Metal(loid) Cycling in Mine-Impacted Sediments of the Northern Idaho Coeur d'Alene River Basin

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AUTHORIZATION TO SUBMIT DISSERTATION

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ABSTRACT

Mining activity along the South Fork of the Coeur d'Alene (CDA) River in northern Idaho has resulted in mine tailings enriched in Pb, As, Ag, Sb, Hg, Cd, and Zn that have contaminated broad areas of the CDA River floodplain and Lake CDA. Without a clear understanding of contaminant redistribution, tailings transport, and metal cycling within this region, sound management decisions to protect environmental quality are difficult. Our objective was to better define the biogeochemical reactions controlling toxic metal cycling within sediments of Lake CDA and wetlands in the Basin. Sediment from contaminated sites in the Lake and Basin wetlands were collected as cores and interstitial water samples obtained using equilibrium dialyzers. Solid phase associations of Fe, S, and As were probed using x-ray absorption (XAS) spectroscopy. In Lake CDA sediments we identified a gradient from oxic conditions at the sediment-water interface to anoxic conditions below 10 cm, thus creating a dynamic redox environment that controls metal(loid) sorption and solubility. The oxic cap at the sediment-water interface traps many of the contaminant metal(loids) decreasing their flux into the overlying water column. However, flood events bury the oxic cap materials transitioning them to a suboxic zone in which reductive dissolution of the oxides releases metal(loid)s into the sediment interstitial water. High Fe:S ratios inhibit the formation of metal(loid)-containing sulfide precipitates in the anoxic zone, thus resulting in chronically and acutely toxic concentrations of soluble metals within the sediment interstitial water. In contrast, constantly saturated wetlands within the Basin do not maintain an oxic sediment cap and concentrations of metal(loid)s in sediment interstitial waters are consequently much lower than those in Lake CDA sediments. This series of reactions and processes presents a dilemma for lake management since promoting reduced conditions at the sediment-water interface in Lake CDA is an unacceptable method to decrease porewater metal(loid) concentrations. Decreased soluble metal(loid) concentrations in the sediments will only occur by minimizing the transport of contaminated materials to Lake CDA.

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TABLE OF CONTENTS

CHAPTER 1

Metal(Loid) Diagenesis In Mine-Impacted Sediments Of Lake Coeur d'Alene, Idaho

CHAPTER 2

Arsenic Cycling In Freshwater Sediments Of Lake Coeur d'Alene, Idaho

CHAPTER 3

Internal Cycling And Benthic Flux Of Trace-Metals In Mine-Waste Impacted Sediments Of Lake Coeur d'Alene, Idaho

CHAPTER 4

Seasonal Redox Changes And Impact On Stability Of Mine-Waste, Lower Coeur d'Alene River, Idaho

APPENDIX

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

Metal(loid) Diagenesis in Mine-Impacted Sediments of Lake Coeur d'Alene, Idaho[1]

ABSTRACT

Mining activity along the South Fork of the Coeur d'Alene River in northern Idaho has resulted in fluvial mine tailings enriched in Pb, As, Ag, Sb, Hg, Cd, and Zn deposited on the lakebed of Lake Coeur d'Alene, thus serving as a potential benthic source of inorganic contaminants. Our objective was to characterize the dominant solid phase materials and diagenetic processes controlling metal(loid) solubilities, and thus their potential release to the overlying water column. Aqueous and solid concentrations of metal(loid) contaminants were examined along with distinct species of Fe and S within sediments and interstitial water. A gradient from oxic conditions at the sediment-water interface to anoxic conditions below 15 cm exists at all sites, resulting in a dynamic redox environment that controls the partitioning of contaminants. Fluvial deposition from frequent seasonal flood events bury ferric oxides residing at the sediment-water interface leading to reductive dissolution as they transition to the anoxic zone, consequently releasing associated metal(loids) to the interstitial water. Insufficient sulfur limits the formation of sulfidic minerals, but high carbonate content of this mining region buffers pH and promotes formation of siderite. Diagenetic reactions create

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[1] Toevs, Gordon R., Morra, Matthew J. Polizzotto, Matthew L., Strawn, Daniel G., Bostick, Benjamin C., and Fendorf, Scott, (2006), Metal(loid) diagenesis in mine-impacted sediments of Lake Coeur d'Alene, Idaho. Environmental Science and Technology, 40, 2537-2543.

chemical gradients encouraging the diffusion of metal(loids) toward the sediment-water interface, thereby increasing the potential for release into the overlying water.

INTRODUCTION

During the first two-thirds of the 20th century mining in northern Idaho produced over 31 100 metric tons of silver and 7.26 million metric tons of lead (Hoffman 1995), with much of this activity taking place along the South Fork of the Coeur d'Alene (CDA) River in a region known as the Silver Valley (Figure 1.1). Wastes from mining and ore-processing activities were disposed directly into the South Fork of the CDA River, resulting in discharge estimates of mine and mill slimes of over 2 000 metric tons per day in 1964. Until the establishment of tailings ponds in 1968, mine tailings containing high concentrations of Pb, Zn, As, and other trace elements accumulated in stream banks or bars along the river. This material was subsequently transported by river flow and flood events, and distributed throughout the lower CDA River floodplain (Bender 1991). Although mining activities and mining discharges are minimal today, erosion and flood events continue to suspend and transport contaminated material throughout the floodplain and into Lake CDA.

Extensive sampling has confirmed that sediments within Lake CDA are enriched in Ag, As, Cd, Hg, Pb, Sb, and Zn with contamination varying in thickness from a minimum of 17 to a maximum of 119 cm (Horowitz et al. 1992; Horowitz et al. 1993b). In spite of this contamination, lake water quality typically meets state and federal guidelines. The USGS analyzed samples from the euphotic zone and lower hypolimnion collected during a 4-year study that began in 1990 (Woods et al. 1997), finding that concentrations of As, Cd, Hg, Cu, Pb, and Zn never exceeded aquatic, primary contact for recreation, or domestic water supply criteria. The Idaho Department of Environmental Quality continued to monitor the euphotic zone for Cd, Pb, and Zn and found similar results (Rothrock 2004). However, the median concentrations of Cu, Pb, and Zn in the interstitial water of the sediments were considered chronically or acutely toxic, suggesting dynamic redox-induced cycling of contaminants within the sediments.

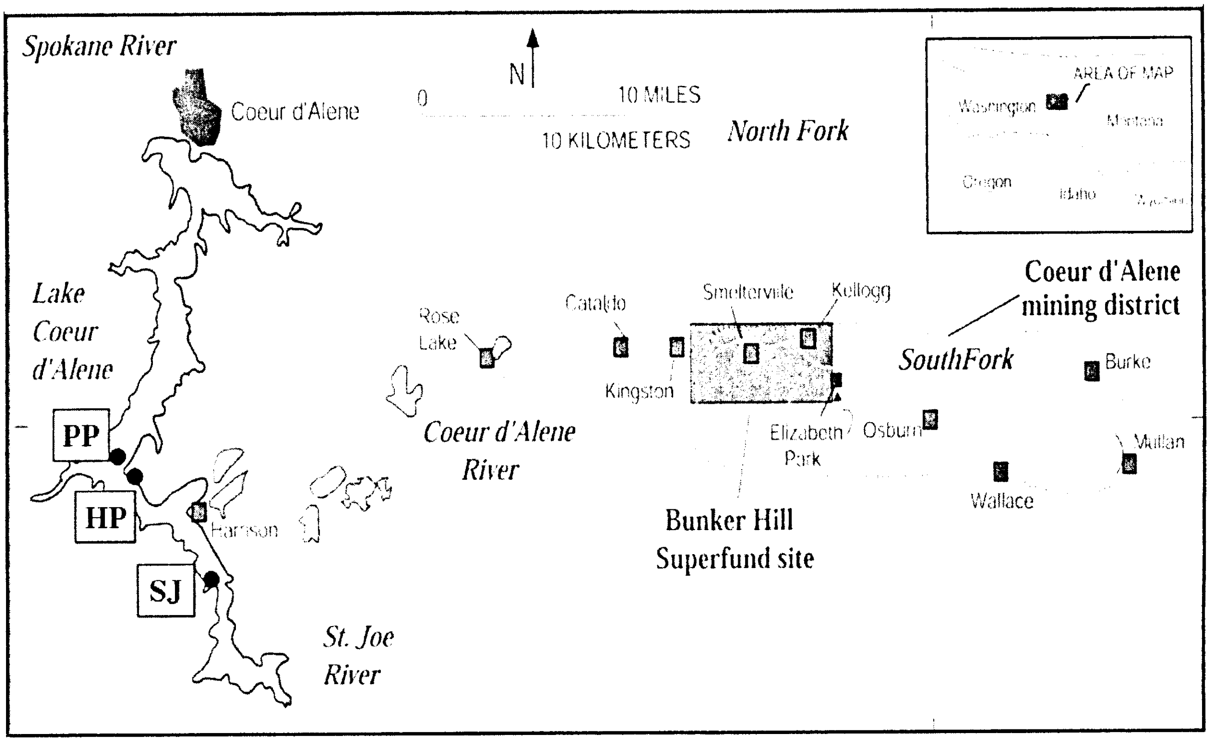

Figure 1.1. Location of the study area in northern Idaho (upper right), Coeur d'Alene (CDA) mining district (inside dotted line), Bunker Hill Superfund Site (inside shaded box), CDA River, two mine waste-impacted sites (HP and PP), and the non-impacted site (SJ) within Lake CDA.

Prior research to characterize sediment geochemistry has produced inconsistent and contradictory results (Horowitz et al. 1999). Surface sediment grab samples collected in Lake CDA and analyzed using selective sequential extraction indicate 95% of the Pb, 90% of the Cd, 80% of the Zn, 75% of the As, and 55% of the Cu are associated with an operationally defined iron oxide phase (Horowitz et al. 1993b). Selective sequential extractions performed on gravity cores from a variety of depositional environments indicated only minor association of metal(loids) with sulfide minerals (Horowitz et al. 1993a). However, others have identified sulfide minerals in sediment cores from Lake CDA and found 50% of the Pb, 63% of the Zn, and 73% of the As are associated with an operationally defined sulfidic phase (Harrington et al. 1998).

One factor contributing to this controversy is the lack of definitive data concerning sediment diagenesis as related to redox changes and sediment depth. Our objective was to characterize Lake CDA sediments using spectroscopic techniques combined with *in situ* interstitial water data, thereby identifying the dominant solid phase minerals and diagenetic processes controlling interstitial water metal(loid) concentrations. This is crucial given that recent studies have confirmed that the sediments are a significant source of contaminant flux (Balistrieri 1998; Kuwabara et al. 2003). Ultimately, our results will facilitate the prediction of contaminant release from the sediments to the overlying water column occurring as a result of redox changes. This is especially important given that increased use of local water resources and population growth in the watershed will likely augment nutrient loading to the Lake.

MATERIALS AND METHODS

Sample Sites.

Two sample sites, Harlow Point (HP) and Peaceful Point (PP), were located in the southern portion of Lake CDA within 1 km of the mouth of the CDA River in an area highly impacted by heavy metals and metalloids (Horowitz et al. 1992; Horowitz et al. 1993a). Since the dominant flow of the Lake is north, a control site was established at the uncontaminated southern end of Lake CDA near the mouth of the relatively pristine St. Joe (SJ) River (Figure 1.1). The water depths at SJ, PP, and HP averaged 6, 19, and 15 m, respectively. Although only data from the May 2002 deployment are presented, similar trends in interstitial water constituents were observed in five additional dialyzer deployments performed from 2001 to 2002.

Materials.

All chemicals were reagent grade and used without further purification. Solutions were prepared using distilled, deionized water. All sampling containers and labware were cleaned with 2% HNO_3 and thoroughly rinsed with deionized water prior to use. Analytical standards and quality assurance standards for ion chromatography (IC) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were purchased from Spex CertiPrep (Metuchen, NJ). Standard Reference Material 2711 from the National Institute of Standards and Technology (Gaithersburg, MD) was used as the total metals standard. Acids used for total metals were all trace-metal grade (Fisher Scientific, Pittsburgh, PA).

Sampling Devices.

Interstitial water was collected *in situ* utilizing Plexiglas equilibrium, dialysis samplers (Hesslein 1976). The dialyzers contained two rows of 25, 10-mL compartments milled on 1.5-cm centers. The compartments were covered with 0.2-µm Osmonics nylon membrane (Westborough, MA), nylon tulle netting, and a matching cover plate held in place with nylon screws. Cores were collected in polycarbonate tubes 10 cm in diameter and 50 cm in length, which upon sample collection were immediately capped on one end with a size 10 rubber stopper and the other with a Fernco style Quickcap (Davison, MI).

Sample Retrieval and Preservation.

Scuba divers inserted the dialyzers vertically into the sediment where they were allowed to equilibrate for 4 weeks, a time deemed appropriate based on field and laboratory studies (Balistrieri 1998; La Force et al. 2000; Winowiecki 2002). Upon retrieval, they were immediately transferred to a boat waiting at the sample site, where interstitial water for anion analysis was removed from the dialyzer cells using a 10-mL syringe and preserved in a sample vial under anaerobic conditions at 4 °C. Interstitial water for cation analysis was removed in a similar fashion and placed in a sample vial containing 4 drops of trace metal grade HNO_3 to maintain a pH of less than 2.5. Cores obtained at the same time were sealed to prevent leaks and oxidation, packed in an airtight container with ice packs, and purged with N_2.

Once in the laboratory, the sediment cores were transferred to an N_2-filled glove box and extruded from the coring tubes with care taken to avoid compaction or elongation. Cores were sub-sectioned at the appropriate depths and homogenized samples placed in vials. The vials were frozen until analysis by X-ray absorption spectroscopy (XAS). Sub-samples for total metals were thawed, transferred to acid-washed crucibles, and dried at 90 °C until a stable weight was achieved. The dry samples were cooled in desiccators, ground with a mortar and pestle, transferred to 10-mL polyethylene vials, and stored in desiccators until analyses were performed.

Analytical Methods.

Samples were microwave-digested with a 9:2:3 ratio of HNO_3, HCl, and HF in accordance with EPA method 3052 (Staff 1994). Recovery precision and accuracy, performed in triplicate on the Standard Reference Material 2711, indicated a relative standard deviation (RSD) of less than 3% and an extraction efficiency greater than 90% for all elements. Triplicate unknown samples were run in each batch digestion and the RSD was generally less than 5%. The digest was filtered using a 0.2-µm Gelman IC Acrodisc syringe filter (Ann Arbor, MI) and volumetrically diluted to 50 mL in preparation for analysis.

Interstitial water anion analyses were performed on a Dionex 500DX Ion Chromatograph fitted with an AS11 Ion Pac column, an AG11 4-mm guard column, and a MFC-1 Metal Trap. The flow rate was 1.0 mL min^{-1} of a 50 mM NaOH eluent. Interstitial water metal(loid) analyses were performed on a Thermal Jarrell Ash ICP-AES. The RSD, as determined by running a standard 10 times, calculating the average, and dividing it into the standard deviation, was less than 4% across all analyses.

Powder XRD patterns were obtained with a Siemens D5000 Diffraktometer system using CuKα radiation operated at 40kV, 30 μA with a fixed 1.0-mm slit and solid-state detector. XRD measurements were taken from 5 to 65 °2θ and a step size of 0.02° 2θ 8.2 sec^{-1}. The Siemens Diffrac^{Plus} Standard (Bruker AXS Inc., Madison, WI) program V2.30 was used for processing data.

Sulfur X-ray absorption near-edge structure (XANES) spectroscopy analyses were conducted at the National Synchrotron Light Source (NSLS) Brookhaven National Laboratory, NY on beamline X-19A under ambient (moist, He-purged) conditions using similar methods to those of Bostick et al. (2005). Homogenized samples from each depth, which had been stored at 4 °C, were mounted onto Glass-fiber filter paper (sulfur-free) and spectra were collected in fluorescence mode using a 1-element PIPS detector. Chemical speciation of sulfur was determined by comparing the spectra of unknowns with reference materials including FeS, FeS_2, methionine, elemental sulfur, thiosulfate, sulfite, cysteic acid, and sulfate (Bostick et al. 2005). Sulfur species were quantified using WinXAS (Ressler 1998), linear combination, and peak fitting (Huffman et al. 1991; Waldo et al. 1991; Beauchemin et al. 2002). Prior to the fitting, the spectral background was removed and the spectra were normalized to the post edge. Initially, all reasonable sulfur standards were included in fitting; standards that were consistently fit with negative or zero fractional contributions were removed from the standard set to reduce the number of variables employed in fitting. Only the XANES region of the spectrum (2465 to 2490 eV) was used in fitting. The quality of fit was inferred from both χ^2 statistics between 200 and 300 and residuals between 5 and 10. The resulting quantification error was ±5%.

Iron XANES and extended X-ray absorption fine structure (EXAFS) spectroscopy analyses were conducted at the Stanford Synchrotron Radiation Laboratory, Menlo Park, CA on beamline 4-3 (8 pole wiggler). Sediments were thawed in an N_2-filled glovebox, packed into Teflon sample holders, and covered with Kapton® tape. Energy selection was maintained by a Si (220) monochromator and energy calibration was performed by assigning a K_α edge position of 7111.0 eV to an in-line Fe(0) metal foil standard. The incident beam was detuned ~50% to reduce contributions from upper-order harmonic energies. Energy scans for XANES analyses were collected from 7050 eV to 7300 eV and energy scans for EXAFS analyses were collected from –200 to +1000 eV about the Fe foil edge; 5 to 6 scans were averaged per sample. Sample EXAFS fluorescence spectra were averaged, background subtracted, and normalized. A spline function was fit through the absorption envelope and subtracted from each spectrum. The resulting EXAFS function (χ) was transformed from eV to k-space (Å^{-1}) and weighted by k^3.

Iron EXAFS and XANES spectra of model compounds were obtained and analyzed in the same manner as unknowns. Known samples included ferrihydrite, goethite, hematite, lepidocrocite, magnetite, green rust-sulfate, green rust-chloride, green rust-carbonate, siderite, vivianite, biotite, hornblende, mackinawite, pyrrhotite, and pyrite. Iron XANES linear combination fitting was performed to determine Fe(II):Fe(III) ratios in the unknown samples.

The accuracy of mineral quantification in natural sediments using linear combination fitting of Fe-XANES and Fe-EXAFS spectra is dependent on the ratio of those minerals having differing densities and mass absorptions, such as Fe-containing sulfides and phyllosilicates. The ratio becomes problematic only when these two fractions have similar abundances in total Fe, but is minimal when one fraction greatly exceeds the other (O'Day et al. 2004). The use of linear combination fitting for mineral quantification in CDA sediments is thus valid as phyllosilicate Fe is 20 times the concentration of sulfidic Fe (Supporting Information Figure 1.9 and Figure 1.3). XRD patterns and EXAFS spectra were used to constrain components for XANES linear combination fitting. Ferrihydrite was used as a proxy for Fe(III) and illite for Fe-phyllosilicate minerals in all sediment samples. Siderite was used as a proxy for Fe(II) in PP and HP sediments and vivianite in SJ sediments. These proxies were used to fit the first-derivative Fe XANES spectra and the Fe(II) to Fe(III) ratio was then determined after subtracting any contribution of the less reactive Fe phyllosilicates.

RESULTS AND DISCUSSION

Element Abundance.

Cores collected near the mouth of the CDA River were substantially enriched in As, Cd, Pb, Zn, Fe, Mn, and S as compared to the non-mining-impacted SJ site (Table 1.1). Measured concentrations of these elements (mmol kg^{-1} ± SE when available, n=2 for this study) fell within the range of previously reported concentrations for Lake CDA sediments: As 1.37 (Horowitz et al. 1995) and 2.68±0.15 (Harrington et al. 1998); Cd 0.222 (Horowitz et al. 1995) and 0.383±0.15 (Maxfield et al. 1974); Pb 15.44 (Horowitz et al. 1995), 18.33±1.16 (Harrington et al. 1998), and 17.86±4.39 (Maxfield et al. 1974); and Zn 36.72 (Horowitz et al. 1995), 45.82±1.91 (Harrington et al. 1998), and 58.13±6.58 (Maxfield et al. 1974).

Redox Conditions.

Identifying the exact sample-cell location at which the sediment-water interface occurs is difficult because it is typically a diffuse and variably stratified boundary (Koschorreck et al. 2003). Lake CDA presents an additional challenge since limited visibility exists on the lake bottom and intermittently aggressive currents are experienced during sampler placement and retrieval. Approximate location of the interface as marked by divers prior to removing the dialyzers and visual signs of sediment contact on the dialyzers upon examination at the surface helped identify the position of the sediment-water interface. Nitrate was only detected in the overlying water column or occasionally in interstitial water near the sediment-water interface (Figure 1.2). Manganese reduction commenced at or just below the sediment-water interface. Interstitial water Mn reached its near-maximum concentration by 5 cm and remained relatively constant with increasing depth. Interstitial water Fe concentrations increased throughout the entire 36-cm profile from the initial detection depth at or within a few centimeters of the sediment water interface. Sulfate concentrations fell below detection limits within 10 cm of the sediment-water interface at PP and HP and within 15 cm at SJ (Figure 1.2). The data in Figure 1.2 are an average of two cells in adjacent dialyzers. In order to indicate the consistency of the trends and variability of the data, both data points for the HP site are shown in Supporting Information Figure 1.5.

Table 1.1. Mean and standard error (n=2) of select element concentrations in Lake Coeur d'Alene near surface sediments collected in May of 2002.

Site/Depth (cm)	Element (mmol kg^{-1})						
	As	Cd	Fe	Mn	Pb	S	Zn
St. Joe							
3-6	0.24±0.05	0.00±0.00	647±21	8.37±1.36	0.137±0.03	21.7±1.7	2.00±0.33
12-18	0.19±0.03	0.00±0.00	605±5	7.21±0.16	0.108±0.01	20.4±1.4	2.09±0.07
24-30	0.18±0.02	0.00±0.00	519±13	7.99±0.01	0.083±0.03	12.8±1.3	1.61±0.07
Peaceful Point							
0-3	4.01±1.98	0.23±0.03	1259±31	123±11	16.5±0.36	46.5±11	48.1±3.7
3-6	1.59±0.20	0.31±0.03	892±79	64.9±0.4	10.0±1.4	47.1±0.31	39.7±3.5
6-12	3.58±0.12	0.33±0.06	1869±3	171±0.8	11.8±0.35	97.4±4.3	42.1±4.3
12-18	2.81±0.42	0.22±0.08	1717±271	154±34	16.1±3.7	110.5±18	44.1±2.8
18-24	2.09±0.39	0.21±0.01	1567±46	150±0.7	23.1±8.2	114±9.1	53.0±9.4
24-30	1.83±0.17	0.20±0.01	1618±33	141±1	28.3±5.1	122±3.3	56.7±5.4
Harlow Point							
0-3	1.90±0.42	0.21±0.00	1377±39	98.9±11	21.0±1.7	95.1±17	51.7±2.7
3-6	1.76±0.45	0.20±0.00	1420±101	104±9.8	21.5±2.4	109±16	51.8±2.6
6-12	1.67±0.15	0.22±0.00	1444±39	114±2.1	24.0±1.5	136±3.0	56.1±1.2
12-18	1.89±0.28	0.25±0.02	1368±41	96.7±13	22.4±0.89	135±6.7	56.1±2.2
18-24	2.11±0.24	0.32±0.05	1343±108	93.7±22	19.6±2.5	126±13	52.6±3.5
24-30	3.04±1.58	0.293±0.03	1529±410	125±47	18.7±5.1	141±60	49.9±11

Several notable differences in chemical composition exist between interstitial water samples obtained from the non-impacted site (SJ) when compared to the contaminated sites (PP and HP). Maximum SO_4^{2-}-S concentrations in the contaminated sites (0.059-0.066 mmol L^{-1}) were higher than those measured in interstitial water samples from the SJ site (0.012 mmol L^{-1}). Manganese concentrations in the contaminated sites were also elevated with HP and PP showing maximum Mn concentrations (0.15 mmol L^{-1} and 0.38 mmol L^{-1}, respectively) 2.6 and 6.6 times greater than those measured in SJ interstitial water (0.058 mmol L^{-1}). In contrast, Fe concentrations in SJ interstitial waters exceeded those of the contaminated sites, despite its having sediment Fe concentrations one-half those of the contaminated sites (Table 1.1).

Redox profiles indicate suboxic conditions exist within the top few centimeters of the sediment-water interface at all sites and that sediments become increasingly anoxic in the remainder of the profiles (Figure 1.2). This is significant, since it is in the suboxic zone (Froelich et al. 1979) that metals coprecipitated with oxyhydroxides are released into the interstitial water through the process of reductive dissolution. Prior research conducted on Lake CDA sediments has variously identified the suboxic zone to occur between 10 and 15 cm from the interface (Horowitz et al. 1993b), within 5 cm of the interface (Balistrieri 1998; La Force et al. 1999), and at the interface (Harrington et al. 1998). Our research confirms that the suboxic zone occurs within 5 cm of the sediment-water interface, indicating that redox conditions control the release of metal contaminants associated with those minerals undergoing reductive dissolution.

