA method included ICP-MS analysis of the samples neat, spiked with 50%, and 100% of the estimated calcium concentrations. This approach was necessary to quantify the extent of the calcium oxide interference and to provide a means for correcting the previously reported Nickel results. As above, the experiment was conducted at the four instrument oxide levels (Table 2). In Figures 1 through 4 below, the measured or observed Nickel concentration is plotted as a function of calcium present or spiked in the sample at various instrument oxide levels. As apparent from the Figures, the positive bias on nickel increases linearly with calcium concentration and regression analysis was used to quantify the effect. The average slope or conversion factor obtained from linear regression analysis of the calcium-nickel MSA experimental data at various instrument oxide levels is also presented in Table 2. The relatively small standard deviations of the slopes at any given instrument oxide level (Table 2) illustrates the reproducibility of the slope or coefficient from sample to sample. In all cases, the relative standard deviation of the slope is less than 15%.

Table 2: Nickel-Calcium MSA Correlation Slope Averages for Variable Oxide Levels

	Slopes (Low Oxides-0.7%)	Slopes (Med Oxides-2.9%)	Slopes (Med Oxides-4.5%)	Slopes (High Oxides-6.5%)
Sample 1660	0.0110	0.0158	0.0201	0.0187
Sample 1663	0.0133	0.0171	0.0215	0.0227
Sample 2994	0.0123	0.0181	0.0230	0.0186
Sample 3060	0.0119	0.0180	0.0275	0.0216
Average:	0.0121	0.0172	0.0230	0.0204
Std Dev:	0.0010	0.0011	0.0032	0.0021

Calcium MSA of Contrived Samples

In the same manner as above, contrived samples were also analyzed for Ni^{60} at multiple concentration levels of calcium. Contrived samples yielded slopes slightly greater than that observed for the pore waters (Figure 5). Although this difference is small, the most likely cause of the discrepancy in the slopes is that there is probably some matrix suppression of the nickel signal in the pore waters while it is absent the contrived laboratory samples.

Effect of Instrument Oxide Level on Correlation

In addition, it was expected that the slopes of trend-lines calculated would be dependent on the oxide conditions of the instrument. If the average slope of the calcium to nickel correlation is plotted as a function of instrument oxide level, a slight correlation is observed (Figure 6). Linear regression analysis of this data yields the following correlation:

$$(\text{Slope of Calcium-Nickel Correlation}) = 0.0016x(\text{\% Oxides Instrument Conditions}) + 0.0124$$

Note that the intercept of this correlation is substantially larger than the slope or coefficient of this correlation. Thus there is minimal effect of instrument oxide conditions upon the slope of the calcium to nickel correlation. However, the effect can be taken in to consideration for samples if the oxide level was recorded at the time of nickel analysis.

Calcium Determinations and Corrected Nickel Calculations

In order to correct previously reported Nickel concentrations, quantification of Calcium in the samples was necessary. Although minimal sample volumes were available, calcium concentrations in pore waters were sufficiently high that the element could be measured by Atomic Absorption Spectrometry (AAS). Calcium results are reported in Table 3 attached. That calcium was determined by AAS and nickel was determined by ICP-MS is immaterial, the bias effect is based upon the amount of calcium actually present in the samples, not the method where by calcium is measured. Additionally, other complications were besetting calcium determinations by ICP-MS such that it was yielding a positive bias for the calcium data (which would have overcompensated the Ni correction and caused an overall negative bias on the nickel results).

The calcium data can then be used to correct the previously reported Nickel results with the following equation:

Nickel Corrected (µg/L) = Nickel Previously Measured (µg/L) – (Corrected Slope)(Calcium Concentration in Sample (mg/L)

Sample analyzed at unknown oxide levels, were conservatively assumed to be analyzed at the highest oxide level used in this study, 6.5%. Calcium and corrected Nickel results are presented in attached Table 3.

APPENDIX D: Sediment Mineralogy Report and Data

8/2/01: Final Report:

Analyses by the H.D. Glass method. The attached spreadsheet contains a new table with the Glass method data. The results are pretty well in line with what we expected. Hughes and Warren (1989) explain the indices that Glass uses. Glass is unable to work any longer, but if he's up to it, Phil DeMaris or I may take these files and his previous Lake Peoria files to Herb's house and obtain his input.

As soon as possible, we will forward electronic copies of the Scintag XRD traces. We need to master the software steps for this transfer.

6/21/01: Draft Report to: Mike Machesky; Associate Professional Scientist
Watershed Science Section; Illinois State Water Survey; 2204 Griffith Dr.; Champaign, IL 61820; 217-333-9322 (-244-3054 FAX); machesky@sws.uiuc.edu.

Samples. The eight samples were 0-6 and 24-30cm samples from 4 borings. The samples had been dried in screw-top plastic bottles. The dried samples were shaken by hand and as much material as possible was transferred into a plastic beaker. The remaining samples in the bottles were soaked in demineralized water for several days, ultrasoned to disperse them, and transferred to the plastic beaker with the dry sample.