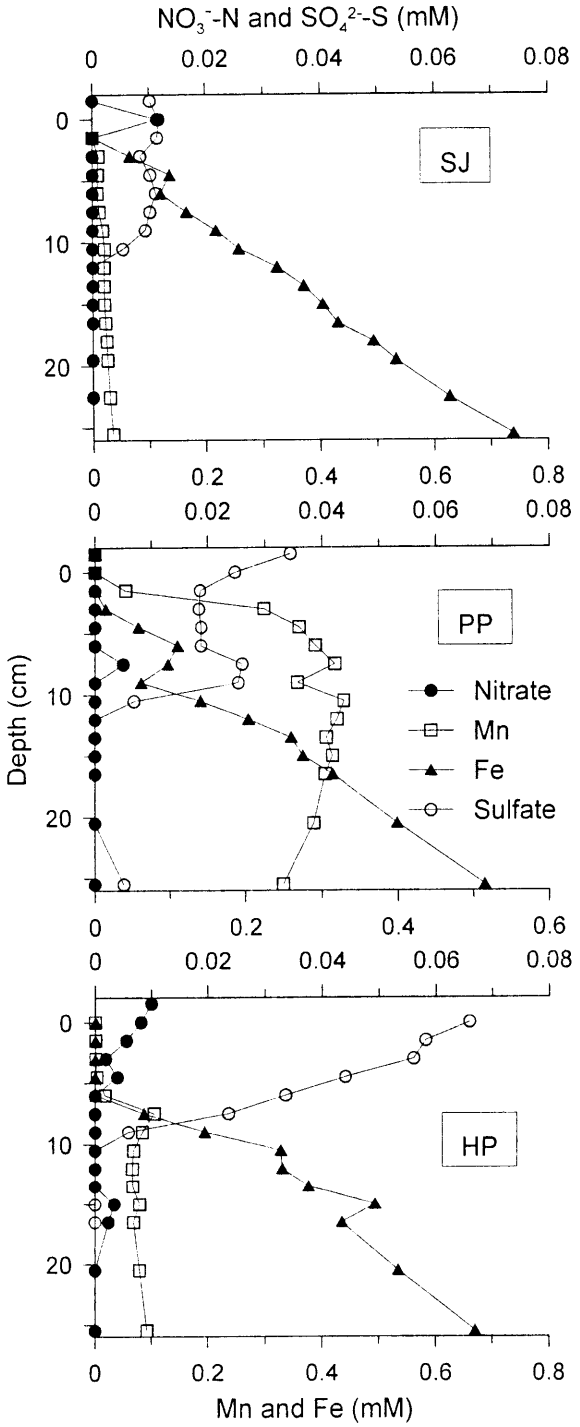

Figure 1.2. Concentrations of redox sensitive species in Lake Coeur d'Alene sediment interstitial water at the control site (SJ) and the two contaminated sites (PP and HP). Each point is an average of two samples obtained from adjacent equilibrium dialyzers in May 2002. Depth increments less than zero (0) indicate concentration above the sediment-water interface. Refer to Supporting Information Figure 1.5 for sample variability.

Sediment Sulfur.

Total sulfur concentrations in sediments obtained at the two contaminated sites (PP and HP) are approximately three to nine times higher than those of the control-site (SJ) (Table 1.1, Supporting Information Figure 1.6). This dissimilarity is expected given the difference in land-use practices occurring within the respective watersheds. Agriculture and logging impact sediment loads in drainages of the SJ watershed, whereas mining activity is the principal determinant of sediment quality for those materials deposited at PP and HP (Horowitz et al. 1993b). The main economic minerals have historically been galena (PbS), sphalerite (ZnS), and argentiferous tetrahedrite [$(Cu,Fe)12Sb_4 S_{13}$]. Most veins contained small amounts of chalcopyrite ($CuFeS_2$), but pyrite (FeS_2) varied among mineral veins (Balistrieri et al. 1999).

Sediment sulfur was speciated in an attempt to identify specific components of the sediment solid phase that potentially participate in metal(loid) retention. XANES data clearly indicate that pyrite was the principle S mineral detected at the contaminated sites (Figure 1.3, Supporting Information Figure 1.8). Although a detrital origin of pyrite is possible (Moore 1994), its presence is more likely explained by diagenetic processes occurring within the sediments. This conclusion is supported by the fact that the control site (SJ) sediments, which are not influenced by mining activity, also contain pyrite at all depths. Other investigators have measured pyrite in the top 0 to 3 cm of lake sediments not subjected to the deposition of mine tailings, although to our knowledge only indirect methods involving selective extraction or dissolution were used (Nriagu et al. 1985; Rudd et al. 1986; Huerta-Diaz et al. 1998).

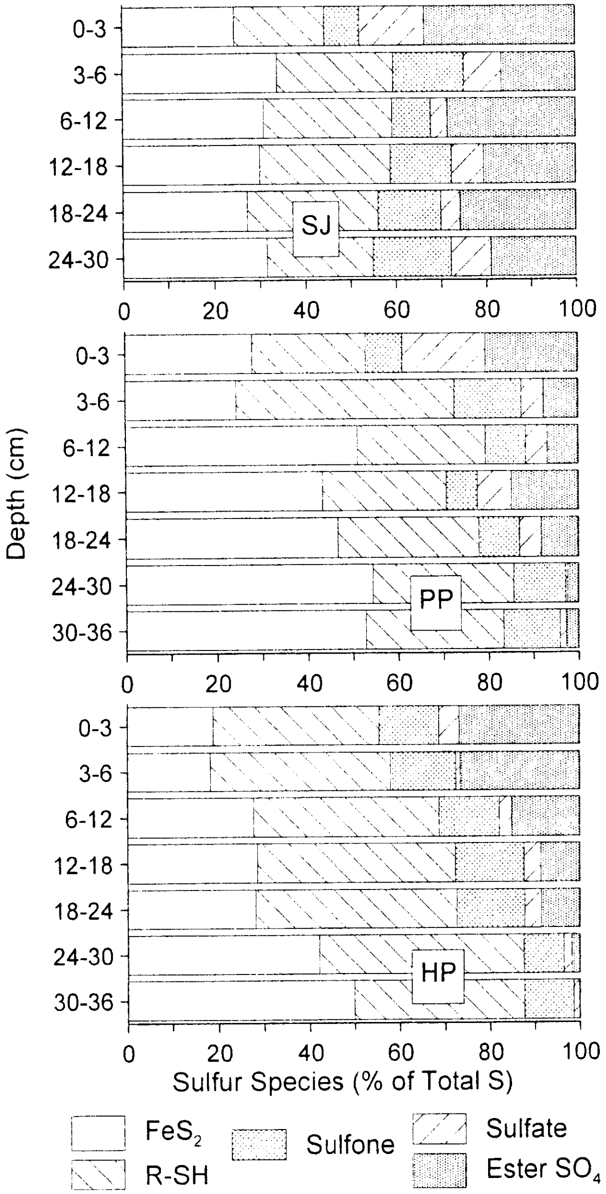

Figure 1.3. Comparison of S species as determined by S-XANES analyses of Lake Coeur d'Alene sediments at the contaminated sites (PP and HP) and the control site (SJ). Data shown for each depth are an average of two spectra from adjacent cores collected May 2002 and have a fitting accuracy of ±5%. Maximum total sulfur within all sediments was less than 0.5% by weight.

Differences in sedimentation rates and pyrite concentrations with depth also point to diagenetic pyrite formation. The sedimentation rate at HP is approximately 0.95 cm yr^{-1}, but only 0.26 cm yr^{-1} at PP (Horowitz et al. 1993a). These sedimentation rates indicate that the top 6 cm of sediment at PP was deposited during the same time period as 24 cm of sediment at HP. This is consistent with the observation that sediment pyrite within these depths comprises 20 to 30% of the total S pool at both sites (Figure 1.3). Greater amounts of pyrite representing between 40 and 50% of the total S occur at depths greater than 6 cm at PP and 24 cm at HP. Such a relationship is anticipated if pyrite is indeed of diagenetic origin, since its production and ultimate distribution within the sediments will be a function of burial time. This trend in pyrite concentration with depth is indeed observed at the PP and HP sites, but is lacking at the uncontaminated SJ site possibly as a result of bioturbation (Boudreau et al. 2001).

Ester bound sulfate decreased with depth at all sites from a high of 34% in the 0- to 3-cm SJ sample to a low of 0.1% in the 30- to 36-cm sample from HP (Figure 1.3). Sulfur in oxidation states consistent with thiols and sulfones showed relatively small changes in percentages of the total sulfur with depth at each site. Increased pyrite percentages with depth are consistently accompanied by a corresponding decrease in organic ester sulfate species. Thus, diagenetic alteration of ester-bound sulfate may be important in the generation of pyrite in these sediments.

Ester sulfate is the most transitory of the organic S pools in sediments and soils (Nriagu et al. 1985; Groscheova et al. 2000), supporting our observation that its contribution to sediment S decreases with depth. Two possibilities exist to explain its disappearance; both pathways ultimately resulting in reduced products potentially involved in FeS_2 formation. In the first of these pathways, ester sulfate is first hydrolyzed by sulfatase enzymes releasing SO_4^{2-} that is subsequently used as a terminal electron acceptor (King et al. 1980; Nriagu et al. 1985; Groscheova et al. 2000). Alternatively, organic oxysulfur compounds such as ester sulfates may serve directly as terminal electron acceptors, generating HS^- or organic sulfides (Altschuler et al. 1983). Although the pathways by which FeS_2 is ultimately formed remain unresolved (Wilkin et al. 1996; Butler et al. 2000), our data indicate that at least a portion of S contained in this mineral originates from the ester sulfate pool.

XANES data indicate the mean value of pyrite in the 30 to 36-cm samples at PP and HP is 50% of the total S (Figure 1.3), which is 34 and 42 mmol FeS_2 kg^{-1} sediment, respectively. The mean Fe concentration at this depth is 1 700 mmol Fe kg^{-1} sediment (Supporting Information Figure 1.7), thus leading to the conclusion that only 2 to 2.5% of the Fe within these samples is associated with pyritic materials. This is surprising given previous investigations using selective sequential extractions indicated that 60 to 70% of the Fe in Lake CDA sediments was associated with an operationally defined sulfidic phase (Harrington et al. 1998). Our results call to question the accuracy of selective sequential extractions and their value in predicting phase partitioning of metal(loid)s. It has been acknowledged that selective sequential extractions are often subject to reprecipitation or readsorption (Belzile et al. 1989), and misinterpretation of results (La Force et al. 2002). This conclusion has significant implications since such extractions also indicated that 60 to 80% of the As, 60 to 70% of the Zn, and 40 to 60% of the Pb are also associated with sulfidic materials (Harrington et al. 1998). Metal(loid) partitioning into and on sulfidic minerals in Lake CDA sediments must be reevaluated given the high Fe to S ratios of the sediments.

Sediment Iron.

The speciation of sedimentary iron, achieved with XAS spectra, offers additional evidence for the diagenesis of sedimentary Fe and S. We chose a conservative approach of fitting the Fe-XANES spectra, relying on XRD and EXAFS (Supporting Information Figures 1.9, 1.10 and 1.11) to constrain the data, and using the minimum number of proxy minerals necessary to quantify Fe(II) and Fe(III) content. Definitive mineral identification is only offered when Fe-EXAFS data were corroborated by Fe-XANES and XRD.

Contaminated sites show an obvious trend in the speciation of solid-phase Fe that reflects changes in sediment redox potentials with depth, with both sites displaying a decrease in Fe(III) minerals below the suboxic boundary and a concomitant increase in Fe(II) solids (Figure 1.4, Supporting Information Figure 1.11). These trends are in agreement with the reducing potential of the sediments as inferred from redox sensitive species in the interstitial water (Figure 1.2). The precipitation of Fe(III) at the sediment-water interface is consistent with an environment of circumneutral pH and oxic conditions (Stumm et al. 1996). The oxic interface is well documented (Horowitz et al. 1993b; Woods et al. 1997) and also supported by our data, as is the circumneutral pH which ranged from 6.0 to 7.4. The pH of the water within this mining district results from a low pyrite to carbonate ratio that buffers the waters of the CDA Basin from the effect of acid-mine drainage (Balistrieri et al. 1999; La Force et al. 2002).

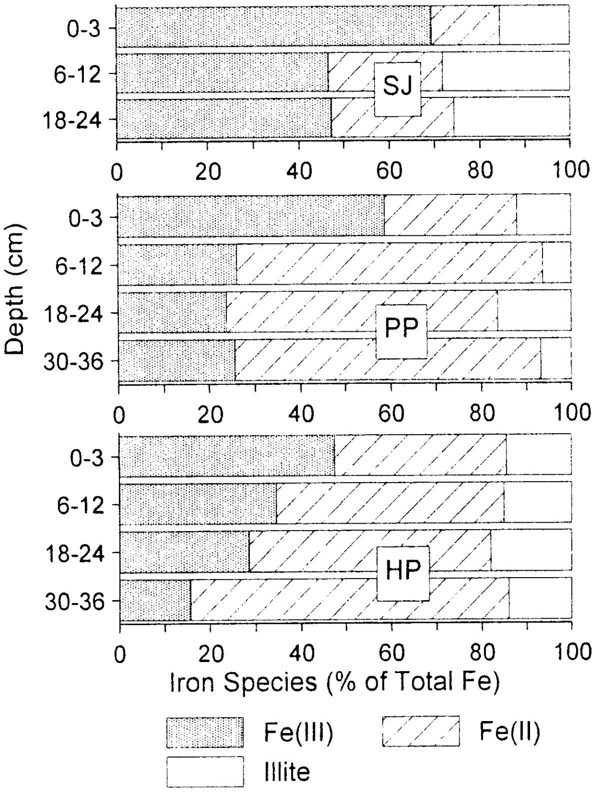

Figure 1.4. Iron XANES analyses of Lake Coeur d'Alene sediments as determined from linear combination fittings of Fe(II) and Fe(III) proxies and illite. Data are from cores collected May 2002 at the control site (SJ) and two contaminated sites (PP and HP). Iron comprised up to 10% of the sample by weight at the contaminated sites.

The Fe(II) to Fe(III) ratio in the sediments at PP and HP increased with depth from 41 to 74% and 52 to 84% of the total iron, respectively (Figure 1.4). A lower deposition rate of 0.26 cm yr^{-1} at PP as compared to 0.95 cm yr^{-1} at HP (Horowitz et al. 1993a) prolongs the residence time of minerals at specific depths in PP sediments, leading to a more distinct demarcation in Fe(II):Fe(III) ratios between sediment samples obtained nearest the sediment-water interface as compared to those secured from lower depths (Figure 1.4 and Supporting Information Figure 1.7). Linear combination of Fe-EXAFS spectra from these sites indicated the majority of the Fe(II) increase was in the form of siderite (Supporting Information Figure 1.9), the presence of which was verified by XRD (Supporting Information Figure 1.10) and XANES (Supporting Information Figure 1.11). Equilibrium speciation performed using

Minteq Visual (USEPA 2004) confirmed siderite was oversaturated below 6 cm at PP and HP. The reduced subsurface environment, high aqueous Fe concentrations (Figure 1.2), and presence of bicarbonate facilitates this precipitation. Dissimilatory metal reducing bacteria (DMRB) have been found in Lake CDA sediments and biological reduction of Fe(III) minerals in the sediments has been verified (Cummings et al. 1999; Cummings et al. 2000). Thus, a cycle of Fe-diagenesis is established where Fe(III) minerals buried by depositional events undergo reductive dissolution in the suboxic and anoxic sediments, forming Fe(II) that precipitates as siderite or diffuses to the oxic zone and reprecipitates as an Fe(III) mineral.

The presence of siderite in surface samples is consistent with its predominance as a gangue mineral in the CDA mining district (Balistrieri et al. 1999) and as such, siderite-rich materials were deposited directly in or nearby the CDA River and its tributaries. Resistance to dissolution is due to circumneutral pH (Duckworth et al. 2004) and active iron cycling which increases the stability field of siderite in oxic environments (Whittemore et al. 1975). This mine-waste material continues to be distributed throughout the basin during flood events, enriching the near-surface sediments with detrital siderite. Thus, continued fluvial deposition accounts for siderite in surface samples at PP and HP and precipitation explains its increase in the anoxic sediments.

Although diagenesis results in a dominance of Fe(II) minerals in the anoxic, contaminated sediments, some Fe(III) minerals persist throughout the sediment cores even at depths of 18-24 cm (Figure 1.4). Bioturbation was not evident at the contaminated sites (Horowitz et al. 1993b) so it is improbable that incorporation of Fe(III) is occurring as a result of this mechanism. However, differential reduction potentials of iron minerals (Stumm et al. 1996), surface passivation (Moore 1994; Roden et al. 1996; Benner et al. 2002), and the inhibitory effect of co-reacted ions, particularly heavy metals on Fe(III), affect its availability for reduction both abiotically and by DMRB (Zachara et al. 2002).

Similar evidence of an oxic sediment-water interface containing the maximum amount of Fe(III) transitioning to suboxic and then anoxic sediments having decreased Fe(III) and increased Fe(II), was obtained for non-mine-impacted SJ sediments (Figure 1.4). However, bioturbation evident at this site (Horowitz et al. 1993a) most likely causes redistribution of solid phase minerals (Boudreau et al. 2001). Although Fe(III) minerals persist in the suboxic and anoxic zones, Fe(III) reduction is extensive, resulting in interstitial water Fe concentrations that are higher than those in contaminated sediments (Figure 1.2) despite the fact that total sediment iron concentrations are lower (Table 1.1). Deposition of mine-impacted sediments at the contaminated sites has thus altered sediment mineralogy such that resulting diagenetic reactions significantly modify interstitial water chemistry as compared to the non-impacted site.

Many diagenetic reactions involving Fe include dissolution (Bingham et al. 2002) such that coprecipitated or sorbed metal(loids) are released into the interstitial water where they become more bioavailable (Di Toro et al. 1992) and free to diffuse into the overlying water column (Balistrieri 1998). Alternatively, these ions may be scavenged by oxides (Benner et al. 2002; Zachara et al. 2002) or precipitate as sulfides at the anoxic boundary (Di Toro et al. 1992), the later being unlikely in Lake CDA sediments because of high Fe to S ratios. Ferric (hydr)oxides at the sediment water interface thus restrict contaminant migration, but diagenetic reactions that occur during sediment burial and exposure to reducing conditions release metal(loid)s into the interstitial water. Metal(loid) cycling between the solid and aqueous phases in Lake CDA is thus a dynamic process intimately tied to diagenetic reactions involving Fe minerals within the sediments.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

Figures of Replicate samples of redox sensitive elements; total sulfur and total iron by weight, S-XANES spectra, Fe-EXAFS fitting from the HP site, XRD fitting from the PP site and the Fe-EXAFS spectra are available immediately following the References for Chapter 1.

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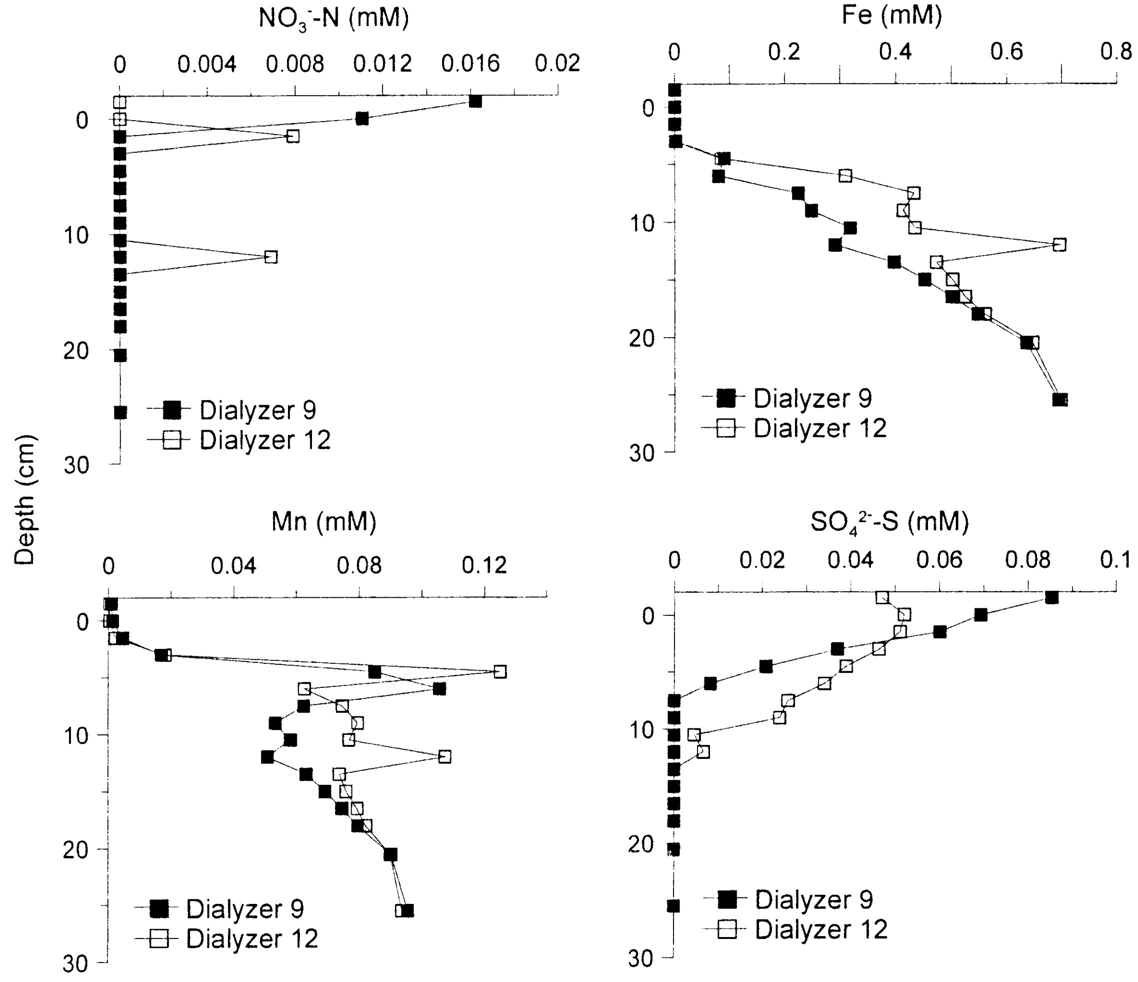
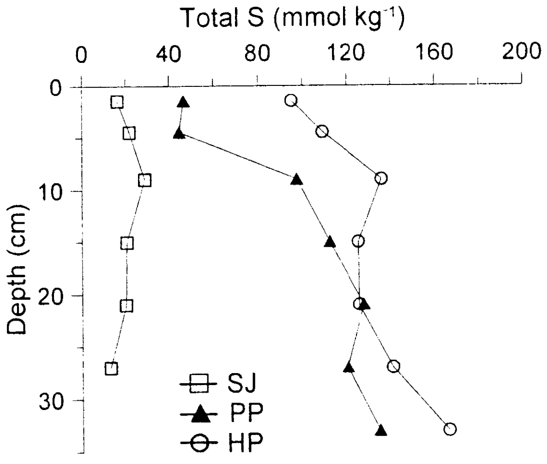
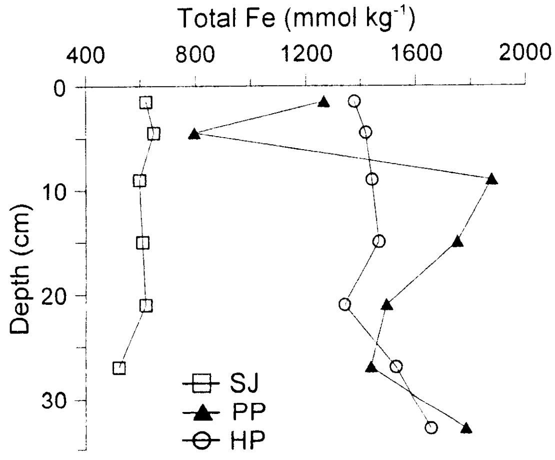
SUPPORTING INFORMATION



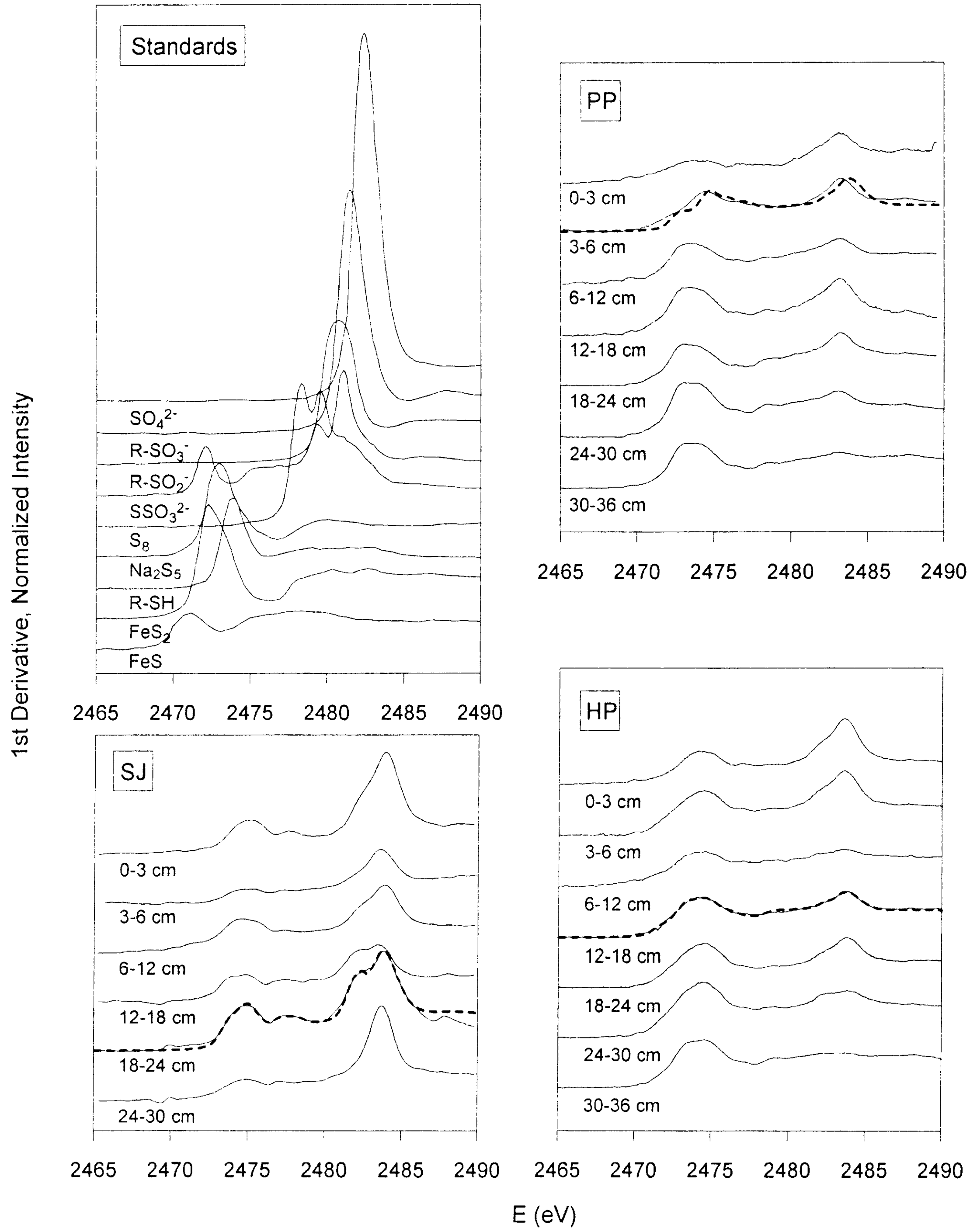
Supporting Information Figure 1.5. Replicates of redox sensitive species from the Harlow Point site, May 2002 deployment, indicating the consistency of the trends and reproducibility of dialyzer samples. These trends are consistent with those found during four deployments from 2000 to 2002. Depth increments less than zero (0) indicate concentrations above the sediment-water interface.