Sample preparation. Once all the samples had been transferred to plastic beakers and diluted with demineralized water, the suspensions were ultrasoned for one min. and poured through a 325 mesh (44µm) screen. About half of the samples had clay lumps that had to be diluted and ultrasoned a second time. General references for these methods can be found in Hughes and Warren (1989), Hughes, Moore, and Glass (1994), and Moore and Reynolds (1997).

The +44µm coarse silt and fine sand were discarded, and the <44µm fraction was stirred and split into two aliquots. One sample was placed in a 40mL centrifuge tube, centrifuged, and the clear supernate was discarded. The second aliquot of each sample was returned to its numbered beaker, diluted, and "washed" with demineralized water.

Smear slides. The centrifuged sediment plugs were thoroughly mixed and spread evenly on a glass XRD slide. They were air-dried and then placed in an ethylene glycol atmosphere for at least two days.

<2µm sedimented slides. About half of the beakers of <44µm aliquots flocculated and settled clear. These were poured off and fresh water was added to fill the beaker. Based on the thickness of the sediments in the bottom of the beaker after overnight settling, the concentration in the beakers was adjusted to a column height of sediment:water of 1:8. A small amount of sodium hexametaphosphate was added as dispersant, and the samples were stirred and allowed to settle for about 15 min. An eyedropper full of the settled slurry was transferred to labeled slides and allowed to dry. The dried samples were placed in an ethylene glycol atmosphere for at least two days before xraying them.

XRD analysis. The smear slides were run on a Scintag with a 0/0 goniometer. An open dish of ethylene glycol was placed next to the samples and a small cover was placed over the sample changer to maintain full glycolation during the XRD scans.

The sedimented slides were run on a GE and the Scintag diffractometers.

Quantitative analysis. The Scintag DMS© computer programs were used to collect peak areas for each of the minerals, and the areas were entered into an Excel© spreadsheet. A set of peak conversion factors is used to convert the clay mineral peak areas into percentages for each of the clay minerals. The clay minerals and nonclay minerals are calculated separately to a total of 100%. A similar set of correction factors is used to calculate percentages of each of the nonclay minerals, and a clay index (CI) is calculated as the sum of the corrected clay mineral peaks divided by the sum of the corrected clay mineral peaks + the sum of the corrected nonclay mineral peaks. This number is a measure of the ratio of clay minerals to nonclay minerals, and it varies from zero (no clay minerals) to 1.0 (no nonclay minerals present. Peak areas from the <2µm sedimented slides analyzed on the Scintag were collected in the same way, entered into the spreadsheet, and percentages were calculated in the same way. The only nonclay calculations that are normally run on <2µm slides are recording the intensity of the major calcite and dolomite peaks.

Samples run on the GE diffractometer are calculated with H.D. Glass' method. We collected these percentages and indices, because most of the earlier ISGS XRD work on Lake Peoria sediments have been done by Glass.

Discussion.

The tables show that the samples contain abundant expandables, and significant illite, kaolinite, and chlorite. The nonclay fraction is dominated by quartz with lesser amounts of plagioclase, calcite, dolomite, K-feldspar, and small amounts of hornblende in some samples. The average percentages and std deviations for each mineral from the smear slide preparations were %expandables= 55% ± 6.8%; %illite = 27% ± 4.5%; %kaolinite+chlorite = 17% ± 2.6%; %kaolinite = 5.4% ± 1.7%; %chlorite = 12% ± 1.6%; %hornblende = 0.7% ± 0.8%*; %quartz = 65% ± 8.0%; %K-feldspar = 6.9% ± 2.1%; %plagioclase = 14% ± 7.3%; %calcite = 4.4% ± 3.2%; and %dolomite = 8.5% ± 1.7%.

The average percentages and std deviations for each mineral from the <2µm slide preparations were %expandables= 63% ± 4.5%; %illite = 30% ± 4.4%; %kaolinite+chlorite = 7.1% ± 0.6%; %kaolinite = 3.1% ± 0.4%; %chlorite = 4.0% ± 0.5%.

The expandables that we calculate is roughly equivalent to smectite or montmorillonite. The Glass method normally reports a percentage for kaolinite and chlorite together, while our work on the Scintag normally allows us to separate out a percentage for each of the individual minerals. Both methods are reported in the table.

*Note: Only 4 samples showed detectable hornblende.

Determining the ratio of clay to nonclay minerals.

Ideally, bulk percentages of each of the minerals in a sample can be estimated by xraying a random bulk powder of the sample. However, the clay mineral intensities from samples such as these would be too low to provide meaningful percentages. We use a combination of methods to precisely define the clay and nonclay mineral fractions, and various methods can be used to determine the absolute nonclay percentages and then convert the clay mineral percentages to bulk percentages. The simplest estimate of clay-to-nonclay mineral ratios is the clay index (CI), and it has been used here.