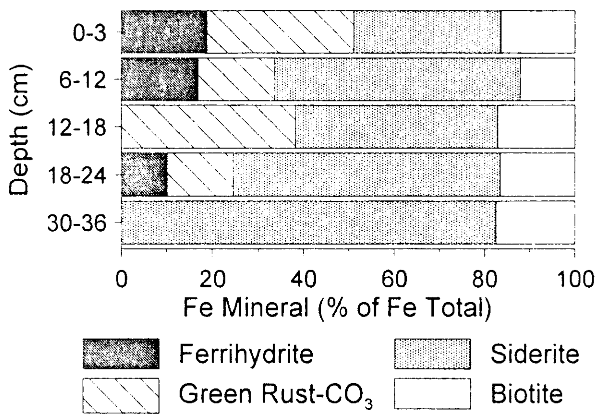
Supporting Information Figure 1.6. Total S concentration of Lake Coeur d'Alene sediments in the control site (SJ) and the two contaminated sites (PP and HP). Total S determined by ICP analysis of sediment microwave digestions. Each point is an average of two samples from adjacent cores collected May 2002.



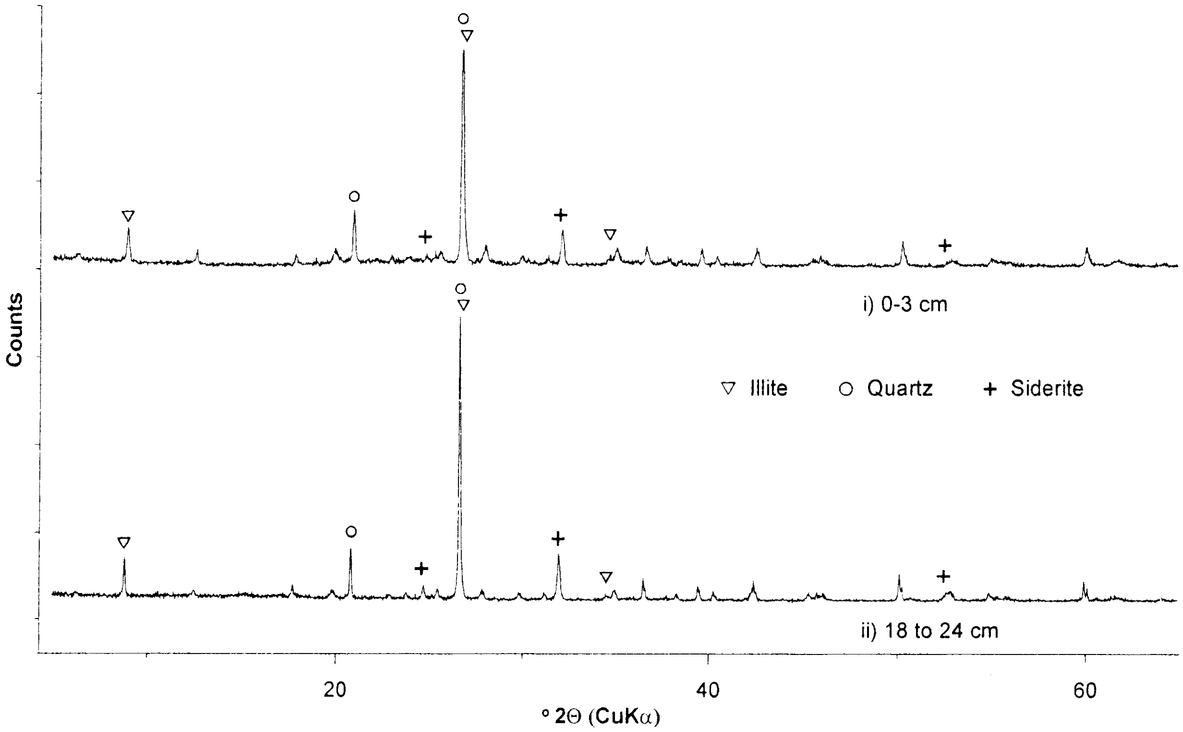
Supporting Information Figure 1.7. Total Fe concentrations of Lake Coeur d'Alene sediments in the control site (SJ) and the two contaminated sites (PP and HP). Total Fe determined by ICP analysis of sediment microwave digests. Each point is an average of two samples from adjacent cores collected May 2002.



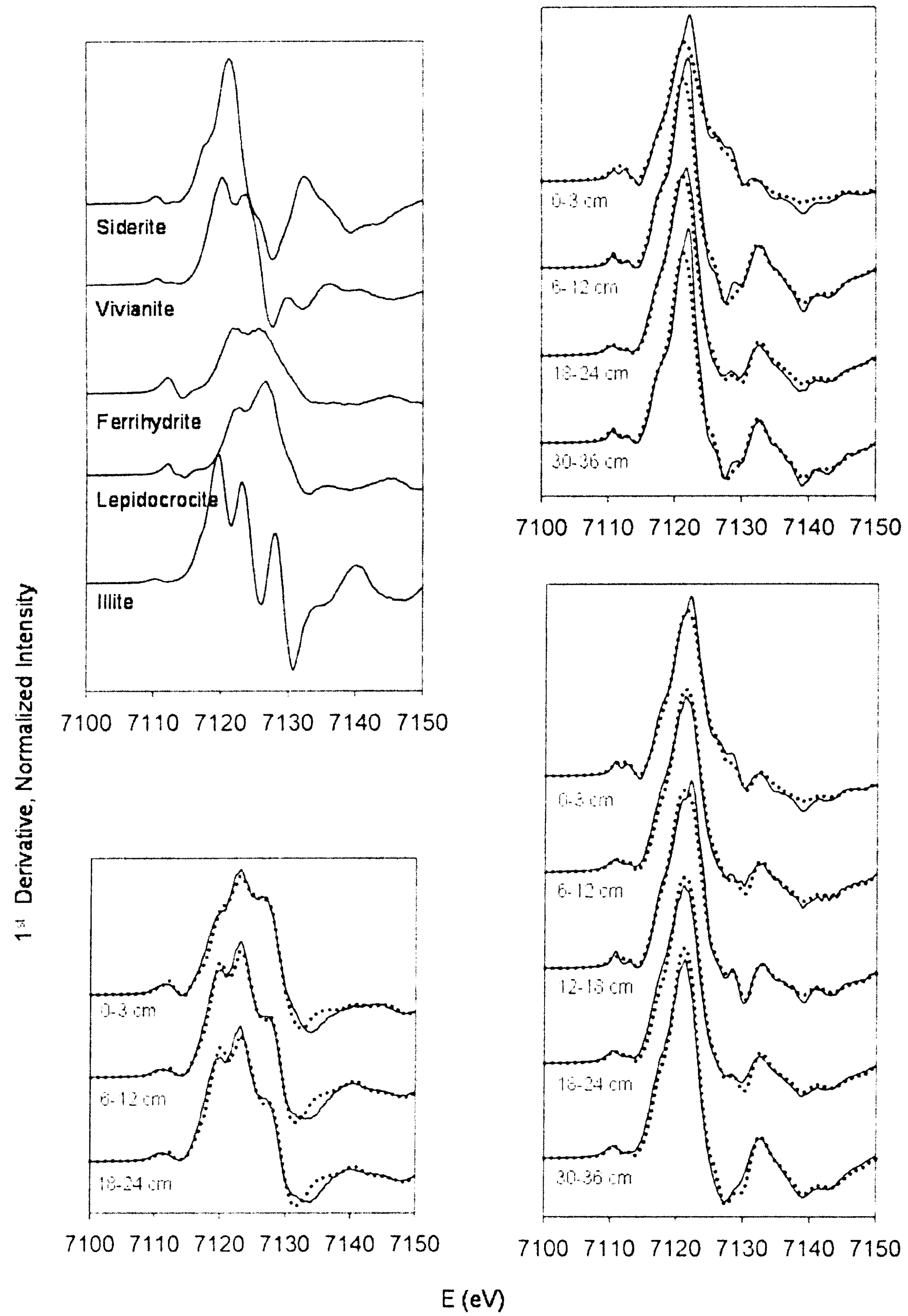
Supporting Information Figure 1.8. S XANES standards and spectra of Lake Coeur d'Alene sediments. Data are from cores collected May 2002 and analyzed at the Brookhaven advanced light source. The dashed lines are representative fitting curves.



Supporting Information Figure 1.9. Iron-EXAFS linear combination fitting for spectra from Harlow Point (HP) indicating the increase in siderite with depth. Minerals other than siderite and illite have not been verified by an additional independent technique. Data are from a core collected May 2002.



Supporting Information Figure 1.10. XRD patterns identifying the presence of various minerals at Peaceful Point, Lake Coeur d'Alene. Data are from a core collected May 2002.



Supporting Information Figure 1.11. Fe XANES standards and spectra of Lake Coeur d'Alene sediments. Data are from a core collected May 2002.

CHAPTER 2

Arsenic Cycling in Freshwater Sediments of Lake Coeur d'Alene, Idaho

ABSTRACT

Lake Coeur d'Alene (CDA), Idaho has been the collecting bed for significant quantities of As resulting from upstream mining activities, yet little is know about the geochemical cycling of this toxic element in these fresh-water sediments or its potential to pollute the overlying water of this heavily used recreational lake. Our objective was to determine the biogeochemical processes controlling solid and aqueous phase As concentrations within Lake CDA sediments. Sediment cores from two contaminated sites were collected by divers and interstitial water samples obtained using equilibrium dialyzers. Total solid phase and interstitial water concentrations of As and other elements were determined, and solid phase As associations probed using x-ray absorption near edge structure (XANES) spectroscopy. Maximum dissolved As concentrations in the sediment porewater (7.34 μM at Harlow Point and 15.38 μM at Peaceful Point) exceeded the EPA Criterion Continuous Concentration by 367% and 768%, respectively, yet diffusion to the overlying water column was mitigated by sorption to iron oxyhydroxides at the oxic sediment-water interface. However, As-bearing sulfidic gangue minerals that have been transported to the lake by flood events undergo dissolution at the oxic interface and the concomitant efflux of sulfate from the sediments exacerbates the high Fe:S ratio that has been

previously reported. This high Fe:S ratio limits the formation of sulfides in the anoxic zone allowing As to remain in solution at these dangerously elevated levels. Depositional events bury oxides containing sorbed As transitioning them to suboxic or anoxic regions where they undergo dissolution, releasing As to the interstitial water. As a result of continuous As trapping at the sediment-water interface and its release upon burial from additional sediments transported by flood events, decreased concentrations of interstitial water As in Lake CDA sediments are not likely to occur unless As-bearing mineral inputs are eliminated.

INTRODUCTION

Lake Coeur d'Alene (CDA) is a natural lake of glacial origin located in Northern Idaho, USA. The two main rivers feeding the lake are the St. Joe River that lies within a relative pristine watershed and the CDA River, the receiving water body for the South Fork of the Coeur d'Alene River drainage (Woods et al. 1997). The world-class mining district known as the Silver Valley is located within this South Fork drainage. During the first 70 years of the 20th century, mining in this district produced over 1 billion troy ounces of silver and 8 million tons of lead (Hoffman 1995). As a result of this activity, mine tailings and mill slurries contaminated with Pb, As, Cd, Zn, and other metal(loid)s have accumulated throughout the flood plain of the CDA River and in the sediments of Lake CDA. Annual and episodic flood events continue to resuspend, transport, and redeposit these sediments both in the river and in the lake (Bender 1991; Box et al. 2005).

In 1993, Horowitz (1993a) estimated that contamination within the lake sediments exceeded 75 million metric tons and covered 85% of the lakebed. Although these lake sediments are heavily contaminated, the overlying water column, with the exception of Zn, generally meets EPA standards for primary contact, recreation (Woods et al. 1997). However, this is not the case for the highly bioavailable, dissolved trace metals such as Cu, Pb and Zn (Di Toro et al. 1992; Ruby et al. 1996) found in the sediments at concentrations that exceed the Criterion Maximum Concentration (CMC) or the Criterion Continuous Concentration (CCC) for (Woods et al. 1997; Balistrieri 1998). Although As is an element of extreme importance globally because of its toxicity and mobility, it has received little attention in these highly contaminated sediments.

Arsenic is a metalloid that contaminates soils, sediments, and aquifers and is toxic to both plants and animals (Eisler 1994; Morton et al. 1994). In 1993, Horowitz (1993a) estimated that 11 500 metric tones of As had been transported to Lake CDA and deposited to the sediments. Inorganic As is often released through the oxidation of sulfide-bearing materials, such as those found in the CDA mining district (Fryklund 1961; Fryklund 1964; Gott et al. 1980), and can persist as an oxyanion in its trivalent, arsenite, and pentavalent, arsenate forms. Arsenite is considered the more toxic of the two anions (Hindmarsh et al. 1986), having adverse effects on aquatic species at concentrations of 0.25 μM (Eisler 1994). In oxic conditions both arsenate and arsenite sorb to iron and manganese oxyhydroxides (Mok et al. 1990; Waychunas et al. 1993; Manning et al. 1996; Fendorf et al. 1997), limiting their diffusion into the overlying water (Brannon et al. 1987; De Vitre et al. 1991). Arsenite will also precipitate as an arsenic-sulfide in anaerobic zones where adequate sulfur and carbon sources exist (Rittle et al. 1995; O'Day et al. 2004). Increased concentrations of As at redox boundaries have been repeatedly observed in stratified water columns and sediments (Kuhn et al. 1993; Azcue et al. 1995). Redox transformations and adsorption processes thus control the fate, transport, and bioavailability of arsenic in many environments, and have been identified as potential contributors to As geochemical cycling in CDA sediments (Cummings et al. 1999).

Prior As research on Lake CDA sediments has been limited to quantifying As in the sediments (Horowitz et al. 1992; Horowitz et al. 1993a); bench studies to determine the potential for As release under changing redox conditions (Harrington et al. 1998; Cummings et al. 1999); and characterization of sediment interstitial water concentrations as part of a larger study (Woods et al. 1997). Unfortunately, we lack a comprehensive understanding of the biogeochemical processes governing As cycling within these sediments, thus limiting our predictive capabilities and ability to make informed management decisions. Our objective was to delineate the biogeochemical processes controlling solid and aqueous phase As concentrations within Lake CDA sediments by quantitatively and qualitatively characterizing As distributions. Processes controlling the release and accumulation of As in natural systems such as Lake CDA are of tremendous importance given the widespread nature of As contamination within the environment.

MATERIALS AND METHODS

Sample Sites.

Two sample sites, Harlow Point (HP) and Peaceful Point (PP), were established in the southern portion of Lake CDA, within 1 km of the mouth of the CDA River, in an area highly impacted by heavy metals and metalloids (Horowitz et al. 1992; Horowitz et al. 1993a). Horowitz (1993a) took cores from this same general area in 1990 and reported that contaminated sediments extended to 119 cm near HP and 41 cm near PP. The water depths at PP and HP averaged 19 and 15 m, respectively. Although only data from the May 2002 deployment are presented, four deployments were performed from 2001 to 2002 yielding similar results. For a map of the greater study area, please refer to Figure 1.1.

Materials.

All chemicals were reagent grade and used without further purification. Solutions were prepared using distilled, deionized water. All sampling containers and labware were cleaned with 2% HNO_3 and thoroughly rinsed with deionized water prior to use. Analytical standards and quality assurance standards for ion chromatography (IC) and inductively coupled plasma (ICP) spectroscopy were purchased from Spex CertiPrep (Metuchen, NJ).

Sampling Devices.

Interstitial water was collected *in situ* utilizing Plexiglas equilibrium dialysis samplers (Hesslein 1976). The dialyzers contained two rows of 25, 10-ml compartments milled on 1.5-cm centers. The compartments were covered with 0.2-μm Osmonics nylon membrane (Westborough, MA), nylon tulle netting, and a matching cover plate held in place with nylon screws. Cores were collected in polycarbonate tubes 10 cm in diameter and 50 cm in length, which upon sample collection were immediately capped on one end with a size 10 rubber stopper and the other with a Fernco style Quickcap (Davison, MI).

Sample Retrieval and Preservation.

SCUBA divers inserted the dialyzers vertically into the sediment where they were allowed to equilibrate for 4 weeks, a time deemed appropriate based on field and laboratory studies (Balistrieri 1998; La Force et al. 2000; Winowiecki 2002). Upon retrieval, they were immediately transferred to a boat waiting at the sample site, where interstitial water for anion analysis was removed from the dialyzer cells using a 10-mL syringe and preserved in a sample vial under anaerobic conditions at 4 °C. Interstitial water for cation analysis was removed in a similar fashion and placed in a sample vial containing 4 drops of trace metal grade HNO_3 to maintain a pH of less than 2.5. Cores obtained at the same time were sealed to prevent leaks and oxidation, packed in an airtight container with ice packs, and purged with N_2.

Once in the laboratory, the sediment cores were transferred to an N_2-filled glove box and extruded from the coring tubes with care taken to avoid compaction or elongation. Cores were sub-sectioned at the appropriate depths and homogenized samples placed in vials. The vials were frozen until analysis by X-ray absorption spectroscopy (XAS).

Particle Size Analysis.

Particle size analysis (PSA) was performed on sub-samples of core sections dried at 90 °C until a stable weight was achieved. The dry samples were cooled in a vacuum desiccator and stored there until removal for weighing. The particle size analysis procedure included sample dispersion using sodium hexametaphosphate (SHMP) and sonification (Gee et al. 1986). The sand and silt fractions were separated from the clay fraction by centrifugation, pouring off the supernatant containing the clay fraction after each sonification/centrifugation sequence. The sequence was repeated until the supernatant was clear. The supernatant was filled to volume in a sedimentation cylinder, stirred, and an aliquot was removed by pipette and dried to determine the clay fraction. Separation of the sand and clay was accomplished by wet sieving and subsequent drying of the two fractions. Accuracy as determined by totaling the fractions and comparing to the original sample weight exceeded 95%.

Analytical Methods.

Core sub-sections were thawed, transferred to acid-washed crucibles, and dried at 90 °C until a stable weight was achieved. The dry samples were cooled in a vacuum desiccator, ground with a mortar and pestle, transferred to 10-mL polyethylene vials, and stored in a vacuum desiccator except when removed to transfer an accurately weighed sample to a digestion container. Samples were microwave-digested with a 9:2:3 ratio of HNO_3, HCl, and HF in accordance with EPA method 3052 (Staff 1994). Recovery precision and accuracy, performed in triplicate on the Standard Reference Material 2711, indicated a relative standard deviation (RSD) of less than 3% and digestion recovery efficiency greater than 90% for the data presented. Triplicate unknown samples were run in each batch digestion and the RSD was generally less than 5%. The digest was filtered using a 0.2-µm Gelman IC Acrodisc syringe filter (Ann Arbor, MI) and volumetrically diluted to 50 mL in preparation for analysis.

Total C, N, and S were determined by dry combustion on an Elementar VarioMax elemental analyzer (Elementar, Germany). Dried sub-samples of the homogenized core sections were weighed into crucibles and combusted at 1 100 °C for total C, N, and S (Nelson et al. 1996). Organic carbon was determined from similar subsamples after the inorganic carbon was removed by treatment with $FeCl_2{\cdot}4H_2O$ (Loeppert et al. 1996). After treatment, the crucibles were dried at 105 °C overnight and then analyzed for organic C by combustion at 1 050 °C. Inorganic C was determined by difference. Standards were run every 10 samples to verify calibration and duplicate unknowns were included to determine precision.

Anion analyses on interstitial water were performed on a Dionex 500DX Ion Chromatograph fitted with an AS11 Ion Pac column, an AG11 4-mm guard column, and a

MFC-1 Metal Trap. The flow rate was 1.0 mL min^{-1} of a 50 mM NaOH eluent. Dissolved metal(loid) analyses were performed on a Thermal Jarrell Ash ICP-AES. The reported values are the average of duplicate samples. Arsenic analysis was performed on a HP 4500 ICP-MS with a flow rate of 0.5 mL min^{-1} after a 5:1 dilution accomplished by a peristaltic pump. Reported concentrations are the average of three replicate measurements of each sample. In order to avoid airborne contamination, ICP-MS sample preparation was performed in a positive pressure clean hood and the auto-sampler was housed in a HEPA enclosure. Detection limits were calculated at two times the standard deviation of the low standard and are as follows: Mn, 0.0001 mM and Fe, 0.0007 mM (ICP-AES); SO_4^{2-}, 0.005 mM (IC); and As, 0.006 μM (ICP-MS). Detection limits for the total metal digest elements in mmol kg^{-1} were: As, 0.0004; Mn, 0.0221; Fe, 0.1025; and S, 0.0540 (ICP-AES).

Arsenic X-ray absorption near edge structure (XANES) spectroscopy was performed at the Stanford Synchrotron Radiation Laboratory on beamline 11-2. The storage ring was operated at 3.0 GeV and at currents between 40 and 100 mA. Incident and transmitted intensities were measured with 15-cm N_2-filled ionization chambers. Sample fluorescence was measured with a 13-element Ge detector containing a 6-μm Ge filter. The incident beam intensity was detuned approximately 50% to reject higher order harmonic frequencies and to prevent detector saturation. Arsenic K-edge spectra were internally calibrated with sodium arsenate (11 874 eV). The spectra were collected from 200 eV below the K-edge (11 867 eV) to 1 000 eV above the edge. The spectral processing and data analyses were done with the program SixPack (Webb 2002). The background was removed from the spectra and then normalized using a Gaussian fit for the pre-edge and a quadratic fit for the post-edge. The first derivatives were used for principle component analysis (PCA) and target transformation.

Spectra of model compounds including arsenate (as Na_2HAsO_4), scorodite ($FeAsO_4 \cdot 2H_2O$), arsenite (as $NaHAsO_2$), realgar (AsS), orpiment (As_2S_3), and arsenopyrite (FeAsS) were obtained and analyzed in the same manner as the unknowns.

PCA has proven to be a successful method to determine the statistical variance within an experimental data set composed of a group of unknown samples (Ressler et al. 2000; Beauchemin et al. 2002). Instead of using a priori information for fitting unknown spectra, this method reduces the data set to a significant number of components. The number of components necessary to reconstruct the sample spectra from HP and PP was determined from the PCA indicator value, which reaches a minimum between primary components and experimental noise (Beauchemin et al. 2002). After PCA analysis, the spectra were compared to the standards using target transformation. Target transform fits of standards with spoil values of less than 2.5 were selected as good fits. Based on these criteria, arsenopyrite, arsenite, and arsenate were selected as standards, and were subsequently used for least square fitting of the unknown spectra to quantify the proportion of each As species in the samples.

RESULTS AND DISCUSSION

Element Abundance.