The next-easiest way to improve the estimate of clays to nonclays would be to make an XRD of a random bulk powder of the sample, and then determine the total percent carbonate minerals by dissolving them with acetic acid and determining the weight loss due to dissolution. A nonclay factor is calculated as the % carbonates by weight loss divided by the % carbonates calculated from XRD on a 100% basis. This factor is multiplied by each of the nonclay mineral percentages from XRD, and the bulk percentage of clay minerals is determined as 100 – the sum of the absolute percentages of nonclay minerals. The 100%-basis clay mineral percentages from XRD of a smear preparation can be proportioned into absolute percentages. This calculation would be improved by separating out a finer size fraction such as <16µm, although a series of sizes would have to be tested to ensure that the top size was coarse enough to include all the clay minerals in the samples. It is also possible to use an XRD peak common to all the clay minerals to estimate total clay mineral percentages from a random bulk preparation.

The data from these determinations are well within the expected range of composition of these materials. The variation between different samples appears to be within the normal variation for these sediments.

Appendix D References

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Moore, D.M., and Reynolds, R.C., Jr. (1997). X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Second Edition. New York: Oxford University Press.

Table D-1. Summary of XRD results.

ISGS Sample No	ISWS Sample No.	%E	%I	%K+C	%K	%C	%H	%Q	%Kf	%Pf	%Cc	%D	CI
6A196ASMG	RM177, 0-6cm	50	32	18	4.4	14	0.0	65	10	12	2.2	10	0.77
6A196BSMG	RM177, 24-30cm	56	29	15	3.7	12	1.9	73	4.9	10	1.1	8.6	0.82
6A196CSMG	RM171, 0-6cm	60	23	16	3.9	12	0.7	61	5.5	14	11	8.5	0.73
6A196DSMG	RM171, 24-30cm	42	36	22	8.4	14	0.0	63	6.5	20	2.0	9.2	0.75
6A196ESMG	RM169, 0-6cm	53	27	20	6.8	13	0.0	64	11	10	4.5	11	0.78
6A196FSMG	RM169, 24-30cm	56	27	17	7.1	10	1.9	49	4.6	31	8.6	4.9	0.80
6A196GSMG	RM164, 0-6cm	66	21	13	4.0	8.9	0.9	76	6.4	6.2	2.5	7.9	0.84
6A196HSMG	RM164, 24-30cm	59	25	17	4.7	12	0.0	71	6.9	10	4.1	8.0	0.85
	average	55	27	17	5.4	12	0.7	65	6.9	14	4.4	8.5	0.79
	std dev	6.8	4.5	2.6	1.7	1.6	0.8	7.9	2.1	7.3	3.2	1.7	0.04
Key: %E, I, K+C, K, and C = % expandables, illite, kaolinite + chlorite, kaolinite (alone), and chlorite (alone);													
	%H, Q, Kf, Pf, Cc, and D = % hornblende, quartz, K-feldspar, plagioclase feldspar, calcite and dolomite.												
	CI is the clay index = corr. Sum of clay intensities/(corr sum clays + corr sum nonclay intensities).												
Samples are <2um sedimented slides.	**Station, depth interval**	%E	%I	%K+C	%K	%C		No meaningful calculations are					
6A196A2g	RM177, 0-6cm	65	29	5.9	2.9	2.9		possible for nonclays, CI.					
6A196B2g	RM177, 24-30cm	58	35	7.1	3.2	3.8							
6A196C2g	RM171, 0-6cm	60	32	7.8	3.0	4.7							
6A196D2g	RM171, 24-30cm	58	34	7.8	3.5	4.2							
6A196E2g	RM169, 0-6cm	67	27	6.5	2.5	4.1							
6A196F2g	RM169, 24-30cm	60	32	7.3	3.6	3.7							
6A196G2g	RM164, 0-6cm	72	21	7.3	3.4	3.9							
6A196H2g	RM164, 24-30cm	64	29	7.4	2.9	4.5							
	average	63	30	7.1	3.1	4.0							
Key: As at top.	**std dev**	4.5	4.4	0.6	0.4	0.5							
Data calculated with H.D. Glass's method (By Phil DeMaris) 7/25/01													
Samples are sedimented <2µm slides, xrayed after 2 days solvation in ethylene glycol.	**Station, depth interval**												
ISGS Sample No	ISWS Sample No.	%E	%I	%K+C	Cc#	D#	DI	VI					
6A196ASMG	RM177, 0-6cm	58	32	10	20	29	2.2	-					
6A196BSMG	RM177, 24-30cm	46	39	14	-	-	1.9	40+					
6A196CSMG	RM171, 0-6cm	61	30	9	-	-	2.2	43+					
6A196DSMG	RM171, 24-30cm	47	40	13	-	-	2.1	31+					
6A196ESMG	RM169, 0-6cm	58	31	11	?	?	1.9	?					
6A196FSMG	RM169, 24-30cm	55	35	10	-	?	2.3	39+					
6A196GSMG	RM164, 0-6cm	53	37	10	12	13	2.4	?					
6A196HSMG	RM164, 24-30cm	60	29	11	17	21	1.8	42+					
	average	55	34	11	16	21	2	39					
	std dev	5.7	4.2	1.7	4.0	8.0	0.2	4.7					
Key: %E, I, K+C = % expandables, illite, kaolinite + chlorite; Cc# and D# = peak counts for calcite and dolomite;													
DI and VI = diffraction and vermiculite indices, respectively (Hughes & Warren, 1989, ISGS IMN 102, p. 47-57.													


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