The sediments were substantially enriched in Mn, Fe, S, and As (Figure 2.1, A-H) when compared to the previously reported concentrations of these elements (mmol kg^{-1}) in non-mine impacted sediments of Lake CDA: Mn 9.101 (Horowitz et al. 1992), 6.353 (Harrington et al. 1998), 7.857 (Toevs et al. 2006); Fe 608.81 (Horowitz et al. 1992), 494.96 (Harrington et al. 1998), 590.26 (Toevs et al. 2006); As 0.053 (Horowitz et al. 1992), 0.160 (Harrington et al. 1998), 0.202 (Toevs et al. 2006); and S 19.413 (Toevs et al. 2006). Our measured concentrations of Mn, Fe, S, and As in Lake CDA sediments generally fell within the ranges previously reported for these elements (Horowitz et al. 1992; Harrington et al. 1998; La Force et al. 1999).

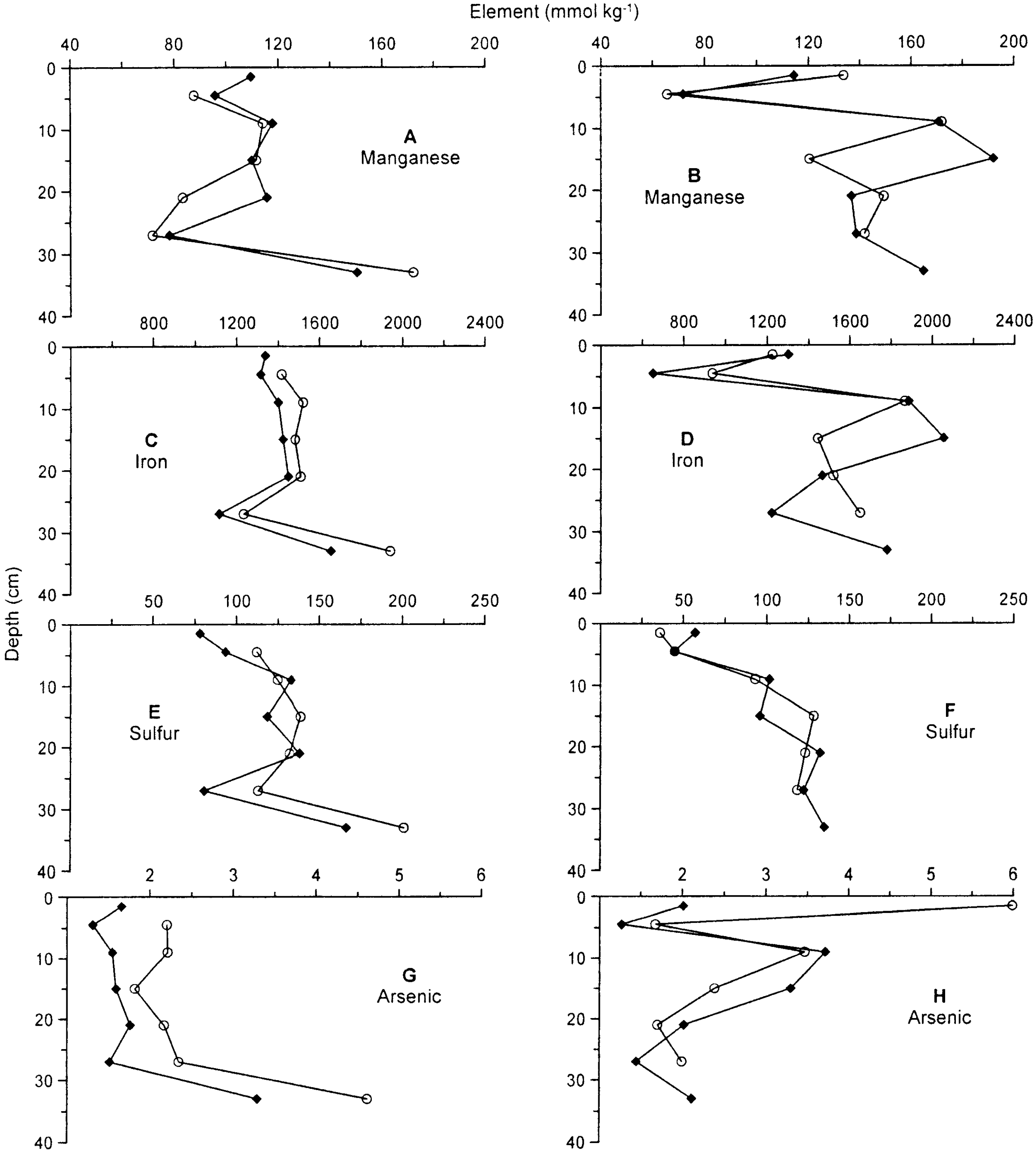


Figure 2.1, A-H. Sediment concentrations of Mn, Fe, S, and As at the contaminated sites, Harlow Point (HP) and Peaceful Point (PP). Results are shown for the total element digests of sub-sampled sections of duplicate cores analyzed on ICP-AES. The cores were collected in May of 2002.

Sediment concentrations of total Mn and Fe vary with depth at both HP and PP, but the trends of such changes differ dramatically between the sites (Figure 2.1, A-D). This apparent inconsistency is a function of differing sedimentation rates at the two sites, with HP receiving approximately four times the deposition load of PP (Horowitz et al. 1993a). Valid comparisons in total Mn and Fe therefore, require consideration of depositional differences. For example, the 33-cm data points from HP in Figure 2.1, A and C (sub-sample taken from 30 to 36 cm) correspond to the 9-cm data points in Figure 2.1, B and D from PP (sub-sample taken from 6 to 12 cm), because less sediment is deposited on an annual basis at PP. In order to facilitate comparison of corresponding depths, depth normalized-profiles for Mn, Fe, S and As are shown in Figure 2.2, A-D. When the normalized depths are compared, changes in Mn concentrations are quite similar. Trends in total Fe for the two sites do not follow as closely in absolute concentrations as Mn, but minima and maxima are present near the same respective normalized depths. Thus, total elemental concentrations of Mn and Fe reflect a historical record of the material originally deposited. Post-depositional remobilization may modify but does not completely erase the original deposition signature, an observation in agreement with Horowitz et al. (1993a).

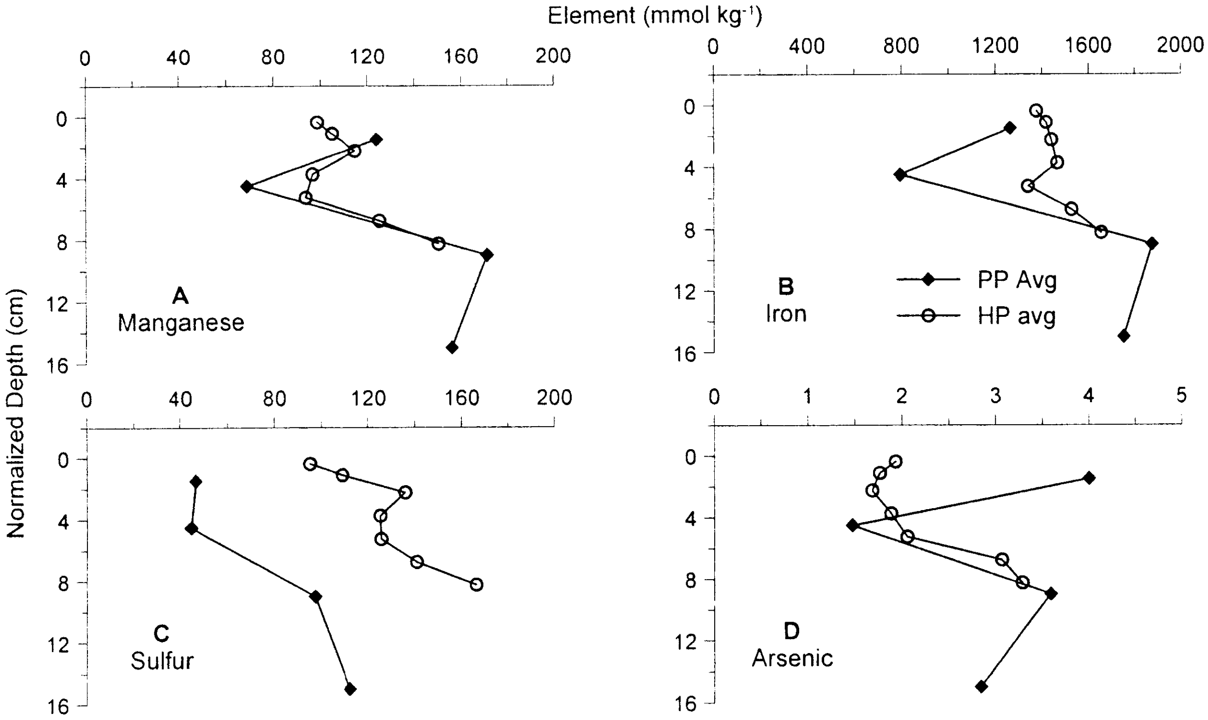


Figure 2.2, A-D. Sediment concentrations of Mn, Fe, S, and As at the contaminated sites, Harlow Point (HP) and Peaceful Point (PP). Results are shown for the total element digests of sub-sampled sections of duplicate cores analyzed on ICP-AES. The cores were collected in May of 2002.

Total S concentrations increase with depth for both sites, but PP sediments contain only about half the amount of total S as HP sediments (Figure 2.2, C) indicating that diagenetic reactions are occurring, and these reactions strongly influence total S concentrations. Similarly, diagenetic processes are obvious for As at the normalized depths of 1.5 cm where enrichment is evident at PP (4.00 mmol As kg^{-1}) when compared to HP (1.76 mmol kg^{-1}) (Fig. 2.2, D). This observation is in agreement with other reports that found As enrichment at PP (Horowitz et al. 1992; Nicholas et al. 2003). Unlike S, such diagenetic changes do not completely obscure As depositional trends occurring deeper in the sediment profile (Figure 2.2, D).

Differences in S solid phase concentrations and surface enrichment of As at PP indicate diagenetic reactions are occurring in these sediments, thus supporting our previous work where Fe and S diagenetic processes were identified (Toevs et al. 2006). Diagenetic reactions are active in altering total concentrations of some elements, but are not as obvious in total Fe and Mn profiles because large sediment concentrations mask our ability to detect relatively small amounts of mobilization and reprecipitation. Diagenetic reactions, depositional events, and their influence on As cycling are the seminal issues to be discussed in the ensuing sections.

Sediment Redox.

Changes in sediment redox potential with depth control many diagenetic processes that affect As cycling. Therefore, identifying the proximity of redox boundaries to the sediment-water interface is an important parameter to determine zones where redox-initiated, diagenetic reactions occur. The exact location of these zones is often difficult to determine as this interface is typically a diffuse and variably stratified region (Koschorreck et al. 2003). The 1.5-cm resolution of the dialyzer cells permits the relative spatial determination of aqueous concentrations and gradients. However, insertion into the lake sediments occurs under zero visibility preventing divers from identifying the exact location of any one individual sample-cell.

We used various parameters observed during dialyzer retrieval and sample analyses to establish the sediment-water interface, including the: approximate depth of insertion marked by a clip placed on the dialyzer by divers prior to removal from the sediment; cell where iron oxidation occurred after sample removal and exposure to oxygen; and cell where Mn concentrations increased. Collectively, this information was used to establish and verify the sediment-water interface, which is referred to as a depth of zero in all figures displaying aqueous concentrations of constituents in sediment porewaters. Negative depths refer to the overlying water column.

Duplicate samples of aqueous concentrations for Mn, Fe, and SO_4^{2-}-S, all redox sensitive species, are presented in Figure 2.3, A-F. Nitrate-N was detected at the sediment-water interface indicating oxic conditions prevail in the surface sediments. Manganese was detected within 4 cm of the sediment-water interface at both sites (Figure 2.3, A-B) indicating suboxic conditions had been established, and SO_4^{2-}- S decreases to background concentrations by 10 cm indicating anoxic conditions (Froelich et al. 1979). These general redox boundaries were confirmed throughout the course of this project, which spanned two years and four seasonal dialyzer deployments. Figure 2.4, shows a representation of these redox boundaries.

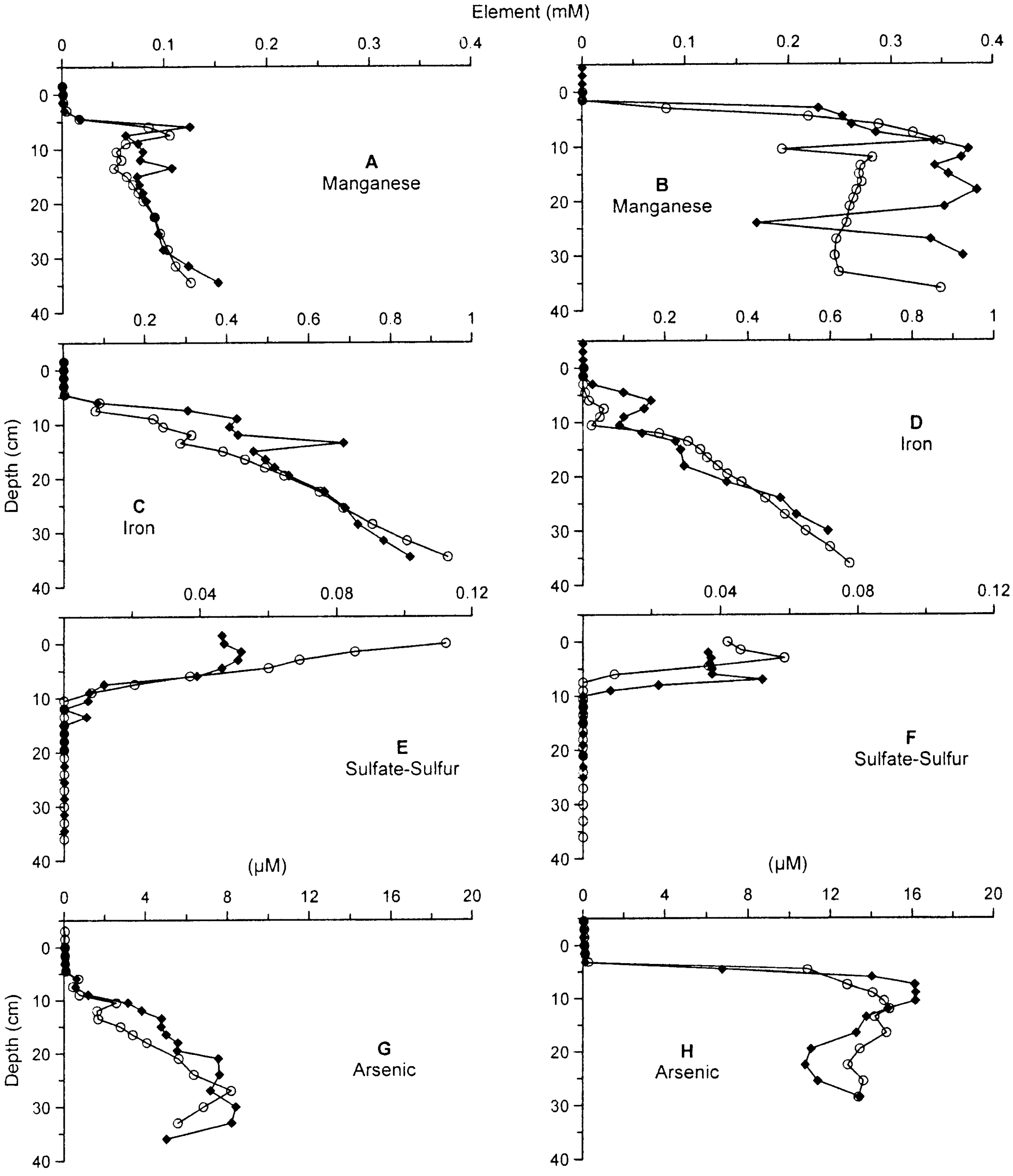


Figure 2.3, A-H. Aqueous concentrations of As, Mn, Fe, and SO_4^{2-} in the sediments and overlying water column from duplicate dialyzers placed at the two contaminated sites, HP and PP. The data points less than zero depth represent the overlying water. The samples were collected in May of 2002. Manganese and Fe were analyzed by ICP-AES, SO_4^{2-} by IC, and As by ICP-MS. Notice As abscissa is in units of µM

Thus, redox processes in the sediments at HP and PP change from oxic to anoxic in a narrow zone near the sediment-water interface (Figure 2.3, A-F). Since the elements of interest with respect to As cycling (i.e., Fe and S) are redox sensitive, geochemical cycling of As would be expected to occur in this dynamic region. The oxic zone promotes oxyhydroxide formation, metal(loid) sorption, and sulfidic mineral dissolution; the suboxic zone promotes dissolution of oxyhydroxides and release of sorbed metal(loids); and the anoxic zone is the location of sulfidic mineral precipitation (Froelich et al. 1979; Manning et al. 1996; Fendorf et al. 1997; Wilkin et al. 2006).

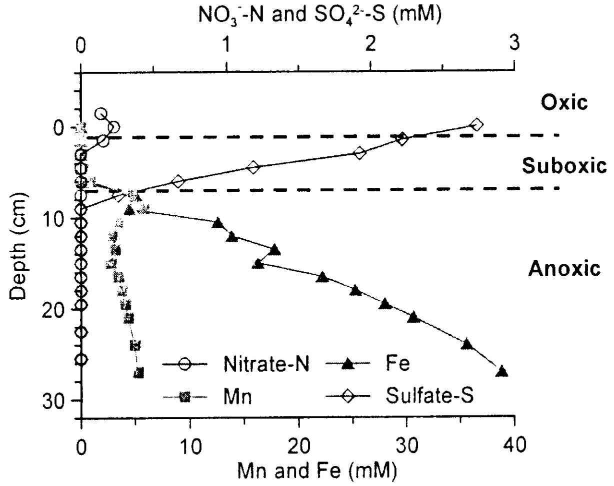


Figure 2.4. A representative redox profile for Lake Coeur d'Alene sediments and overlying water column. Seasonal and site differences were minimal. The dashed lines indicate the operationally defined redox boundaries.

Although the redox reactions are well defined, common depositional events increase the complexity of this system. Additionally, HP has a sediment accumulation rate that is four times greater than PP (Horowitz et al, 1993) which has dramatic implications as to the length of time sulfidic minerals remain in an unstable environment. Figure 2.5 is an illustration that demonstrates this difference where a sedimentation rate of 2 cm yr^{-1} (Site 1) is compared to 0.5 cm y^{-1}. The illustration indicates it takes sediments less than 8 years to transition by burial below the suboxic/anoxic boundary at Site 1, but at Site 2 those same sediments remain in the upper suboxic zone. Thus, Lake Coeur d'Alene sediments have well defined redox boundaries, but because of frequent depositional events, the redox cycle and particularly the As cycle is dramatically different between the two sites.

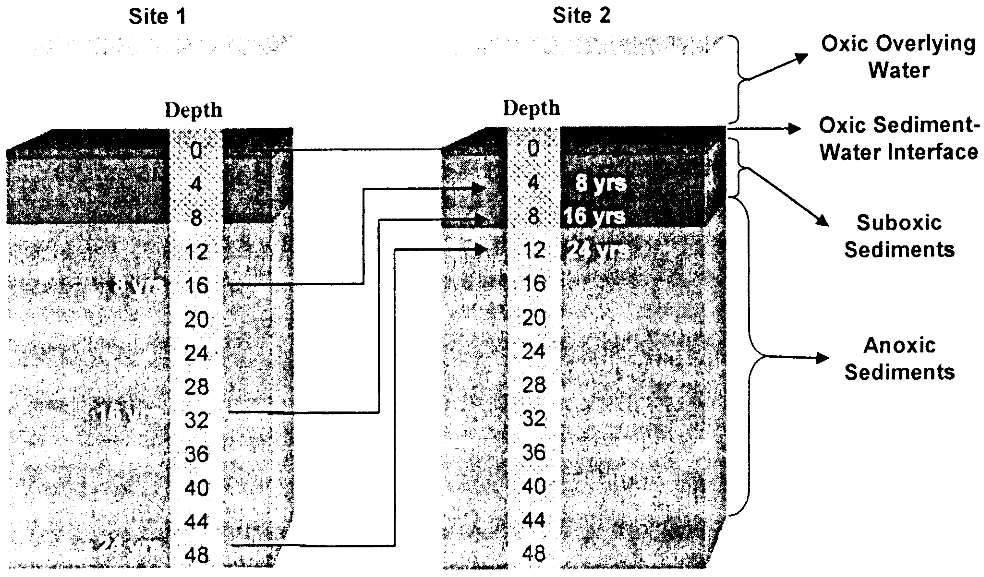


Figure 2.5. This is an illustration of two sediment profiles with similar redox conditions but differing sedimentation rates. Site 1 receives 4 times the sediment as Site 2. The arrows joining the two profiles correspond to similar age deposits and demonstrate the time difference the sediments remain in the oxic and suboxic zones prior to transition by burial to the anoxic zone.

Porewater Arsenic.

Arsenic appears in the interstitial water of HP at 5 cm, showing a continuous increase to approximately 25 cm where the maximum concentration of 8.4 μM was detected (Figure 2.3, G). The trend at PP is very different, as after the first detection of As in the interstitial water at 5 cm, the maximum concentration of 16.2 μM was measured within the next few centimeters (Figure 2.3, H). Once this maximum is established, the remainder of the profile has some variation, but the aqueous concentrations of As always exceed those found at HP.

Interstitial concentrations of As at HP are 367% and PP 768% of the Criterion Continuous Concentration (CCC) of 2.0 μM adopted for the protection of freshwater biota (Whitman 2002), thus creating a significant threat to this ecosystem (Di Toro et al. 1992; Eisler 1994). A clear understanding of the processes that promote As release and maintain such high dissolved As concentrations in the porewater is required for making management decisions that will decrease the threat As poses to lake biota and water quality.

The dissolution of Fe-oxyhydroxides containing sorbed As appears to be responsible for the observed increase in dissolved As concentrations with depth in the sediment (Figure 2. 3, G-H), consistent with results from other investigators (Cummings et al. 1999; Matin et al. 2002). In the anoxic zone, we would expect the reduction of SO_4^{2-} and the precipitation of FeS_2 or other sulfides containing the appropriate stoichiometric ratios of metal(loids) from the aqueous phase (Rittle et al. 1995). These sulfidic minerals normally sorb, coprecipitate, or precipitate As from solution (Morse 1994), thereby decreasing dissolved concentrations. However, in previous studies we concluded that high Fe:S ratios greatly limit the percentage of metal(loid)s precipitated as sulfidic minerals in Lake CDA (Toevs et al. 2006). This limitation supports our present data indicating that without precipitation of As-bearing sulfidic minerals in the anoxic zone, concentrations of dissolved As in the sediments of Lake CDA will remain at these toxic levels.

Even with these high concentrations of As in the interstitial water, both sites indicate As diffusion to the overlying water column is minimal as the concentration falls to less than 0.01 μM within the upper 3 cm of the sediments. Arsenic sorption occurs on oxyhydroxides at both HP and PP as indicated by the simultaneous decline of Fe and As in the interstitial water near the oxic interface (Figure 2, C-D and G-H). Oxic sediments at the sediment-water interface are known to promote the formation of Fe-oxyhydroxides having a high sorption capacity for As (Waychunas et al. 1993; Manning et al. 1996; Fendorf et al. 1997; Manning et al. 1998; Raven et al. 1998). Arsenic sorbed at the oxic sediment-water interface will thus transition to the anoxic region, with the deposition of additional sediment, where reductive dissolution releases soluble As to the porewater, effectively trapping As in an environment where limited S prevents precipitation.

Reactions whereby As is released and remains in soluble form in the anoxic region of the sediment are further enhanced by oxidative reactions occurring at the sediment-water interface, through possibly two mechanisms. Oxic environments promote the dissolution of arsenic sulfides and the concomitant release of SO_4^{2-} and As to the aqueous phase (Morse 1994). Thus, As-bearing sulfidic minerals transported to Lake CDA and deposited to the oxic surface layer of sediment may undergo dissolution, simultaneously losing SO_4^{2-} and further exacerbating the already high Fe:S ratios in this system. This efflux of SO_4^{2-} has also recently been observed in As-contaminated sediments in Bangladesh (Polizzotto et al. 2006). Upon dissolution, released As would sorb and concentrate on the oxides in this oxic zone and therefore be readily available for release by way of reductive dissolution when the sediments are buried by additional depositional events. This two-step process in which As trapped in the oxic zone is released in soluble form in an anoxic, S-limited environment virtually ensures that soluble As in the sediment porewaters of Lake CDA will remain at toxic levels. Support for the proposed pathways involving oxidative and reductive processes is offered in the following sections in which reactions and depositional events at HP and PP sites are compared and contrasted. The differences between the two sites are important because they reflect the consequences of dissimilar rates of sediment deposition and how such variation impacts As cycling.

Site Factors.

The distinct As profiles and differences in maximum As concentrations between the sites indicate reactions occurring at PP are more conducive to As release and accumulation in the interstitial water than HP (Figure 2.3, G-H). We have already established that redox boundaries are similar at HP and PP, making it clear other factors are responsible for the difference in dissolved As concentrations. One factor potentially responsible for this difference is the concentration of total As in the sediments. The highest total As concentrations do indeed occur at the lower depths in HP sediment (Figure 2.1, G), the approximate region in which the highest soluble As concentrations occur (Figure 2.3, G). Likewise, if the surface enrichment zone is excluded from the PP comparison, the highest total As concentrations (Figure 2.1, H) occur near the same sediment depths as the maximum porewater concentrations (Figure 2.2, H). However, there are no consistent relationships beyond those maxima indicating that total As does not control soluble concentrations at other depths.

A second possibility accounting for the differences in soluble As concentrations within the porewater is mineralogical variation in the deposited sediments resulting from sediment sorting relative to the mouth of the CDA River. As there is little doubt the CDA River is the point source for the contaminated sediments (Horowitz et al. 1993a), any mineralogical differences would not be related to parent material. However, particle surface area and associated distinctions in chemical reactivity may differ between the two sites. To explore this possibility, we compared the particle size distribution and found the silt fraction composed 70% or more of the sediment weight at all sampled depths at both sites. As would be expected due to the distance from the mouth of the CDA River, PP sediment consistently contained more clay: 8.1% more for 6-12 cm at PP compared to 30-36 cm at HP (corresponding depths for differing sedimentation rates) and 9.7% more for 0-3 cm at PP compared to 6-12 cm at HP. This difference in clay content, and thus surface area, indicates the sediments at PP could be more susceptible to dissolution of sulfidic minerals at the oxic interface, increasing formation of oxyhydroxides and subsequent sorption of As. These events would lead to additional oxyhydroxide transfer to the suboxic zone where reductive dissolution would release the sorbed As to the dissolved phase. Thus, particle size could be one factor contributing to the increased As at PP.

A third possibility that would contribute to the disparity in soluble As concentrations would be variations in total amounts of organic C. Higher concentrations of organic C would be expected to compress the redox boundaries, due to the increased oxygen demand, and increase reductive dissolution in the suboxic and anoxic zones because of the increased carbon source. The organic C values never exceed 2.7% at either site but are consistently higher at HP, whether depth corrected for sedimentation or depth-wise comparisons are made. Thus, we would expect to find more compressed redox boundaries and increased concentrations of dissolved of Mn and Fe at HP. Changes in interstitial concentrations of Mn, Fe, SO_4^{2-}-S, and As all indicated that the redox zones are more compressed at PP than HP, making it unlikely that OC differences are responsible for observed difference in dissolved As.

Finally, we must consider the impact that dissimilar sedimentation rates have on soluble As concentrations. We must first acknowledge that sulfidic materials, including

FeAsS, contained in sediments deposited at the sediment-water interface could potentially oxidize, the extent of oxidation being a function of sediment residence time in this aerobic environment. Larger or more frequent deposition events would decrease the time available for oxidative diagenetic reactions. Our data as well as that reported by others indicates surface enrichment of As occurs in PP, but not HP sediments (Supporting Information Table 2.1). Increased oxidation of FeAsS at PP releases more As for sorption to oxyhydroxides at the oxic interface, resulting in the observed enrichment of As when compared to HP (Figure 2.2, D). This enrichment at PP occurs because the lower sedimentation rate allows As-bearing sulfidic sediments to reside in the oxic zone for longer periods prior to burial and subsequent transition to stable conditions in the anoxic environment.

If increased oxidation of sulfidic materials is occurring at PP, we would expect differences in S cycling at the two sites. The oxidation of sulfides is indicated at both sites by increased SO_4^{2-}-S in the porewater near the sediment-water interface (Figure 2, E-F). When porewater SO_4^{2-}-S concentrations are compared between HP and PP (Figure 2, E-F), the differences appear to be minor and do not indicate additional oxidation of sulfidic minerals at PP. However, as discussed previously, the solid phase S concentrations at PP are only about half those for HP when the sediment concentrations are depth-normalized (Figure 2.2, C). This trend for lower total S concentrations at PP is consistent with greater dissolution of sulfides in the oxic zone and diffusional losses of SO_4^{2-}-S into the overlying water column. This larger S depletion in the sediments of PP is expected given the lower deposition rates and longer residence times at the sediment-water interface.

The proposed As cycle in the sediment of Lake CDA was inferred from total sediment and porewater concentrations of the relevant elements, and the assumption that sulfidic materials were present in the materials deposited at the sediment-water interface. In the next section, we used XANES analysis to provide direct evidence for oxidation and preservation of FeAsS depending on sediment deposition rates and residence times at the oxic sediment-water interface.

X-ray Absorption Spectroscopy.

Figure 2.6, A-B shows the normalized XANES spectra of sediments from HP and PP with the corresponding Least Square Fitting (LSF) spectra represented by the dotted line. The As in both profiles is variable in oxidation state and percentages of FeAsS. Upon inspection of the spectra and their respective fits, it is apparent that high percentages of FeAsS (>68% of the total As) are found at both sites, but only at specific depths (HP 6-12, 30-36 cm and PP 6-12, 12-18, and 30-36 cm). Recent studies assessing the stability and dissolution of FeAsS have expanded the environmental conditions where dissolution would not occur, but this work has also confirmed the reactivity of fine grained FeAsS in oxic environments (Craw et al. 2003). Geochemical information does not support precipitation of FeAsS (Craw et al. 2003), making it is reasonable to assume FeAsS is detritial and not authigenic. Due to the fine-grained nature of these sediments and the reactivity of fine-grained FeAsS, preservation of this mineral is therefore the consequence of rapid transition by burial through the oxic environment of the surface sediments. The highly variable concentration of FeAsS in the sediments, 0-86% of the total As, (Figure 2.6, A-B) implies that the deposited material had widely variable FeAsS concentrations or the residence time in the oxic zone varied tremendously throughout history. When previously presented total elemental and dissolved As analyses are used in conjunction with the XANES analyses, there are indications the sediment source as well as the time spent at the sediment water interface both play a role in controlling FeAsS concentrations within the sediment.

In determining the conditions that govern which mechanism is most important, it is essential to remember that HP receives four times the amount of deposition as PP. Thus, as discussed previously, the 30-36-cm sample at HP approximately corresponds to the 6-12-cm sample obtained from PP, with both having similar total As concentrations (Figure 2.1, G-H) and Figure 2.2, D. The As-XANES spectra from these two depths are quite similar with 84 to 86 % of the total As in the form of FeAsS (Figure 2.5, A-B), confirming the sediments are likely of the same origin and that little post-depositional alteration has occurred. This is consistent with our previous conclusions based on total elemental analyses and the hypothesis presented by Horowitz et al. (1993a) which stated that Lake CDA sediments are not substantially affected by post-depositional remobilization. These data thus give credence to the claim that one of the reasons FeAsS concentrations within the sediments vary is because the deposited materials originally contained different amounts of FeAsS.

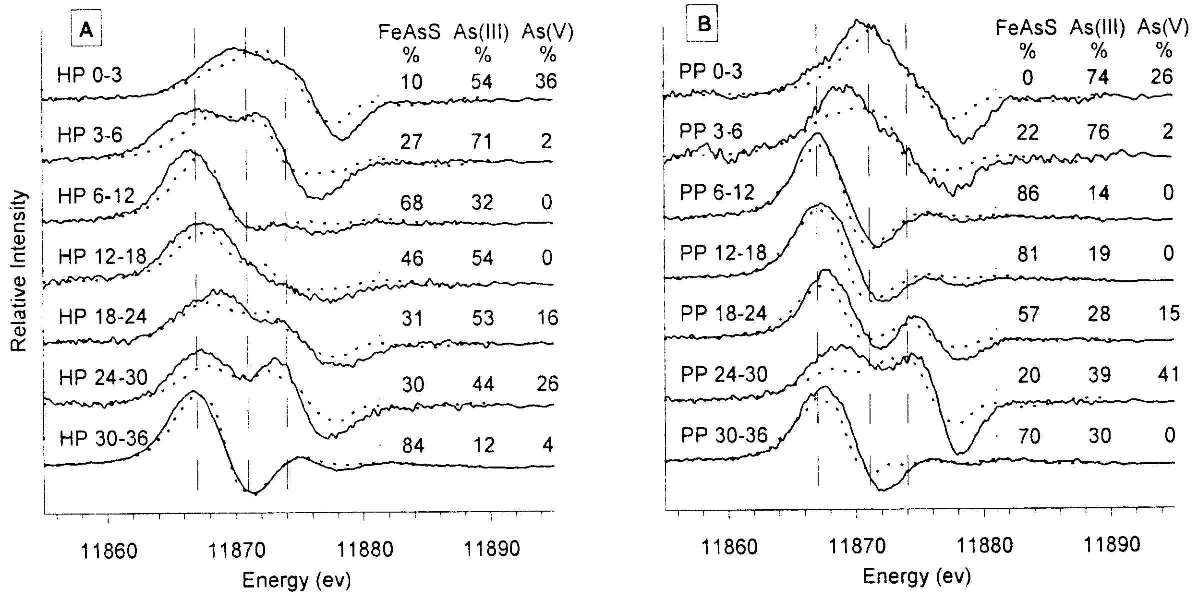


Figure 2.6, A-B. Arsenic-XANES spectra (solid lines) for sub-samples of cores from Harlow Point (A) and Peaceful Point (B) with the Least Square Fitting (LSF) curves (dotted lines) superimposed. The vertical dashed lines represent the inflection energy, from left to right, for FeAsS, As(III) and As(IV), respectively. The percentages of FeAsS, As(III), and As(V) were quantified from the LSF results. Principle Component Analysis was used to reduce the number of fitting spectra. The cores were collected in May of 2002.

If, however, FeAsS concentration differences in the sediment are simply the function of what was in the deposited materials, how can HP sediments in the 6-12 cm sample contain 68% FeAsS, but sediments deposited at the same time and present in the 0-3 cm sample from PP contain no FeAsS (Figure 2.6, A-B)? The 4:1 sedimentation rate difference between the sites leads us to predict that PP sediments present at 2 cm should have the equivalent FeAsS percentage of 68%. This apparent conflict indicates that the depositional event represented in the 6-12-cm sample at HP had sufficient sediment volume to transition the FeAsS from the surface oxic zone to the subsurface suboxic zone where the mineralogical signature was preserved, but the event was not large enough to accomplish this same transition by burial at PP. While the FeAsS was residing in the oxic sediments at PP, two significant events occurred. First, more weathered materials from subsequent, less significant flood events were deposited, diluting the concentration of FeAsS, and second, while FeAsS was residing in the oxic zone, dissolution occurred. Both of these events would serve to minimize the FeAsS signature in the 0-3 cm sample from PP, producing the observed result.

Site comparisons clearly show both sites receive material having similar mineralogical compositions, but FeAsS concentrations within these materials vary widely from one depositional event to another. We contend differences in FeAsS concentration are a function of the size of the flood event as it relates to the source of the mobilized materials. Flooding events in the CDA River Basin are frequent, scouring and mobilizing material along the riverbanks and within the river channel, subsequently depositing this material throughout the floodplain and in Lake CDA (Box et al. 2005). There are considerable qualitative differences in the sediment loads of these flood events, because larger events erode material from different sources than smaller flood events. Riverbed sediments are more typically scoured, mobilized, and transported during the lesser flood events, whereas larger flood events transport floodplain soils previously protected by their elevation above the river. Different weathering processes are active in the two environments giving the respective eroded materials distinct geochemical signatures (Box et al. 2005), signatures which we contend are partially responsible for the observed variation in As-XANES spectra.

Some examples of these differing sediment sources and loads and how they are reflected in the XANES spectra are the flood events occurring in January 1996 and January 1974. The January 1996 flood event was the second largest event recorded since the Cataldo gauge was established in 1911. This flood event produced suspended-sediment loads that were two orders of magnitude greater than three other flood events from 1995 to 1997 (Box et al. 2005), depositing sediment now found in HP cores at 6-12 cm and PP cores at 0-3 cm.

This large flood event eroded soils having relatively high FeAsS concentrations, thus yielding an As-XANES spectrum for HP showing 68% FeAsS (Figure 2.6, A). Since 1996, lower river flows primarily eroded highly weathered riverbed and stream bank sediments producing the spectra observed for HP samples obtained from 0-3 and 3-6 cm. As expected, these spectra indicate only 10-27% of the As is present in the form of FeAsS (Figure 2.6, A). High FeAsS percentages are not observed at 0-3 cm in PP sediment samples not only because of FeAsS oxidation, but also because smaller depositional loads of sediment with lower percentages of FeAsS diluted the signature of material deposited by the 1996 flood.

A second flood event that provides additional evidence for the proposed As cycle is that of 1974, the largest event ever recorded at the Cataldo gauge. The magnitude of this event would be expected to produce signatures similar to the 1996 event not only because the sediment load would include less weathered sources with higher FeAsS content, but also because the amount deposited would transition the sulfidic materials through the oxic zone and into the suboxic zone by burial where they would retain their sulfidic signature. We propose that sediment from the 1974 flood is found in HP cores at 30-36 cm and in PP cores at 6-12 cm. Consistent with the above-described events, both As XANES spectra show materials with high concentrations of FeAsS (Figure 2.6, A-B). This indicates the magnitude of this flood event was large enough to preserve the FeAsS signature even at the lower depositional environment of PP.

Major flood events thus have been shown to deposit sediment of a different mineralogical composition than minor flood events (Box et al. 2005) producing historical signatures in Lake CDA sediment. These historical signatures are modified by diagenetic reactions, the extent of which is a function of sediment deposition rate. Major flood events depositing large amounts of sediment promote rapid burial and preservation of any contained reduced minerals such as FeAsS. Soluble As release in the sediments is a sequential process whereby sediments first reside in an oxic zone near the sediment-water interface and then transition upon burial to a suboxic or anoxic zone deeper in the sediment. Lower deposition rates at PP allow for longer residence times in the oxic surface sediment layer, promoting more extensive oxidation of reduced minerals, SO_4^{2-} efflux, and the formation of additional oxides and oxide precipitates that undergo reductive dissolution when buried. As a result, higher concentrations of dissolved As closer to the sediment-water interface are found at PP when compared to HP. The release of soluble As in reduced sediment of Lake CDA is especially significant, because a S limitation prevents As sorption or precipitation. This series of reactions and processes presents a dilemma for lake management since aerobic conditions at the sediment-water interface serve to trap As, preventing its flux into the overlying water; however, burial and reductive dissolution of the trapped As produces toxic As concentrations in the anoxic sediment porewater. Since promoting reduced conditions at the sediment-water interface is an unacceptable method to decrease porewater As, decreased soluble As in the sediments will only occur by minimizing As inputs to Lake CDA.

SUPPORTING INFORMATION

A table summarizing results of prior research regarding Fe, As, and S concentration in the sediments of the two study sites is available immediately following the References for Chapter 2.

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SUPPORTING INFORMATION

Supporting Information Table 2.1. A summary of present and prior concentrations of Fe, As, and S in the sediments at or near Harlow Point (HP) and Peaceful Point (PP). The data indicate agreement of As enrichment and S depletion in the surface sediments at PP when compared with HP.

Date	**Site**	**Sample Description**	**Fe**	**As**	**S**
			(%)	**(mmol kg^{-1})**	**(mmol kg^{-1})**
Horowitz et al. (1992)	#128, near HP	2 cm surface grab sample	8.7	6.41	N/A
Horowitz et al. (1992)	#119, near PP	2 cm surface grab sample	6.5	8.81	N/A
Winowiecki (2002)	HP	0-5 cm, homogenized	7.5	1.88	128.91
		0-25 cm average	7.6	1.94	139.93
Winowiecki (2002)	PP	0-5 cm, homogenized	5.86	4.99	32.81
		0-25 cm average	6.91	3.42	59.77
Toevs et al. (2006)	HP	0-3 cm, homogenized	7.7	1.90	99.69
		0-35 cm average	8.2	2.18	123.70
Toevs et al. (2006)	PP	0-3 cm, homogenized	7.1	4.01	24.72
		0-35 cm average	8.3	2.57	81.70

CHAPTER 3

Internal Cycling and Benthic Flux of Trace-Metals in Mine-Waste Impacted Sediments of Lake Coeur d'Alene, Idaho

ABSTRACT

Lake Coeur d'Alene, Idaho, USA is a natural freshwater lake containing sediments highly enriched with Cd, Cu, Fe, Mn, Pb, Zn, and other trace metals transported from upstream mining district. The potential for these contaminants to negatively impact benthic organisms and degrade lake water quality through the process of solid phase-dissolution and subsequent diffusion of contaminants to the overlying water column is of great concern. Our objective was to characterize geochemical parameters controlling interstitial concentrations of Cd, Cu, Ni, Pb, and Zn in order to determine the threat of these metals to benthic communities and the potential for release to the overlying water. Total heavy metal concentrations in the sediment and dissolved heavy metals in sediment interstitial water as obtained using equilibrium dialyzers were quantified for two contaminated sites. Dissolved trace metal concentrations of Cd, Cu, Pb, and Zn in the interstitial water exceeded the level EPA has recognized as chronically damaging, and in most cases exceed the level determined to be acutely toxic to benthic organisms. Lead exceeded the Criterion Continuous Concentration by 400 times within 3 cm of the sediment-water interface and Zn exceeded that standard by forty times at 7.5 cm at one site. All of the metals except Ni demonstrate large

increases in concentrations from the sediment water interface (SWI) to the anoxic boundary, indicating the source of the dissolved metals is likely the reduction of oxides containing sorbed contaminants. Benthic flux calculations suggest the sediments to be a source of Cd, Cu, Pb, and Mn at both sites, and Zn to act as a source at one site, but a sink at the other. Dissolved trace-metal concentrations in these contaminated sediments are thus acutely and chronically damaging to benthic organisms and a potential contaminant source to the overlying water. This process of metal release from oxidized materials transitioning by burial to a reduced zone deeper in the sediment will continue until transport and deposition of additional contaminated materials are eliminated.

INTRODUCTION

Lake Coeur d'Alene, Idaho, USA is a natural freshwater lake that lies at the mouth of the Coeur d'Alene (CDA) River. The CDA River drains a watershed that includes the Silver Valley, a mining district that ranks as one of the world's leading producers of Ag and one of the United States' major producers of Pb and Zn (Bennett et al. 1989). Mining began in the district in the late 1800's and for the first two-thirds of the twentieth century, mining and ore-processing wastes were deposited directly into the South Fork of the CDA River. These materials, highly enriched in Ag, As, Cd, Cu, Fe, Mn, Pb, Sb, and Zn (Bender 1991), were distributed throughout the channel and floodplain of the lower CDA River and CDA Lake. Regulation stopped the dumping of mine-wastes into the South Fork of the CDA River in 1968, but periodic flooding within the CDA River basin continues to redistribute this contaminated material (Box et al. 2005). Horowitz et al (1992, 1993a) estimated that by 1990 there were already 75 million metric tons of metal-enriched sediments in Lake CDA.

In 1989, 172 surface grab samples were collected in Lake CDA to conclude 85% of the lake bed was contaminated and that trace metals in the surface sediments were largely associated with oxides (Horowitz et al. 1992). Twelve gravity cores obtained in 1990 at various depths and in a variety of depositional environments revealed some locations had trace-element enrichment exceeding 119 cm in the bed sediments and virtually no benthic activity in the contaminated zones (Horowitz et al. 1993a). Interstitial concentrations of dissolved of Cu, Pb, and Zn secured during this same time period using equilibrium dialyzers showed that all three metals exceeded the Criterion Maximum Concentration (CMC) established by EPA (Woods et al. 1997). Balistrieri (Balistrieri 1998) performed preliminary benthic flux calculations utilizing the above mentioned dialyzer samples and additional data from sediment cores, producing preliminary evidence that the sediments may be a source of dissolved trace metals that is equal to, or in some cases greater than the CDA River. In 1999, the first direct studies of benthic flux were conducted in a pilot study (Kuwabara et al. 2000), confirming the potential for the bed sediments to be a significant source of trace metals. In spite of extensive sediment contamination, the overlying water column, with the exception of Zn, generally meets EPA standards (Woods et al. 1997) (Rothrock 2004).

Therefore, there is not only a critical need to characterize the dissolved trace metal profiles, but it is also necessary to evaluate the processes responsible for the heretofore-mentioned toxic concentrations of dissolved trace metals and determine the barriers that prevent their diffusion into the overlying water column. Diagenetic processes relevant to metal(loid) cycling in Lake CDA have been studied (Harrington et al. 1998; Harrington et al. 1998; Cummings et al. 1999; Toevs et al. 2006a) and indicate significant changes in solid phase associations from the surface sediment to the near surface sediments. The combined results of these studies indicate an oxic cap is present at the sediment water interface, with the transitions from Mn, to Fe, and finally SO_4^{2-} reduction occurring in less than 10 cm (Toevs et al. 2006a). We proposed that these redox changes in combination with frequent depositional events exert a major influence on Fe (first article) and As (second article) cycling.

The influence of redox changes on the phase distribution of other metals is relatively unknown. Although solid phase concentrations of trace-metals have been measured extensively in Lake CDA sediments, it is soluble concentrations that are of interest when determining the threat of these metals to benthic communities and the potential for metal release to the overlying water column. Soluble-metal concentrations are most bioavailable and hence have the greatest impact on benthic organisms (Di Toro et al. 1992). Soluble-metal concentrations and the associated concentration gradients across the sediment-water interface are also the driving force for benthic flux. However, the paucity of dissolved-metal data within these sediments precludes the ability to evaluate recovery plans for benthic activity and makes benthic flux calculations tenuous.

Our objective was to characterize geochemical parameters controlling interstitial concentrations of selected trace elements in order to determine the threat of these metals to benthic communities and the potential for release to the overlying water column. To achieve this objective, we: quantified dissolved metal concentrations in the sediment and the overlying water column; determined the depths and spatial differences of dissolved constituents at two contaminated sites; proposed diagenetic processes potentially responsible for the dissolved metal profiles; and calculated benthic fluxes to determine if the sediments are a source or a sink for the dissolved contaminants.

MATERIALS AND METHODS

Sample Sites.

Two sample sites near the mouth of the Coeur d'Alene (CDA) River, Harlow Point (HP) and Peaceful Point (PP), were chosen because they are significantly contaminated with mine waste (Horowitz et al. 1992; Horowitz et al. 1993a). Both sites continue to receive additional sedimentation of metal(loid)-containing materials during frequent and episodic flood events. The water depths at these sites are 15 and 19 m, respectively. A non-mine waste-impacted site located near the mouth of the pristine St. Joe River was used as a reference for background levels of metals in the sediments (Toevs et al. 2006a).

Materials.

All chemicals were reagent grade and used without further purification. Solutions were prepared using distilled, deionized water. All sampling containers and labware were cleaned with 2% HNO_3 and thoroughly rinsed with deionized water prior to use. Analytical standards and quality-assurance standards for ion chromatography (IC) and inductively coupled plasma-atomic emission spectroscopy (ICP) were purchased from Spex CertiPrep (Metuchen, NJ). Standard Reference Material 2711 from the National Institute of Standards and Technology (Gaithersburg, MD) was used as the total metals standard. Acids used for total metals were all trace-metal grade (Fisher Scientific, Pittsburgh, PA).

Equilibrium Dialyzers and Sediment Cores.

Interstitial water was collected in situ utilizing Plexiglas equilibrium dialysis samplers (Hesslein 1976). The dialyzers contained two rows of 25, 10-mL compartments milled on 1.5-cm centers. The compartments were covered with 0.2-μm Osmonics nylon membrane (Westborough, MA), nylon tulle netting, and a matching cover plate held in place with nylon screws. SCUBA divers inserted the dialyzers vertically into the sediment where they were allowed to equilibrate for 4 weeks, a time deemed appropriate based on field and laboratory studies (Balistrieri 1998; La Force et al. 2000; Winowiecki 2002). Upon retrieval, they were immediately transferred to a boat waiting at the sample site, where interstitial water for anion analysis was transferred from the dialyzer cells to a HDPE sample vial using a 10-mL syringe. The sample vials were preserved under anaerobic conditions at 4 °C. Interstitial water for cation analysis was transferred in a similar fashion and placed in a sample vial containing 4 drops of trace metal grade HNO_3 to maintain a pH of less than 2.5.

The exact location of the SWI is difficult to determine as this interface is typically a diffuse and variably stratified region (Koschorreck et al. 2003) and additionally, insertion into and retrieval from the lake sediments took place under zero visibility. The 1.5-cm resolution of the dialyzer cells permits the spatial determination of aqueous concentrations and gradients, but identifying the precise depth is difficult. This challenge was resolved by analyzing various signatures observed during retrieval and sample analyses to establish the sediment water interface (SWI). These signatures include the approximate depth of insertion marked by a clip placed on the dialyzer by divers prior to removal from the sediment; the cell where iron oxidation occurred after sample removal and exposure to oxygen; and the cell where Mn concentrations increased. Collectively, this information was used to establish the SWI, which is referred to as zero depth on all figures displaying aqueous concentrations. Negative depths refer to the overlying water column.

SCUBA divers collected sediment cores in polycarbonate tubes with a diameter of 10 cm and a length of 50 cm. The tubes were inserted into the sediment, a Fernco-style Quickcap (Davison, MI) was placed over the exposed end, the tube was extracted from the sediment, and a size 10 rubber stopper was placed in the tube. The cores were immediately transferred to a waiting boat where they were sealed to prevent leaks and oxidation, packed in ice packs in an airtight container, and purged with N_2 for transport to the laboratory. Once in the laboratory, the cores were transferred to an N_2-filled glove box and extruded from the coring tubes with care taken to avoid compaction or elongation. Cores were sub-sectioned at the appropriate depths and homogenized samples placed in acid-washed HDPE vials. The vials were frozen until analysis.

Analytical Methods.

Frozen, homogenized core sub-sections were thawed, transferred to acid-washed crucibles, and dried at 90 °C until stable weights were achieved. The dry samples were cooled in a vacuum desiccator, ground with a mortar and pestle, transferred to 10-mL polyethylene vials and stored in a vacuum desiccator except when removed to transfer an accurately weighed sample to a digestion container. Samples were microwave-digested with a 9:2:3 ratio of HNO_3, HCl, and HF in accordance with EPA method 3052 (Staff 1994). Recovery precision and accuracy, performed in triplicate on the Standard Reference Material 2711, indicated a relative standard deviation (RSD) of less than 3% and extraction efficiency greater than 90% for the data presented. Triplicate unknown samples were run in each batch digestion and the RSD was generally less than 5%. The digest was filtered using a 0.2-μm Gelman IC Acrodisc syringe filter (Ann Arbor, MI) and volumetrically diluted to 50 mL in preparation for analysis.

Concentrations of NO_3^- and SO_4^{2-} in the samples collected with the equilibrium dialyzers was determined using a Dionex 500DX Ion Chromatograph fitted with an AS11 Ion Pac column, an AG11 4-mm guard column, and a MFC-1 Metal Trap. The flow rate was 1.0

mL min^{-1} of a 50 mM NaOH eluent. The samples were preserved at 4 °C under N_2 gas until transferred to the auto-sampler vials. Standards were included with the unknowns to monitor calibration and drift, and analysis was completed within 24 h.

Dissolved metal(loid) analyses were performed on a Thermal Jarrell Ash ICP-AES. Reported values are the average of two replications from each cell. Detection limits for each element were calculated at two times the standard deviation of the low standard. The RSD, as determined by running a standard 10 times, calculating the average, and dividing it into the standard deviation, was less than 4% across all analyses. Standards were run every 15 samples to verify calibration and were also included in the unknowns to monitor drift. Dissolved trace-metal analyses were performed on a HP 4500 ICP-MS with a flow rate of 0.5 mL min^{-1} and a dilution of 5:1 via peristaltic pumps. The reported concentrations are the average of three replications from each sample. In order to avoid airborne contamination, ICP-MS sample preparation took place in a positive-pressure clean hood and the auto-sampler was housed in a HEPA enclosure. Detection limits were calculated at two times the standard deviation of the low standard.

Porosity was determined by extruding fresh, unfrozen cores in precise increments and sectioning into pre-weighed drying tins. The tins were subsequently reweighed and dried at 105 °C until a stable weight was achieved. The weight of the water was determined by difference between the wet and dry sediment sections. The porosity was calculated by dividing the volume of water by the total volume of the saturated sediment (Danielson et al. 1986). The density of the sediment and water were assumed to be 2.65 g cm^{-3} and 1.0 g cm^{-3}, respectively.

RESULTS AND DISCUSSION

Element Abundance.

Total metal digests of cores collected from HP and PP found the sediments were substantially enriched in As, Cd, Pb, Zn, Fe, Mn, and S when compared to the non-mine impacted area (St Joe) of Lake CDA (Table 3.1). The reported values are in general agreement with other studies designed to quantify the mine-waste materials which have been transported to the lake (Horowitz et al. 1992; Horowitz et al. 1993a).

Table 3.1. The elemental range, median, mean, and standard deviation of depth averaged duplicate cores, 30 cm in length. The cores were taken from a non-mine impacted site (St. Joe) and from two mine waste-impacted sites (Harlow Point and Peaceful Point). The cores were collected in May of 2002 and the data is from microwave digestions analyzed on ICP-AES.

Statistics	**Element (mg kg^{-1})**						
	As	**Cd**	**Fe**	**Mn**	**Pb**	**S**	**Zn**
St. Joe Site							
Range	9-17	0-0.17	28270- 37330	390-530	12-255	370-700	100-150
Median	15.3	0	34280	440	23	640	140
Mean	14.8	0.04	33906	483	48	591	139
± *SD(n=9)*	3.36	0.07	34282	440	23	639	142
Harlow Point Site							
Range	100-350	22-40	62360-108370	3940-9460	2820-5295	2500-6450	2550-3970
Median	140	25.6	79660	6058	4561	3999	3560
Mean	162	28.3	80865	5982	4369	4021	3480
± *SD(n=13)*	68.8	6.0	11242	1551	670	1076	363
Peaceful Point Site							
Range	75-450	15-45	36000-114000	3560-10540	1595-6490	1150-4330	2470-4080
Median	160	24.4	81387	7428	3498	3078	3030
Mean	190	26	79978	7264	3582	2955	3080
± *SD(n=13)*	98.6	8.9	23764	2145	1339	1136	493

Dissolved Trace Metal Concentrations.

The aqueous trace- metal profiles of duplicate equilibration dialyzers from the HP site are shown in Figure 3.1, A-E. With the exception of Ni, all of the elements at least at some depths, exceed the continuous and the maximum concentration considered acutely or chronically toxic for freshwater biota. For continuous exposure (CCC), corrected for alkalinity of 5 mg L^{-1} of $CaCO_3$ (Woods et al. 1997), Cd should not exceed 0.09 μg L^{-1} and the recommended maximum concentration (CMC) is 0.37 μg L^{-1} (Whitman 2002). Both of these values were exceeded at the SWI and throughout the profile when analyzed concentrations were above the instrumental detection limit of 0.732 μg L^{-1} (Figure 3.1, A). Copper exceeded both the CCC and the CMC, 0.69 and 0.80 μg L^{-1}, respectively, from the SWI to 3.0 cm (Figure 3.1, B). Nickel (Figure 3.1, C) does not exceed the CCC of 4.13 μg L^{-1} at any point in the HP profile. Lead (Figure 3.1, D) exceeded the CCC and the CMC, 0.07 and 1.82 μg L^{-1}, respectively, at the SWI and throughout the profile, and the maximum soluble concentration at 3.0 cm was 400 times the recommended CCC. Zinc (Figure 3.1, E) exceeds the CCC of 8.97 μg L^{-1} and the CMC of 9.26 μg L^{-1} at the SWI and throughout the profile, and at 7.5 cm exceeds the CCC by forty times. High concentations of Zn were expected since it typically exceed the freshwater aquatic life criteria throughout the overlying water column (Woods et al. 1997; Balistrieri 1998; Rothrock 2004).

When the dissolved-trace metal values are compared to the dialyzer-collected data reported by Balistrieri (Balistrieri 1998), there is general agreement for Cu and Pb. A comparison of our Zn data and the Balistrieri data reveals inconsistencies, but there was concern that sample integrity had compromised the accuracy of this element in the data set used by Balistrieri. No concentrations were reported for Cd or Ni in that report. The differences between the values reported by Balistrieri (Balistrieri 1998) and those reported in this study could reflect inherent variability of the different sample sites, but they could also be a function of seasonal trends, a critical and dynamic component of trace-metal cycling, which to our knowledge, has not yet been addressed.

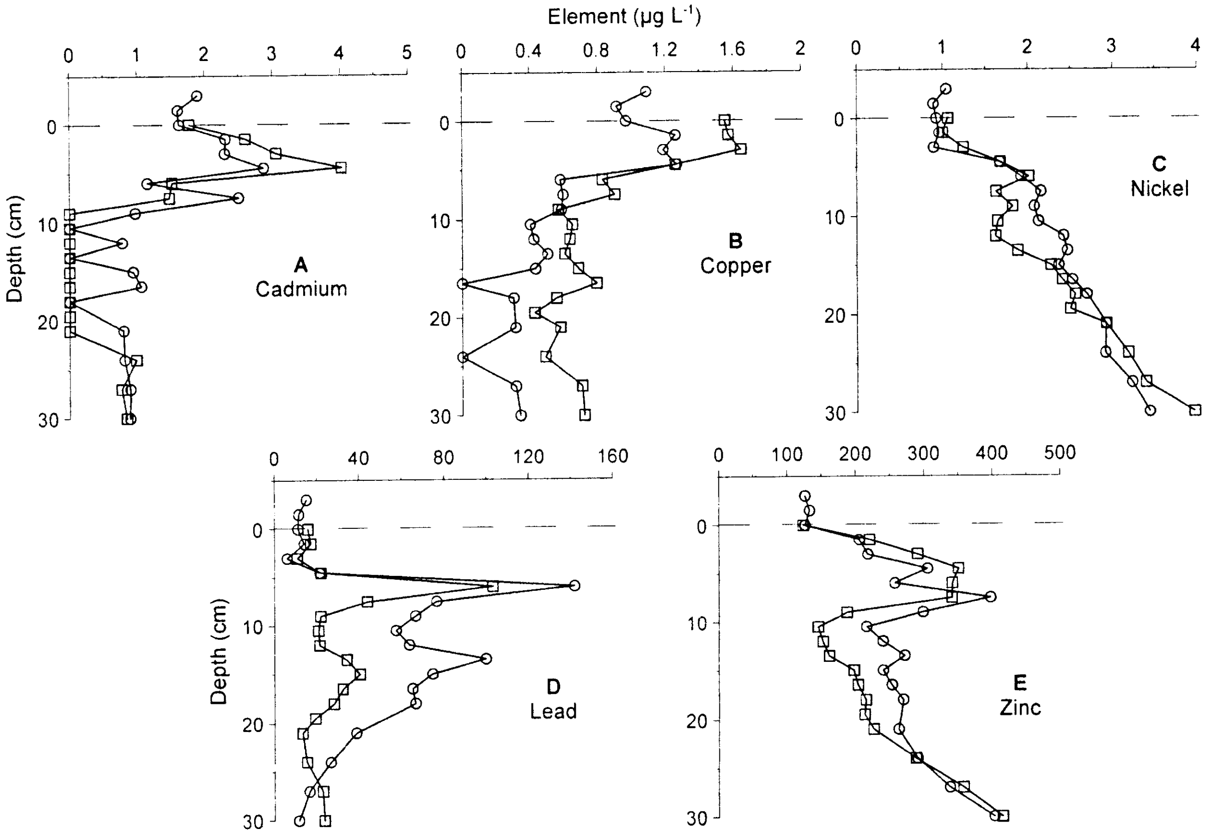

Figure 3.1, A-E. Duplicate profiles of trace metals found in the interstitial water at HP. The samples were collected by equilibrium dialyzers in May of 2002 and analyzed by ICP-MS. The dashed line represents the sediment-water interface.

The aqueous-trace metal profiles of duplicate equilibration dialyzers from the PP site are shown in Figure 3.2, A-E. Changes in interstitial water concentrations of all elements with depth are similar between the sites, the main difference was in absolute concentration of the elements. Cadmium (Figure 3.2, A) had lower values than those reported at HP and more of the data points were below the detection limit. However, all values above detection limits exceed both the CCC and the CMC. The Cu profile (Figure 3.2, B) is similar to that of HP, with the major difference being a slightly higher maximum concentration. Copper exceeds both criteria from the SWI to 3.0 cm and then exceeds the CCC to a depth of 6.0 cm. Nickel (Figure 3.2, C) has a greater maximum concentration than HP and exceeds the CCC beginning at 22.5 cm, but does not exceed the CMC at any point in the interstitial water profile. The dissolved Pb concentrations at PP (Figure 3.2, D) are substantially less that those at HP with the average maximum (30 $\mu g\ L^{-1}$) only one-fourth that of HP (130 $\mu g\ L^{-1}$). However, Pb still exceeds the CCC and the CMC at the SWI and throughout the profile. The maximum concentration of Zn at PP (Figure 3.2, E) is substantially less than HP, but again the dissolved concentrations exceed both the CCC and the CMC at the SWI and throughout the profile. Our data are similar to those previously reported for a sampling performed at East Point, a site near that of PP (Balistrieri 1998). As with HP, differences between the two data sets may reflect inherent variability or seasonal variation.

Regardless of the absolute differences between our two sites or between our data and that of other investigators, the range in concentrations of dissolved trace metals at the SWI and in these sediments clearly show that a number of different metals pose a significant threat to the benthic community and the overlying water column. These acute and chronic dissolved concentrations would certainly explain the low densities of macroinvertebrates observed by Horowitz et al. (1993a) and Kuwabara et al. (2003), and the dynamic profiles indicate the importance of diagenetic reactions. Understanding the processes controlling metal solubility is a key component for effective management of Lake CDA and other bodies of water with similar contamination.

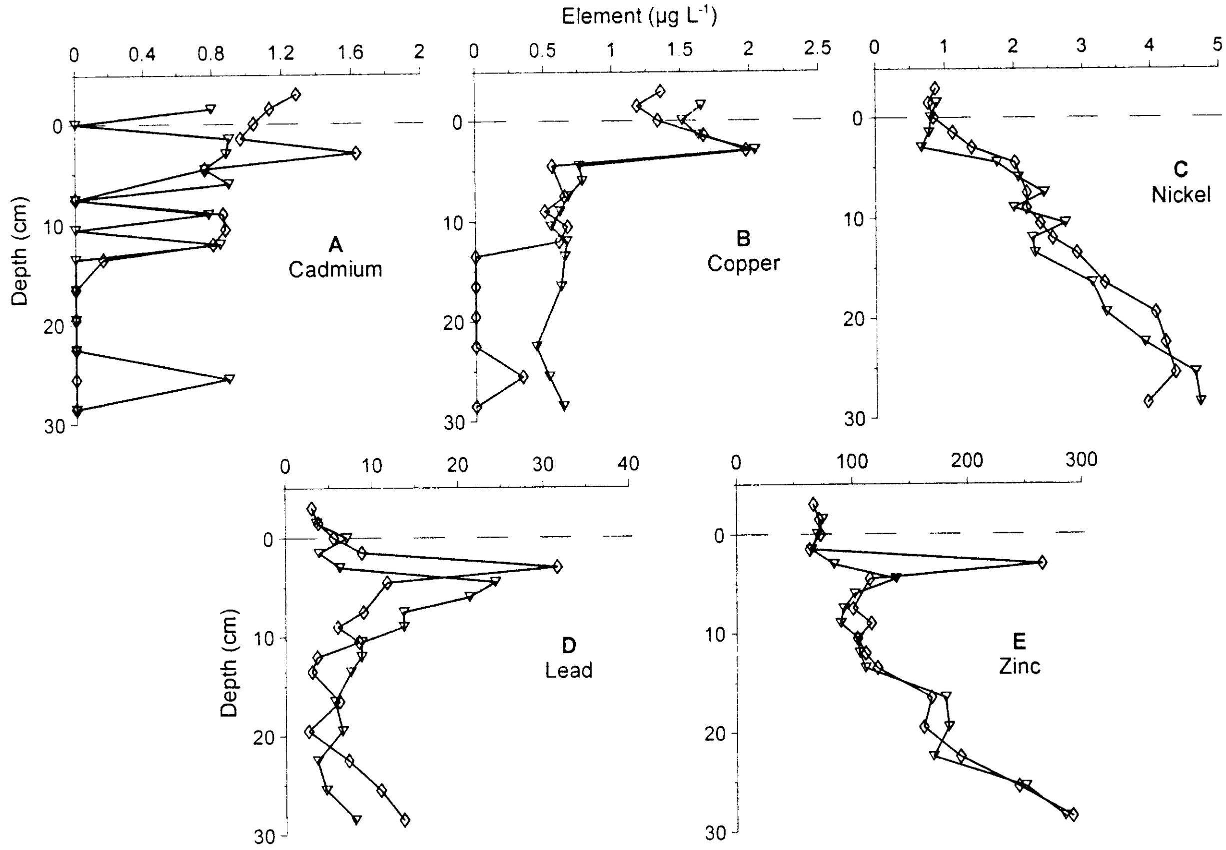

Figure 3.2, A-E. Duplicate profiles of trace metals found in the interstitial water at PP. The samples were collected in equilibrium dialyzers in May of 2002 and analyzed by ICP-MS. The dashed line represents the sediment-water interface.

Diagenetic Processes.

The processes commonly impacting the fate of trace metals in similar freshwater environments are: sorption onto or co-precipitation with Mn and Fe oxyhydroxides in the oxic zone; release from Mn and Fe oxyhydroxides during reductive dissolution in the anoxic zone; sorption onto r co-precipitation with sulfidic minerals in the anoxic zone; formation of organic matter-metal complexes; and oxidation state changes across redox boundaries that often affect their solubility (Balistrieri et al. 1994; Morse 1994). In order to facilitate the identification of which processes are likely occurring at various depths in Lake CDA sediments, the dissolved concentrations of redox-sensitive species are compared in Figure

3.3, A-C. The inserts in these figures facilitate a more detailed depth comparison of the redox boundaries, which upon examination reveal subtle differences between HP and PP.

Dissolved Mn (Figure 3.3, A) increased in the interstitial water sample taken from a depth of 3.0 cm at HP and reached its near-surface maximum of 6 mg L^{-1} by 6 cm. Dissolved Fe (Figure 3.3, B) began to increase at 4.5 cm and generally continued to increase throughout the profile reaching a maximum of 42 mg L^{-1} at 30 cm. Sulfate (Figure 3.3, C) begins to decrease in the interstitial water directly below the SWI and is below the detection limit by 12 cm, indicating the maximum depth we would expect to find significant sulfidic mineral precipitation. The depths at which redox processes alter interstitial concentrations of Mn, Fe, and SO_4^{2-}-S serve as reference points for discussing diagenetic processes potentially responsible for the observed trace-metal concentration profiles. The HP site will be discussed first and then it will be compared with PP to determine which processes appear to be common and which seem to be impacted by differences in redox boundaries.

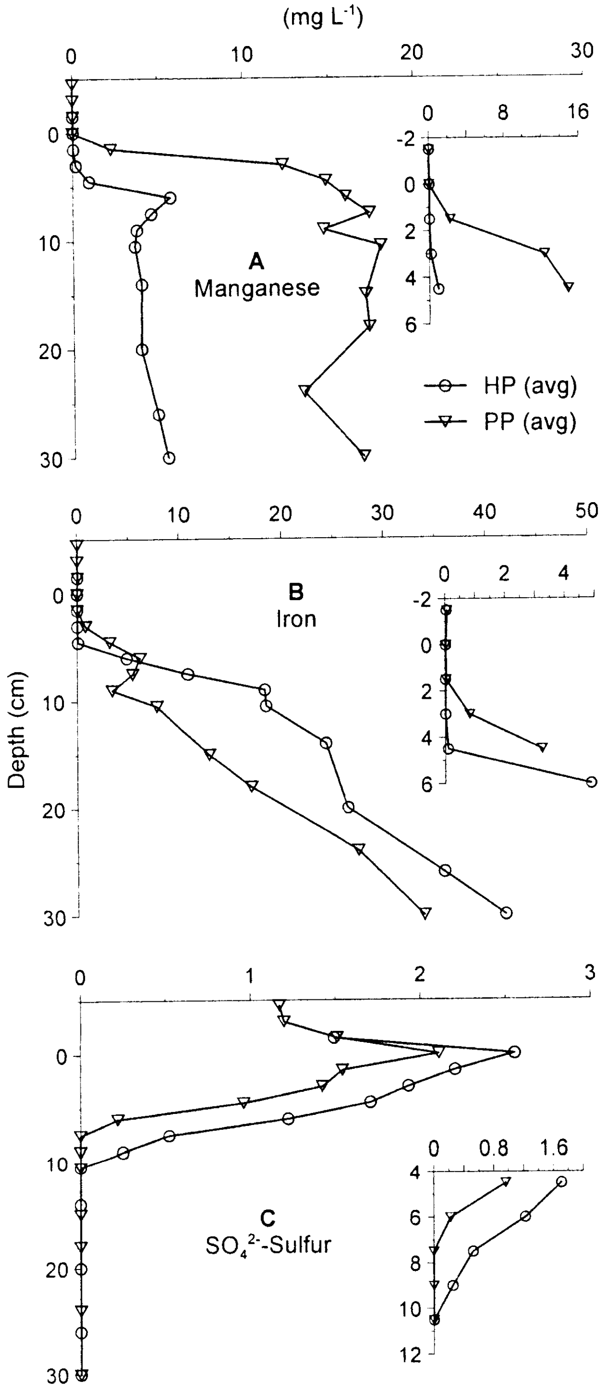

Figure 3.3, A-C. Average interstitial water profiles of redox sensitive species from HP and PP indicating the transition from oxic to anoxic sediments. The inserts allow for a precise identification and comparison of the redox boundary between the two sites. The samples were collected in equilibration dialyzers in May of 2002. Iron and Mn were analyzed by ICP-AES and SO_4^{2-}-S was analyzed by IC.

Dissolved Cd at HP (Figure 3.1, A) reaches its near-surface maximum of 4.0 mg L^{-1} at 4.5 cm, slightly above the Mn near-surface maximum at 6.0 cm. This close depth proximity with dissolved Mn would indicate a Mn-oxyhydroxide association and subsequent release when this oxide undergoes reductive dissolution. Previous studies have studied the adsorption characteristic of various trace metals (Tessier et al. 1985) and found that Cd release was highly correlated with Mn-oxyhydroxide dissolution. Tthe trace metals analysis of grab samples from CDA sediments likewise found the majority of Cd was associated with an operationally defined oxide phase (Horowitz et al. 1992). Another possible source for Cd would be the reduced ore materials which would be unstable in the near-surface, oxic environment. Although literature indicates the formation of oxic rinds can promote long-term stability in oxic conditions and minimize their dissolution (Moore 1994), these rinds may in and of themselves be a source of trace metals when additional sedimentation transitions these materials to the suboxic and anoxic zones of the sediments (Toevs 2006b).

The aqueous profiles for Cd at sediment depths above the maxima are surprising in that Cd is not removed from the interstitial water in the oxic zone near the SWI. An oxic environment at the SWI supports the formation of Fe and Mn oxides that act as sorbents of dissolved trace metals (Tessier et al. 1985). We previously reported that As diffusion to the overlying water column is prevented by sorption to Fe-oxyhydroxides in these sediments (Toevs 2006b). One possibility for the elevated levels of Cd at the SWI is incomplete cycling of Mn, a process typical in sediments where the suboxic zone is near the SWI. This close proximity allows soluble Mn to diffuse into the overlying water column prior to Mn-oxyhydroxide formation, thus preventing concomitant sorption of trace metals (Shaw et al. 1990). This kinetic limitation on Mn oxidation decreases the formation of Mn-oxyhydroxides, possibly limiting Cd sorption on Mn minerals within the oxidized zone at the SWI.

The Cd profile at about 8 cm shows a decrease in dissolved concentrations that corresponds to the zone of SO_4^{2-} reduction (Figure 3.3, C) and presumably, the formation of amorphous Fe-sulfides. Sulfides demonstrate a large sorption capacity for trace metals, such as Cd, that have a preferential coordination to sulfur ligands rather than oxygen (Balistrieri et al. 1994). Previous investigations have shown that pyrite concentrations increase with depth as a result of diagenetic reactions occurring in Lake CDA sediments (Toevs et al. 2006a). Copper concentrations in sediment interstitial water are relatively constant from the SWI to the maximum at 3.0 cm (Figure 3.1, B) indicating that once Cu is in the dissolved phase, sorption processes are ineffective in preventing diffusion to the overlying water column. As with Cd, the dissolved concentrations of Cu decrease in the zone of SO_4^{2-} reduction, fluctuating near the CCC of 0.69 $\mu g\ L^{-1}$ for the remainder of the profile. Both Cu and Cd solid phases thus appears to be stable in the anoxic zone or at the very least, dissolution in this zone is offset by sorption or precipitation.

The Ni profile (Figure 3.1, C) is unique when compared to the other four elements in Figure 3.1 in that the slope is fairly consistent from the surface to the maximum depth, with relatively minor changes at the suboxic-anoxic boundary. As with Cd and Cu, it appears there is insufficient sorption in the oxic zone to remove the dissolved phase from solution, thus establishing the opportunity for diffusion into the overlying water column. This incomplete sorption is consistent with nickel's lack of affinity for oxides as reported by McKenzie (McKenzie 1980), where Ni had the lowest affinity for Mn-oxyhydroxides and second lowest affinity Fe-oxyhydroxides when compared to the sorption of Mn, x, x, x, and x. Regardless of the low sorption affinity, dissolved Ni was positively correlated with dissolved Mn and Fe in Hall Lake (Balistrieri et al. 1994) and appears to be highly correlated with dissolved Fe at HP (Figure 3.3, B). The limited change in the slope of dissolved Ni across the suboxic-anoxic boundary is possibly because Ni has less affinity for sulfur ligands than do reduced species of Cu(I), Pb(II), and Zn(II) (Stumm et al. 1996). Therefore, the Ni profile seems to correlate well with dissolved Fe, and the low affinity for Mn and Fe-oxyhydroxides is insufficient to remove it from solution in the oxic zone. Additionally, the low affinity of Ni for sulfur ligands appears to prevent removal from the aqueous phase in the anoxic zone.

The Pb concentration profile in HP interstitial water (Figure 3.1, D) indicates a significant source of dissolved Pb at 5 cm and effective sorption above and below this maximum concentration. The maximum concentration of Pb coincides very well with maximum Mn concentration (Figure 3.3, A) and also with the rapid increase of dissolved Fe (Figure 3.3, B). Both of these oxyhydroxides would be expected to contribute to dissolved Pb concentrations as previous studies (McKenzie 1980) found Pb had the strongest binding affinity on Mn and Fe-oxyhydroxides on all the trace metals tested with the exception of Cu on goethite. This same affinity for oxides would account for the decrease in dissolved Pb in the oxic zone. Another mechanism for Pb removal from the aqueous phase is the formation of pyromorphite which can form rapidly in soils when Pb(II) and HPO_4^{2-} ions are present (Scheckel et al. 2003) and have been shown to be sparingly soluble (Ruby et al. 1994) The decrease in dissolved Pb concentrations in the anoxic zone is consistent with the Cd and Cu profiles at this depth, again coinciding with the zone of sulfate reduction.. The bimodal shape of the dissolved Pb profile at HP indicates an additional source of Pb in the anoxic sediments or if not an additional source, removal from solution has been outstripped by contributions to the dissolved phase. Regardless of the reason, dissolved Pb remains in solution at levels that are chronicly and acutely toxic throughout the remainder of the profile at HP.

The Zn profile is similar to the Ni profile in that the highest dissolved concentrations are found at the deepest depth and, as with the other elements discussed, sorption processes in the oxic zone are insufficient to remove Zn from solution (Figure 3.1, E). Zinc concentrations appear to be positively correlated with dissolved Mn and Fe profiles above the anoxic boundary and the poorly defined depth of release, similar to Cd, could indicate multiple solid-phase sources. This would be in agreement with the association reported in Hall Lake (Balistrieri et al. 1994), where dissolution of both Mn and Fe oxides correlated well with dissolved Zn. This would also be supported by the high solubility of Zn(II) in water of circumneutral pH.

The dissolved Zn profile exhibits a rapid decrease at 8 cm coinciding with the zone of sulfate reduction and therefore, sulfide production (Figure 3.3, C). Zinc's affinity for sulfur ligands would account for the decrease in dissolved Zn in this zone. After reaching this minimum in the anoxic zone, Zn concentrations continue to increase throughout the remainder of the profile indicating there is a solid-phase source in the anoxic zone and insufficient sulfide production occurs to precipitate the high concentration of this dissolved metals. Although the responsible processes cannot be determined with certainty, it is clear that dissolved Zn exists at acute and chronic concentrations detrimental to biota at the SWI and throughout the remainder of the profile.

An overall comparison of dissolved trace-metal concentrations at HP and PP indicates that PP has lower maxima of Cd, Pb, and Zn, but higher maximum concentrations of Cu and Ni (Figure 3.2, A-E). Even though the Pb maximum at PP is about 20% of the HP maximum, Pb still exceeds both the CCC and the CMC at the SWI and throughout the profile (Figure 3.2, D). As with Pb, the Zn maximum at PP is lower than found at HP, but this element also exceeds the CCC and the CMC at the SWI and throughout the profile (Figure 3.2, E). Thus, although absolute concentrations of Pb and Zn differ considerably between the two sites, both HP and PP interstitial waters contain dissolved trace-metal concentrations that have acute and chronic toxicity.

One noteworthy difference between the two sites is the depth of maximum concentrations and the depth where these maxima decrease. We can explain this dissimilarity by noting that the depth to the suboxic-anoxic boundary differs between the sites, with PP sediments exhibiting Fe-reducing conditions at least 2 cm closer to the SWI than HP (Figure 3.3, B). The depth of this boundary does not alter the observed trends in soluble trace-metal concentrations, it only changes the depths at which changes occur, thus indicating that the diagenetic processes involved in the release of trace metals to the dissolved phase are similar. According to the freshwater aquatic standards, these dissolved concentrations of Cd, Cu, Pb, and Zn are problematic for any meaningful attempt towards restoration of a benthic community. The additional problem of potential diffusion of these dissolved species to the overlying water will be addressed in the following section.

Molecular Diffusion.

As discussed in the previous section, diagenetic reactions occurring in these mine-impacted sediments produce acute and chronic concentrations of dissolved trace metals in the interstitial water. If these soluble concentrations are greater than those in the overlying water column, diffusional processes promote transport of dissolved metals from the sediments into the lake water. If dissolved concentrations in the overlying water column are greater than those in the interstitial water, diffusional processes favor transport of dissolved metals to the sediments at which time the sediments act as a sink for dissolved trace metals.

Molecular diffusion, the process responsible for diffusive flux across the SWI, is usually calculated from Fick's First Law as applied to the sedimentary environment:

$$J_S = -\phi\, D_S \left(\frac{\delta C}{\delta x} \right)$$

where J_S is the benthix flux (g cm^{-2} d^{-1}), ϕ is the sediment porosity just below the sediment-water interface, D_S is the diffusion coefficient for the element in the sediment (cm^{2} d^{-1}), and ($\delta C/\delta x$) is the concentration gradient of the element across the sediment-water interface (g cm^{-4}) (Berner 1980). Diffusion coefficients in the sediment (D_S) are related to molecular diffusion coefficients in water (D_0) as follows:

$$D_S = D_0 /(\phi * F)$$

where F is the sediment resistivity. For high porosity sediments as in Lake CDA, F can be estimated as ϕ^{-3} (Ullman et al. 1982). Therefore,

$$D_S = D_0 / \phi^{-2}$$

The diffusion coefficient (D_0) is determined from the species of the metal, which will depend on the pH, redox potential, and the presence of complexing ligands. The calculations are based on Cd(II), Cu(II), Ni(II), Pb(II), Zn(II), and Mn(II). The diffusion coefficients at 25° C in units of cm^{2} d^{-1} for Cd, Cu, Ni, Pb, Zn, and Mn are 0.619, 0.633, 0.587, 0.816, 0.618, and 0.594, respectively (Li et al. 1974). These coefficients are then corrected for the water temperature of 9.5° C resulting in the corrected coefficients of 0.320, 0.327, 0.303, 0.422, 0.319, and 0.307, respectively. For a complete discussion of the assumptions made and temperature corrections based on the Stokes-Einstein, relationship refer to the article by Balistrieri (Balistrieri 1998).

Once the corrected diffusion coefficients in water (D_O) have been calculated, the diffusion coefficient in the sediments (D_S) can be calculated by taking into account the porosity (ϕ) of the sediment. The porosity was determined from wet and dry difference and was 82.2% at HP and 91.7% at PP. One factor that can significantly change D_S is bioturbation in the near-surface sediments can range from a factor of 1.3 to 2.5 times larger than D_O (Carignan et al. 1985) . However like Horowitz (1992) and Kuwabara (2000), we identified individual sedimentation layers throughout the contaminated core sections indicating a virtual absence of bioturbation. Therefore, no adjustment is made to D_S to accommodate the effect of bioturbation.

To determine the concentration gradient across the SWI ($\delta C/\delta x$), the concentration of the dissolved metal must be determined above and below the SWI. The use of equilibrium dialyzers with a spatial resolution of 1.5 cm has limitations in that the gradient changes across this dynamic interface are undoubtedly more exponential than linear, but even with this recognition, these calculations are very useful to establish trends and benchmarks for future work. The gradient is calculated using the following formula:

$$\delta C / \delta x = \left[(Me^{2+})_{BW} - (Me^{2+})_{IW}\right] / \Delta d$$

where $(Me^{2+})_{BW}$ is the concentration of the dissolved metal (Me^{2+}) at the bottom of the water column just above the interface (g cm^{-3}), $(Me^{2+})_{IW}$ is the concentration of the dissolved metal in the interstitial water just below the interface (g cm^{-3}), and Δd is the distance between the location of the bottom water and the interstitial water (cm). For this data set, the bottom water concentration is the average of the cell located at 0 cm and the one located at -1.5 cm, the interstitial water is the concentration in the cell at a depth of 1.5 cm, and the diffusional distance across the SWI is 0.75 cm.

A summary of the benthic flux calculations is shown in Table 2. Positive numbers indicate the sediments are a source of metals to the overlying water column and negative numbers indicate the sediments are a sink. As with the Kuwabara report, (2000) these benthic flux calculations (Table 1) generally found the sediments to be a source of Cd, Cu, Pb, and Mn at both sites. The sediments at HP were also a source of Zn, but PP sediments are predicted to act as a sink, as dissolved Zn in the overlying water column was high enough to prevent its diffusion. However, dissolved Zn concentrations used in these calculations, 72.2 and 72.4 $\mu g\ L^{-1}$ in sampler 15A and 15 B, respectively, are consistent with the Zn concentrations reported for the water of Lake CDA (Balistrieri 1998; Kuwabara et al. 2000; Rothrock 2004). This indication of the sediments acting as a sink at PP gives additional significance to recent studies indicating remediation to reduce dissolved trace metal concentrations up-gradient from a potential source of dissolved metals can actually increase the release from the down-gradient source, minimizing or negating the benefits of the remediation (Kuwabara et al. 2003), as any reduction in overlying concentrations would impact the direction and magnitude of benthic flux. Thus, the issue is complex but cannot be dismissed when discussing lake management and remediation plans.

Table 3.2. Summary of molecular diffusive benthic fluxes from HP and PP based on molecular diffusion coefficients from Li and Gregory (1974). The samples used for calculations were collected by equilibrium dialyzers in May of 2002.

Sample	Molecular Diffusive Flux (µg cm^{-2}y^{-1})					
	Cd	Cu	Ni	Pb	Zn	Mn
		Harlow Point Site				
HP#6B	0.078	0.037	0.006	0.418	8.63	4.70
HP#11A	0.095	0.002	-0.007	0.192	11.1	0.319
		Peaceful Point Site				
PP#15A	-0.017	0.060	0.042	0.788	-1.25	616
PP#15B	0.071	0.007	-0.009	-0.272	-1.05	0.835

Although flux calculations give indications that the sediments act as a source for the metals studied, additional monitoring with increased resolution, as has been recently demonstrated through the use of gel probes and microsensors (Koschorreck et al. 2003; Leermakers et al. 2005), would resolve the present ambiguity. However, the dissolved metal data demonstrate that concentrations of Cd, Cu, Pb, and Zn in the interstitial water exceed the level EPA has determined to be a chronically damaging, and in most cases exceed the level determined to be acutely toxic to benthic organisms. It is also evident that all of the metals except Ni have large increases in concentrations from the SWI to the anoxic boundary, indicating the source of the dissolved metals is likely the reduction of oxides containing sorbed contaminants. With the exception of Ni and Zn, once the sediments have transitioned across the anoxic boundary, dissolution and sorption processes appear to be in equilibria or the dissolved concentrations decrease. This would suggest the oxic boundary and the dissolution and sorption processes occurring there are contributing to these high concentrations of dissolved metals in the interstitial water when those same oxides transition to this anoxic zone with additional sedimentation. This process of metal release from oxidized materials transitioning to a reduced zone deeper in the sediment will continue until transport and deposition of contaminated materials are eliminated.

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CHAPTER 4

Seasonal Redox Changes and Impact on Stability of Mine-Waste, Lower Coeur d'Alene River, Idaho

ABSTRACT

The Coeur d'Alene Mining district is world-class in the production of numerous metals, but this mining legacy has contaminated broad areas of the Coeur d'Alene River floodplain and Lake Coeur d'Alene. The potential for eutrophication to promote dissolution of the mine-wastes within the lake sediments and subsequent diffusion of the contaminants to the overlying water is of great concern. Our objective was to determine the impact reduction potential has on dissolved trace metal concentrations and therefore, the potential to degrade water quality. A pond was located with similar solid-phase contamination as found in the lake sediments. We monitored dissolved metals in the interstitial water during an annual cycle by analyzing seasonal samples collected with equilibrium dialyzers. Surface and bottom water samples were also collected and analyzed. The analytical results were unexpected as all monitored, dissolved trace-metal concentrations in the interstitial water were lower than levels observed in Lake CDA, which has a continuously oxic sediment-water interface. Dissolved Pb in the pond sediments was only 7.1% that found in the lake sediments, 10.10 and 141.9 $\mu g\ L^{-1}$, respectively, and Zn was only 3.5% of the Lake maximum, 18.88 and 530.5 $\mu g\ L^{-1}$, respectively. However, Zn concentrations in the surface water of the pond experienced

shifts covering two orders of magnitude, 78 to 8 688 µg L^{-1}, respectively, and the bottom water concentrations were typically greater than those found in the lake. When compared to Lake Coeur d'Alene, conditions in this mine-waste impacted pond increased some dissolved metal concentrations in the overlying water, but substantially lower concentrations of dissolved metals were found in the sediment interstitial water. This study therefore strongly implicates reductive dissolution of the oxic cap when buried by additional sediment as the source of dissolved contaminants in the lake sediments and confirms the paramount importance of minimizing future transport of mine-waste sediments to the lake.

INTRODUCTION

The Coeur d'Alene Mining district is one of the richest sources of lead, zinc, silver and antimony in the world. Mining began in the late 1800's and by 1983 extensive contamination from mining activities led to the establishment of a 54-km^2 Superfund site, which as of that date was the largest site established. The mine wastes were not confined to the Superfund site as a large portion of the material, the mill slimes, had been deposited directly into the South Fork of the Coeur d'Alene River. These sediments were simultaneously and subsequently transported down the entire length of the Coeur d'Alene River and into Lake Coeur d'Alene. The ores in the Coeur d'Alene mining district are mostly sulfides of silver, lead, and iron with interlaced arsenic, antimony, cadmium, cobalt, and mercury (Sprenke et al. 2000). In 1993 Horowitz et al. (1993) confirmed that 85 million metric tons of these mine-wastes had been transported to Lake Coeur d'Alene (CDA) and were residing in the lakebed sediments. The potential for these sediments to contaminate the overlying water, which with the exception of Zn typically meets the EPA guidelines for freshwater lakes, has resulted in numerous publications and extensive studies.

One of the major concerns is that eutrophication will potentially release metal(loid) contaminants (Woods et al. 1997) by eliminating the oxic zone present at the sediment water interface (SWI). It is proposed that suboxic and anoxic conditions will promote reductive dissolution of solid materials that currently scavenge metal(loid)s and prevent them from entering the overlying water. Our goal was to first locate a small body of water contaminated by mine waste similar to that contained in Lake CDA sediments, but possessing an oxic interface for only a portion of the year. The interstitial water would then be monitored through an annual cycle to determine concentration changes of dissolved metals, and therefore the effect redox changes had on mine-waste stability. Because of extensive contamination and the presence of numerous wetland areas, the lower CDA River floodplain is a suitable area to consider for a monitoring site.

The lower 42 km of the CDA River is a broad floodplain that appears to be the remnants of a once much larger glacial lake. This section of the river is deep and slow with a gradient of only 0.19 m km^{-1}. Mill slimes contaminating the CDA River are quite susceptible to redistribution because of their very uniform particle size, with the <0.125-mm fraction composing up to 90% of the sample (Sprenke et al. 2000). For example, the tremendous input of mill slimes from the South Fork of the Coeur d'Alene River to the main stem of the CDA River reduced the river depth at one monitored location from 12-15 m in 1910 to 3-5 m in 1930. Consequently, frequent and episodic flood events transported and distributed this reservoir of contaminants in the river, throughout the flood plain, and into the numerous small lakes and wetland areas which are common features of this ecosystem. We established a monitoring site in a pond where there were indicators of active redox cycling to quantify changes in soluble metal concentrations within the sediment and the overlying water. Our objective was to use this simulation as a means to predict what might occur in Lake CDA should it become eutrophic and anaerobic.

MATERIALS AND METHODS

Sample Site.

A sample site was chosen near the center of a wetland located on Mike Schlepp's farm near Medimont, Idaho. The owner of the surrounding farm ground indicated the site has been continuously inundated since the early 1900's when the Post Falls dam was constructed, which is important for replicating sediment conditions similar to that of Lake (CDA). The water depth fluctuated from 1 meter in the early spring, to 2 meters throughout the summer, and decreased to 1 meter again in the late fall. Prior to establishing the site, sediment contamination and dissolved metal concentrations in the interstitial water from three locations within the wetland were compared. There were only minor differences in the contaminant levels and dissolved metals, indicating that a wetland with uniform contamination and geochemistry had been located.

Materials.

All chemicals were reagent grade and used without further purification. Solutions were prepared using distilled, deionized water. All sampling containers and labware were cleaned with 2% HCl, soaked in 1% HNO_3, and thoroughly rinsed with deionized water prior to use. Analytical standards and quality assurance standards for ion chromatography (IC) and inductively coupled plasma-atomic emission spectroscopy (ICP) were purchased. Standard Reference Material 2711 from the National Institute of Standards and Technology (Gaithersburg, MD) was used as the total metals standard for the acid digests. Acids used for total metals were all trace-metal grade (Fisher Scientific, Pittsburgh, PA).

Equilibrium Dialyzers and Overlying Water Samples.

Interstitial water was collected *in situ* utilizing Plexiglas equilibrium, dialysis samplers (Hesslein 1976). The dialyzers contained two rows of 25, 10-mL compartments milled on 1.5-cm centers. The compartments were covered with 0.2-μm Osmonics nylon membrane (Westborough, MA), nylon tulle netting, and a matching cover plate held in place with nylon screws. The dialyzers were inserted vertically into the sediments from a Cataraft (Aire-Ocelot, Boise, ID) using a template to stabilize the dialyzer during placement, a landing board attached to the template to assure uniform depth placement, and interconnected sections of steel tubing that were adjustable for the depth of the overlying water. Rope was attached to the dialyzer to assist in placement and tied off to a buoy to aid in retrieval. The dialyzers were allowed to equilibrate for 4 weeks, a time deemed appropriate based on field and laboratory studies (Balistrieri 1998; La Force et al. 2000; Winowiecki 2002).

Upon retrieval, the dialyzers were transferred to shore and immediately processed on location or in an enclosure located a short distance from the sample site. We removed samples from adjacent dialyzer cells in rapid sequence using a 10-mL syringe and expressed them into a 15-mL HDPE sample vial. Three milliters of the total volume were immediately removed using the same syringe. A lure lock cation exchange cartridge (OnGuard II, Dionex, Sunnyvale, CA) was installed, 2 mL was dispensed to condition the cation-exchange cartridge, and 1 mL was placed in a HDPE vial for anion analysis. Another 3 ml was immediately removed and placed in a 5-mL PPE sample vial (Perfector Scientific, Atascadero, CA) where it was stored under N_2 gas on ice packs until titrated for alkalinity. The remaining sample in the 15-mL HDPE vial was acidified with 0.075 mL of trace metal grade HCl to maintain a pH of less that 2.5 in preparation for metal(loid) analysis by ICP-

AES or ICP-MS. All samples were stored on ice until returning to the laboratory where they were maintained at 4 °C until analysis.

Overlying water samples were collected by submerging acid-washed and rinsed, 250-mL HDPE bottles beneath the water surface, removing the cap, and allowing the bottle to fill. The bottom water samples were collected by using an acid-washed and rinsed, 10-cm by 50-cm polycarbonate core tube and the coring device described below. The air-tight piston was placed flush with the exposed end of the core tube to prevent the capture of surface water. The coring device was lowered until contact was made with the sediment, at which time the air-tight piston was drawn into the core tube to the half-way mark, filling the core tube with bottom water. The coring device was then inserted into the sediment while simultaneously pulling the piston through the remainder of the core tube. The partial sediment core prevented loss of the bottom water while pulling the coring device to the surface, and the piston prevented mixing the bottom water sample with the overlying water. Once the coring device was at the surface, the piston was removed and the bottom water decanted into a 250-mL, acid-washed HDPE bottle. The water samples were immediately transferred to the processing site where they were syringe-filtered with a 2-µm membrane and preserved for analytical analysis as described above.

Sediment Cores.

Sediment cores were collected in polycarbonate tubes with a diameter of 10 cm and a length of 50 cm. The tubes were modified to securely attach to a coring device by drilling a 1-cm hole through the tube diameter and inserting a 1-cm by 12-cm head bolt secured with a hair-pin clip to an insertion assembly attached to sections of quick connect core tube extensions (AMS, American Fall, ID). The core tube extensions allowed adjustment for the depth of the overlying water. Once the core tube was secure, a rope (1 m longer than the length of the steel tubing) with a traveling air-tight piston attached was fed through the open end of the core tube, through an opening in the insertion assembly, and secured to the end of the steel tubing to allow easy access. The entire coring device was then lowered in a vertical fashion until contact with the sediment was made. The core tube was then pushed into the sediment while simultaneously pulling the rope, which in turn pulled the air-tight piston. When the piston had traveled the length of the core, the device was returned to the surface in a vertical motion, with the air-tight piston holding the core in place. As the lower end of the core cleared the surface of the water, a Fernco style Quickcap (Davison, MI) was placed over the exposed end and secured. The insertion assembly was then removed from the upper end of the tube, the air-tight piston was removed with care taken not to elongate the core, another Fernco-style Quickcap was placed and secured, and the holes used to insert the headpin were covered with duct tape to prevent spillage and to maintain the redox condition of the core. The cores were stored on ice under N_2 until they were sectioned in an anaerobic glovebox in the laboratory. Throughout the core retrieval, storage, and transport processes every effort was made to maintain a vertical orientation. Once in the laboratory, the cores were transferred to an N_2-filled glove box and extruded from the coring tubes with care taken to avoid compaction or elongation. Cores were sub-sectioned at the appropriate depths and homogenized samples placed in acid-washed HDPE vials. The vials were frozen until analysis. The insertion tool for the dialyzers and the coring assembly were designed and built specifically for this project.

Analytical Methods.

Frozen, homogenized core sub-sections were thawed, transferred to acid-washed crucibles, and dried at 90 °C until stable weights were achieved. The dry samples were cooled in a vacuum desiccator, ground with a mortar and pestle, transferred to 10-mL polyethylene vials, and stored in a vacuum desiccator except when removed to transfer an accurately weighed sample to a digestion container. Samples were microwave-digested with a 9:2:3 ratio of HNO_3, HCl, and HF in accordance with EPA method 3052 (Staff 1994). Recovery precision and accuracy, performed in triplicate on the Standard Reference Material 2711, indicated a relative standard deviation (RSD) of less than 3% and extraction efficiency greater than 90% for the data presented. Triplicate unknown samples were run in each batch digestion and the RSD was generally less than 5%. The digests were filtered using a 0.2-µm Gelman IC Acrodisc syringe filter (Ann Arbor, MI) and volumetrically diluted to 50 mL in preparation for analysis.

Anion concentrations were determined using a Dionex 500DX Ion Chromatograph fitted with an AS18 Ion Pac column, an AG18, 4-mm guard column, and a MFC-1 Metal Trap. The flow rate was 1.0 mL min^{-1} of a 100 mM KOH eluent. A gradient method was used to improve peak separation and decrease elution time. The samples were preserved at 4 °C under N_2 gas until transferred to auto-sampler vials. Standards were included with the unknowns to monitor calibration and drift and analysis was complete within 24 hours.

Dissolved metal(loid) analyses were performed on a Thermal Jarrell Ash ICP-AES. The reported values are the average of three replicates. Detection limits for each element were calculated at two times the standard deviation of the low standard. The RSD, as determined by running a standard 10 times, calculating the average, and dividing it into the standard deviation, was less than 4% across all analyses. Standards were run every 15 samples to verify calibration and were also included in the unknowns to monitor drift. Dissolved trace-metal analyses were performed on a HP 4500 ICP-MS with a flow rate of 0.5 mL min^{-1} and a dilution of 5:1 via peristaltic pumps. The reported concentrations are the average of three replications from each sample. In order to avoid airborne contamination, ICP-MS sample preparation took place in a positive-pressure clean hood and the auto-sampler was housed in a HEPA enclosure. Detection limits were calculated at two times the standard deviation of the low standard.

Seasonal Deployments.

To meet the objective of monitoring contaminant stability under varying redox conditions, a sampling sequence was established to capture changing pond conditions. The first deployment took place in February 2004 when the pond was covered with ice and snow and the water level was near the annual minimum. Retrieval took place in March when we simultaneously deployed the second set of dialyzers. The ponds were ice free, the water level had risen slightly, but the ponds were generally devoid of macrophyte growth. The April retrieval and simultaneous deployment found the ponds had increased in depth by approximately 0.5 m since February and some macrophyte growth had extended to the pond surface. It was during this April event when additional sediment cores were removed and preserved for total metal analysis. The May retrieval and simultaneous deployment took place under very similar pond levels as April but macrophytes were becoming abundant and high water clarity allowed us to observe turtles, fish, and muskrats. The June retrieval found the ponds at full pool, about 1.2 m above the February level. The ponds were teaming with aquatic activity, emerging pond grasses, and moss growth at the surface and at depth was apparent. The fifth deployment took place in July when the pond remained at full pool, but with macrophyte, pond grasses, and moss in such abundance that maneuvering the cataraft was difficult. During the August retrieval, the pond level had declined slightly, but vegetation had continued to grow in such abundance that maneuvering to the sample site and sample retrieval were challenging. The September deployment took place with similar water levels as observed in August and pond grasses had extended their growth to approximately 1 m above the water surface, but other vegetation was not as abundant. The water level in the ponds during the November retrieval had declined approximately 0.75 m from full pool and macrophytes and pond grasses were in the advanced stages of senescence allowing easy navigation in the pond.

RESULTS AND DISCUSSION

Element Abundance.

Total metal digests of cores collected from Schlepp Pond found the sediments were substantially enriched in As, Cd, Pb, Zn, Fe, Mn, and S when compared to non-mine impacted sediments of lower CDA basin (Horowitz et al. 1993a; Toevs et al. 2006a). Contamination levels were equal to or greater than those found during a previous monitoring project of the contaminated sediments of Lake CDA (Table 4.1). Median total Cd and Zn concentrations in the sediment of the pond are double, total Pb is approximately 30% greater, and total S concentrations are over twice as high as Lake CDA sediments. The reported values are in general agreement with other studies that quantified mine-waste material that has been transported to the lateral lakes in the lower CDA River basin (Sprenke et al. 2000) and to Lake CDA (Horowitz et al. 1992; Horowitz et al. 1993a).

Table 4.1. Elemental analysis of acid-digested sediments from 2, depth averaged Schlepp Pond cores and averaged concentrations from two Lake Coeur d'Alene mine-waste impacted sites. The cores from Schlepp Pond were collected in April of 2004 and Lake Coeur d'Alene cores were collected in May of 2002. Analyses were performed using ICP-AES.

Statistic	Element (mg kg^{-1})						
	As	Cd	Fe	Mn	Pb	S	Zn
				Schlepp Pond Site			
Range	51-298	26-103	66 900-103 000	6 22-10 3	4280-15100	5590-11100	3750-11000
Median	145	58.6	89 200	7 94	5 440	8 860	7 260
Mean	171	61.5	87 300	8 07	7 39	8 700	7 380
±SD (n=16)	88.5	18.6	10 800	1 13	3 98	1 570	2 270
				Lake Coeur d'Alene Contaminated Sites, Averaged			
Range	94-451	15-44	36 400-116 000	3 600-10 600	1 620-6 490	1 12-6450	2 290-4 080
Median	157	25.6	80 477	6 540	4 130	3 700	3 370
Mean	193	27.5	82 311	6 870	4 010	3 420	3 300
±SD (n=34)	99.4	6.56	17 488	1 990	1 110	1 230	474

Seasonal Redox Environment.

The redox boundaries were determined by the presence or absence of NO_3^-, Mn, Fe, and SO_4^{2-} in the sediment interstitial water following the description of Froelich (Froelich et al. 1979). This method requires accurate identification of the sediment-water interface (SWI) defined as zero in the presentation of all dissolved species data. This boundary was determined by recording the residual sediment line on the dialyzer when retrieved and verifying this position by overlaying the analytical data to verify water-column and subsurface dissolved concentration trends. The data presented in Figure 4.1, A-F are the average of three equilibrium dialyzers for each deployment.

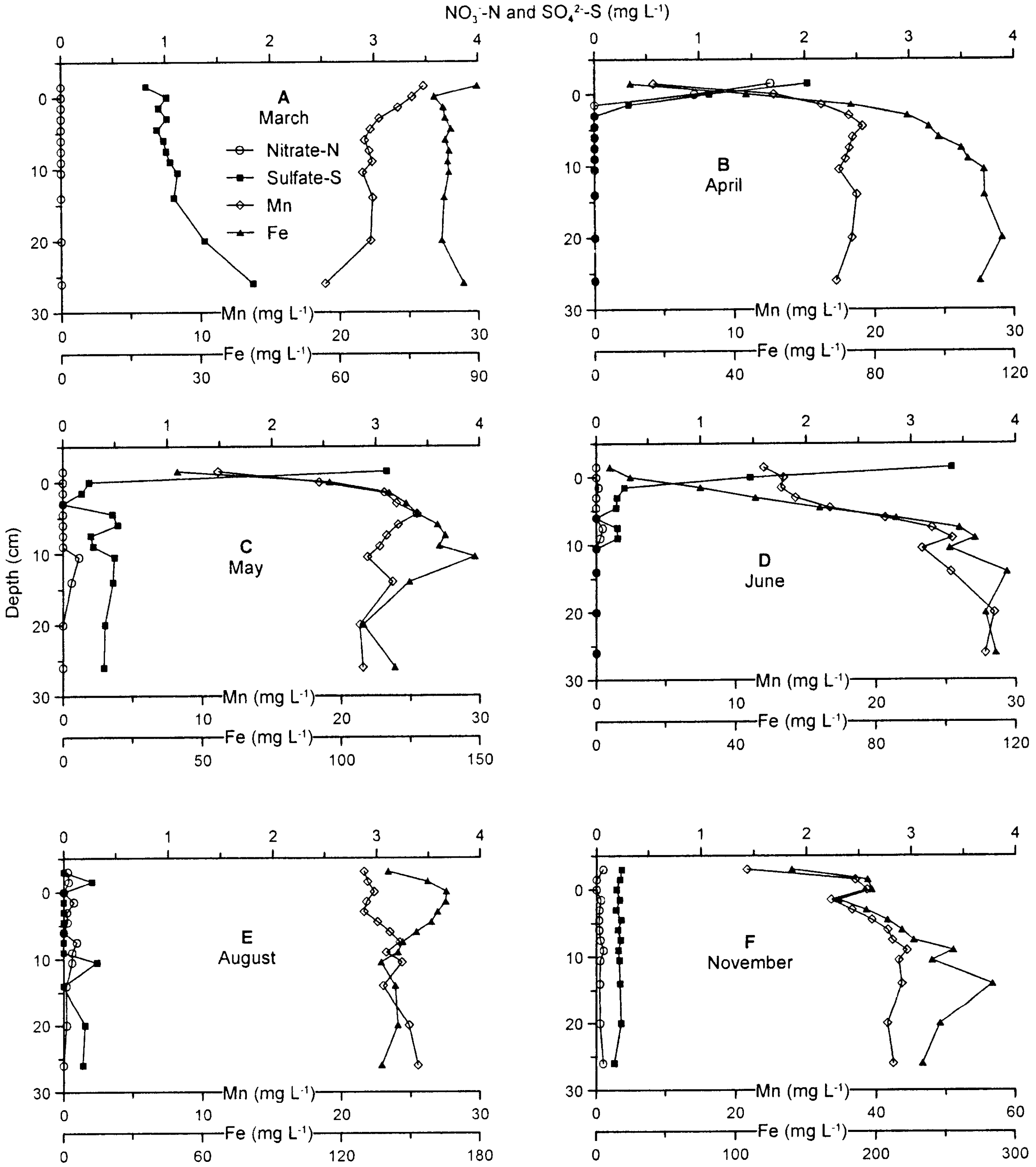

Figure 4.1, A-F. Profiles from averaged concentrations of redox sensitive species present in the interstitial water from six seasonal deployments in Schlepp Pond during 2004. Nitrate and SO_4^{2-} -S were analyzed by IC and Mn and Fe were analyzed by ICP-AES. The average is from three equilibrium dialyzers.

The March data (Figure 4.1, A) show no NO_3^--N, the highest SO_4^{2-}-S levels recorded in the sediments during this study, and relatively low levels of Mn and Fe when compared to the subsequent months. The dissolved concentrations of both Mn and Fe vary little with depth indicating that the reduction potential was uniform throughout the sampled profile. A possible explanation for the observed concentrations of redox-active species is that deployment took place while the surface of the pond was ice covered. This ice cover restricted oxygen diffusion and low temperatures limited microbial activity.

The only deployment in this series where NO_3^--N was detected in the overlying water column was April (Figure 4.1, B), indicating that the SWI was less reduced than at other sampled times of the year, and possibly even oxic. Manganese and Fe both decreased at the SWI indicating the likely formation of oxyhydroxides in this oxic zone, but dissolved Fe increased deeper in the profile when compared to the March data indicating microbial activity was utilizing this terminal electron acceptor (TEA).

Nitrate was not detected in the May samples (Figure 4.1, C), but SO_4^{2-}-S was above detection limits through most of the profile, indicating a sulfate input, internal production by way of mineralization was greater than utilization, or that the sediments were poised above the SO_4^{2-} reduction potential during this period. All of these scenarios may be contributing as the ponds continued to increase in depth from the influx of well-oxygenated CDA River water. Manganese and Fe continued to increase deeper in the sediments, not only indicating additional availability, but also continued demand as a TEA. The June data (Figure 4.1, D) were very similar to those of May except for the absence of SO_4^{2-} deeper in the sediments suggesting that the ratio of SO_4^{2-} utilization as a TEA to any inputs had increased. This June retrieval occurred when the ponds had reached their maximum depth and vegetative growth was rapidly increasing.

In August, both NO_3^--N and SO_4^{2-}-S were absent at the SWI and concentrations were near detection limits throughout the profile (Figure 4.1, E). Dissolved Mn concentrations were comparable to both May and June, but dissolved Fe concentrations had increased. The feature of the August profile that is significant is the return to the nearly vertical shape of dissolved Mn and Fe profiles that were observed in March, indicating uniform reducing conditions in the sediments from the SWI to 26 cm.

The November (Figure 4.1, F) samples showed large increases in dissolved Mn and Fe, a trend counterintuitive to what would be expected as sediment temperatures are expected to decrease microbial activity. One possibility for this increase is plant senescence, which would provide a large, readily available carbon source for the microbial community and also readily reducible iron oxyhydroxides that had accumulated at the soil-root interface of the aquatic plants during the summer months. Another notable feature of the November profiles is the presence of SO_4^{2-}-S from the SWI to the maximum sampled depth as might be expected if oxyhydroxides poise the redox potential and decrease SO_4^{2-}-S utilization.

The analytical data for these redox-sensitive elements show that the ponds display significant changes in the reduction potential but only a brief interval when an oxic SWI was possibly present between the March deployment and the April retrieval. This brief oxic SWI was inferred not only by the presence of NO_3^--N at the interface and in the overlying water, but also because we observed an orange Fe-like precipitate in the first 2 to 3 cells below the SWI of each dialyzer when retrieved from the pond sediments in April. Iron precipitation always occurred inside the cells after sample removal and exposure to O_2, however no other deployment found Fe already precipitated in the cells prior to removal from the sediments. Thus, the presence of Fe at the SWI in March (Figure 4.1, A) and the presence of NO_3^--N in April (Figure 4.1, B) support the theory that dialyzer placement took place when the sediments were Fe-reducing at the SWI (March), but during the ensuing equilibration period the surface sediments became oxic. This increase in redox potential caused the precipitation of the dissolved Fe that had already diffused into the sample cell, resulting in the orange precipitate. These seasonal redox changes at the SWI provide the context in which to explain changes in dissolved trace-metal concentrations.

Dissolved Trace Metal Profiles.

The seasonal deployments described above were designed to monitor the stability of metals in these contaminated sediments under changing redox conditions. Prior research in Lake CDA suggested (Horowitz et al. 1995; Woods et al. 1997) that most trace elements were associated with an operationally defined Fe-oxide phase that would be unstable if placed in an Fe-reducing environment. As the CDA River and floodplain are the point source for the contaminated lake sediments, these pond sediments, which lie within this flood plain, should serve as an excellent proxy for the lake sediments. Therefore, the ICP-MS trace-metal analytical results (Figure 4.2, A-E) indicating concentrations of dissolved metals were dramatically less than those found in Lake CDA sediments (Toevs 2006c) were unexpected.

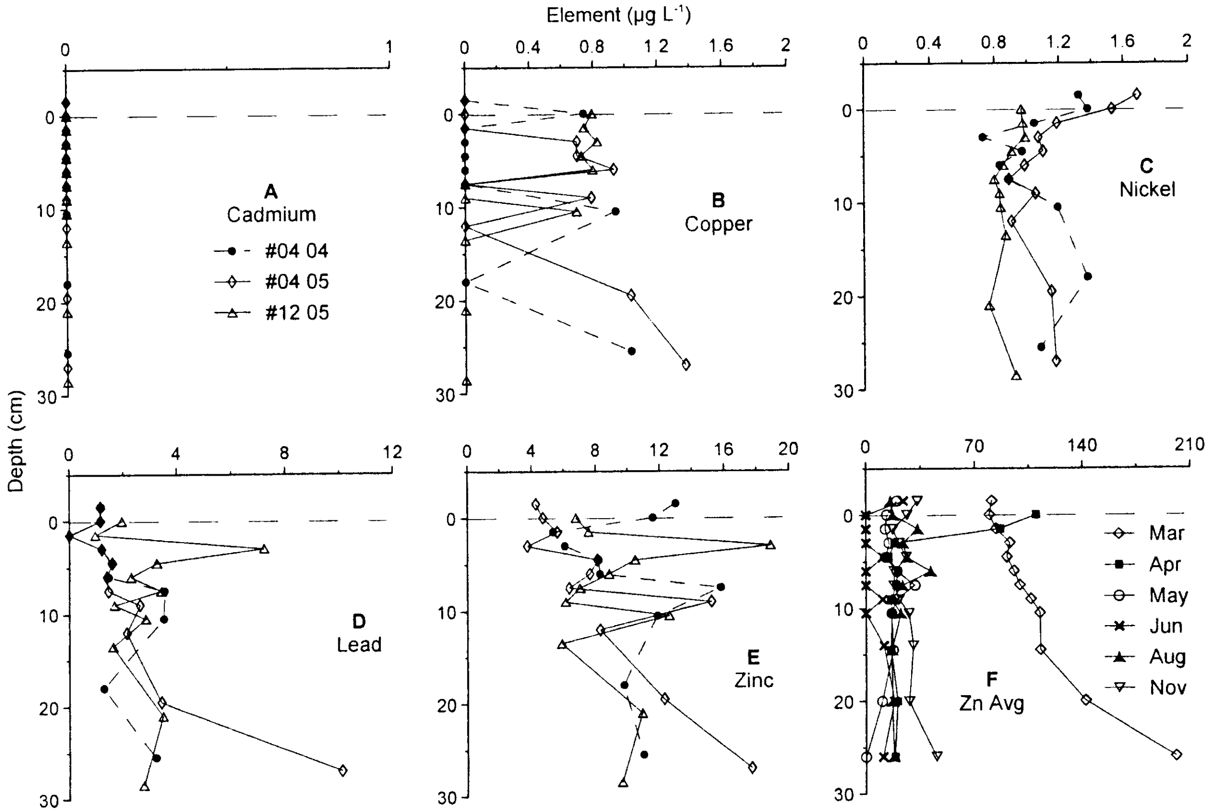

Figure 4.2, A-F. Profiles of dissolved metal concentrations in the interstitial water from Schlepp Pond. Figures A-E are from June 2004 and June 2005 samples analyzed by ICP-MS. Figure F is the average dissolved Zn concentration for six seasonal deployments in 2004 analyzed by ICP-AES. The averages in Figure F are from three equilibrium dialyzers from each deployment.

Cadmium (Figure 4.2, A) was always below the detection limit (0.78 µg L^{-1}) in the pond samples compared to a maximum of 4.02 µg L^{-1} in Lake CDA interstitial waters (Toevs 2006c). Copper (Figure 4.2, B) was also often below the detection limit (0.67 µg L^{-1}), having a maximum concentration of 1.37 µg L^{-1} compared to the lake maximum of 2.04 µg L^{-1}. The maximum Ni concentration in the pond was 1.70 µg L^{-1} (Figure 4.2, C) compared to the lake interstitial water maximum of 4.72 µg L^{-1}. Maximum dissolved Pb concentrations in the pond sediments (Figure 4.2, D) were only 7.1% of the lake maximum, 10.10 and 141.9 µg L^{-1}, respectively. When the June pond samples are compared to the May lake samples, Zn concentrations (Figure 4.2, E) were similarly different with the maximum pond concentration only 3.5% of the lake maximum, 18.88 and 530.5 μg L^{-1}, respectively.

Less damaging biotic effects are anticipated in Schlepp Pond sediments compared to Lake CDA sediments as result of lower maximum concentrations of dissolved metals in the pond interstitial waters. Lake CDA interstitial water concentrations generally exceeded the Criterion Continuous Maximum (CCC) established by the EPA for freshwater biota (Whitman 2002) by several orders of magnitude, but the June interstitial water concentrations in Schlepp Pond, with the exception of Pb, were close to the values considered non-threatening for aquatic biota. It is therefore probable that the differences in dissolved metals is responsible for the lack of benthic activity in Lake CDA sediments and the abundance of activity in these pond sediments. Additionally, the large difference in soluble As concentrations within the interstitial waters is a probable contributing factor to the observed difference in benthic activity, with maximum concentrations of 1 211 μg L^{-1} observed for Lake CDA (Toevs 2006b) and 14 μg L^{-1} for Schlepp Pond (Figure 5.67).

Another noticeable difference is the lack of distinct concentration maxima in the Schlepp Pond profiles when compared to the Lake CDA profiles. Lake CDA commonly showed maxima for Cd, Cu, Pb, and Zn at the oxic-suboxic boundary, which we explained as reductive dissolution of Fe and Mn oxyhydroxides transitioned to lower depths by depositional events (Toevs 2006c). Iron and Mn oxyhydroxides sorbed soluble metals at the continuously oxic SWI and released these metals when buried, thus producing a maximum at the point of reductive dissolution. Lower metal concentrations at deeper depths resulted from anoxic conditions and the formation of iron sulfide precipitates acting as sorbents. Although a slight hint of maxima exist for Pb and Zn (Figure 4.2, D-E), we observed no consistent evidence that similar processes were occurring in Schlepp Pond sediments. We explain this difference by the fact that an oxic SWI existed for only a brief time during the March deployment, thus there was no extended accumulation phase for the metals during the remainder of the year when the SWI was either Fe- or SO_4^{2-}-reducing. In addition, the lack of burial events on a routine basis prevents this sequential sorption-release cycle to occur within the pond sediments.

Our ability to monitor the stability of these contaminated sediments through various redox environments was thus hindered because of two factors, the first of which was the brief period of oxic conditions at the SWI. Secondly, the only element in the interstitial water that was consistently above detection limits on the ICP-AES was Zn. We have presented the Zn profiles for the six seasonal deployments in Figure 4.2, F. Zinc concentrations vary throughout the six deployments from a high of 200.5 $\mu g\ L^{-1}$ in March, which is approximately six times the average, to a low in June when Zn is occasionally below the detection limit of 3.0 $\mu g\ L^{-1}$. Additionally, the April samples indicated Zn began to accumulate in the interstitial water at 1.5 cm and exceeded 100 $\mu g\ L^{-1}$ at the SWI. This sequence may be the result of the oxic conditions experienced during the March deployment. The November to March sequence deserves additional comparison even though these sampling events are not sequential.

As previously described, the November SO_4^{2-}-S profile along with the largest soluble Mn and Fe concentrations (Figure 4.1, F) imply that Fe and Mn oxyhydroxides associated with plant roots are being reduced and that the sediments appear poised in redox at the level of Fe and Mn reduction. In March when the pond is ice covered, SO_4^{2-} continues to accumulate in the interstitial water and soluble Fe and Mn concentrations vary little from the

SWI to the maximum sampled depth, indicating suboxic conditions throughout the sediments. During this same period, Zn is released to the dissolved phase reaching its maximum in the March sample, but Fe is decreasing, reaching its seasonal minimum at this point.

Bostick et al. (2001) showed that oxidation and reduction reactions play a major role in Zn partitioning among various solid phases in CDA mine-wastes, despite the fact that Zn itself is not redox active. Additional investigations by Hansel et al. (2001) clearly demonstrated that plant roots greatly influence Zn partitioning, because of reactions occurring in the rhizosphere. It is possible that Zn associates with Fe oxyhydroxides formed in the rhizosphere of the wetland plants, and as such we would expect a concurrent release of Zn in November during the time when maximum Fe dissolution occurs. As this is not the case, Zn release must be a function of the dissolution of other solid phases. The observation that maximum soluble Zn is produced during March when Fe concentrations are at a minimum and SO_4^{2-}-S concentrations are at a maximum (Figure 4.1, A), suggests the source of Zn cannot be Fe oxyhydroxides, but is possibly a reduced species undergoing oxidative dissolution. This would be consistent with a previous study which found Zn associated with sulfides and carbonates in flooded CDA tailings (Bostick et al. 2001), thus supporting our observations. Additionally, it is entirely possible that rhizosphere reactions play a role in this sequestration in that Zn has been shown to form metal carbonate nodules on the roots of the wetland plant *Phalaris arundinacea* (Hansel et al. 2001). We propose that wide fluctuations in soluble Zn concentrations result from changes in redox as they affect Zn-containing sulfides and carbonates associated with plant roots, thus playing a major role in this wetland system.

Surface and Bottom Water Dissolved Metals.

In addition to the dissolved metals in the sediments, changes in dissolved metal concentrations in the overlying water column were monitored. Table 4.2, A show averaged values of dissolved Pb and Zn concentrations in the surface and bottom water samples from each deployment. The surface-water Pb concentrations were below the detection limit of 8.0 $\mu g\ L^{-1}$ for all months except June. When the June value is compared to the CCC for Pb of 0.07 $\mu g\ L^{-1}$, after adjustment for alkalinity of 5 mg L^{-1} of $CaCO_3$, the Pb values exceed the adopted limit. When dissolved Pb concentrations in the bottom water samples were above detection limits, they also exceeded the CCC. The dissolved Zn concentrations in the surface samples from the seasonal deployments have two orders of magnitude in variation, all of which exceed the CCC of 8.96 $\mu g\ L^{-1}$, after adjustment for alkalinity. The Zn bottom water concentrations are all within the same order of magnitude, but they too exceed the CCC. When the ICP-MS data for June of 2004 and June of 2005 are examined (Table 4.2, B), Cd values were always below the detection limit of 0.78 $\mu g\ L^{-1}$ for both the surface and bottom water. The CCC for Cu is 0.69 $\mu g\ L^{-1}$ after alkalinity adjustment, and is slightly exceeded for all samples. As with the seasonal data, Pb and Zn also exceeded the CCC for freshwater biota.

Table 4.2, A-B. Dissolved trace metal concentrations in the surface water and the bottom water in Schlepp Pond. Table 4.2, A displays averaged values of each seasonal deployment in 2004 for Pb and Zn analyzed by ICP-AES. Table 4.2, B displays the averaged values for five trace metals from the June 2004 and the June 2005 deployments analyzed by ICP-MS.

Sample	Month					
	March	April	May	June	August	November
A						
			Seasonal Lead Concentration ($\mu g\ L^{-1}$)			
Surface	<8	<8	<8	8.90	<8	<8
Bottom	10.560	19.5	<8	9.20	22.6	32.4
			Seasonal Zinc Concentrations ($\mu g\ L^{-1}$)			
Surface	8680	472	95.0	78.0	41.9	75.4
Bottom	683	158	103	210	177	186

	Element ($\mu g\ L^{-1}$)				
	Cd	Cu	Ni	Pb	Zn
B					
			June 2004 Deployment		
Surface	0.000	0.877	0.934	12.1	33.1
Bottom	0.000	0.908	1.62	28.6	250
			June 2005 Deployment		
Surface	0.000	0.811	0.865	12.6	28.30
Bottom	0.000	0.646	1.70	10.5	171

The dissolved metals concentrations for the surface and bottom water of Schlepp Pond show that for all elements except Zn, the concentrations are similar. The high concentrations of soluble Zn in the bottom waters of the pond and the very large changes in concentrations in March and April (Table 4.2, A) are striking. These fluctuations most likely reflect active redox cycling within this zone and the dynamic nature of Zn associations and partitioning with the solid phase (Bostick et al. 2001). In contrast, we did not observe analogous changes in the bottom and surface water for seasonal Pb concentrations (Table 4.2, A). Radically different partitioning of Pb in the rhizosphere of *P. arundinacea* was observed as compared to Zn with plants collected from the CDA floodplain (Hansel et al. 2001). Lead was found to be complexed mainly to organic functional groups, and thus the redox cycling that influences Zn does not exert the same influence on Pb. Active redox cycling within the sediments of Schlepp Pond thus has dramatic effects on soluble Zn concentrations, but such changes are element-specific depending on the solid-phase component associations.

Schlepp Pond and Lake Coeur d'Alene Comparisons.

The contaminated sediments of Schlepp Pond have similar sources as those deposited in Lake CDA and they are equally or more highly enriched in total metals. The most notable differences include median total Cd and Zn concentrations twice those of the Lake and a total Pb concentration approximately 30% higher. One other relevant elemental difference is a total S concentration, which is more than twice that of Lake CDA sediments.

Despite the equivalent or higher levels of contamination, Schlepp Pond interstitial waters consistently contained lower dissolved metal concentrations than Lake CDA interstitial waters. In June 2004 and June 2005 deployments, we found lower dissolved Cd, Cu, and Ni, with Pb and Zn concentrations being only a fraction of those found in the Lake interstitial waters (Toevs 2006c). The influence of the oxic SWI on higher dissolved metal concentrations in Lake CDA sediments cannot be discounted, as dissolved metal concentrations in the pond sediments show little variation with depth indicating the sorption release processes observed in the Lake are absent. Additionally important is the concentration of SO_4^{2-} observed in the ponds is twice that of the lake sediments. This additional SO_4^{2-} would increase sulfide production potential in the anoxic zone and sorption of metals that have strong affinity for sulfur ligands (Balistrieri et al. 1994), thus lowering the dissolved metals in the pond. Finally, as Hansel et al. (2001) found, the root-sediment interface is dynamic and plays an active role in trace-metal sequestration, a process absent in the lake sediments. Differences exist between the sedimentary environment of Lake CDA and Schlepp Pond, but our data confirm the stability of these mine-waste impacted sediments in Fe-reducing environments. Additionally, these data strongly implicate reductive dissolution of the oxic cap upon burial as the source of dissolved contaminants in the lake sediments and confirm the paramount importance of minimizing future transport of mine-waste sediments to the lake.

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APPENDIX

FIGURES FOR LAKE COEUR D'ALENE

Redox Elements

Replicates of Redox Elements

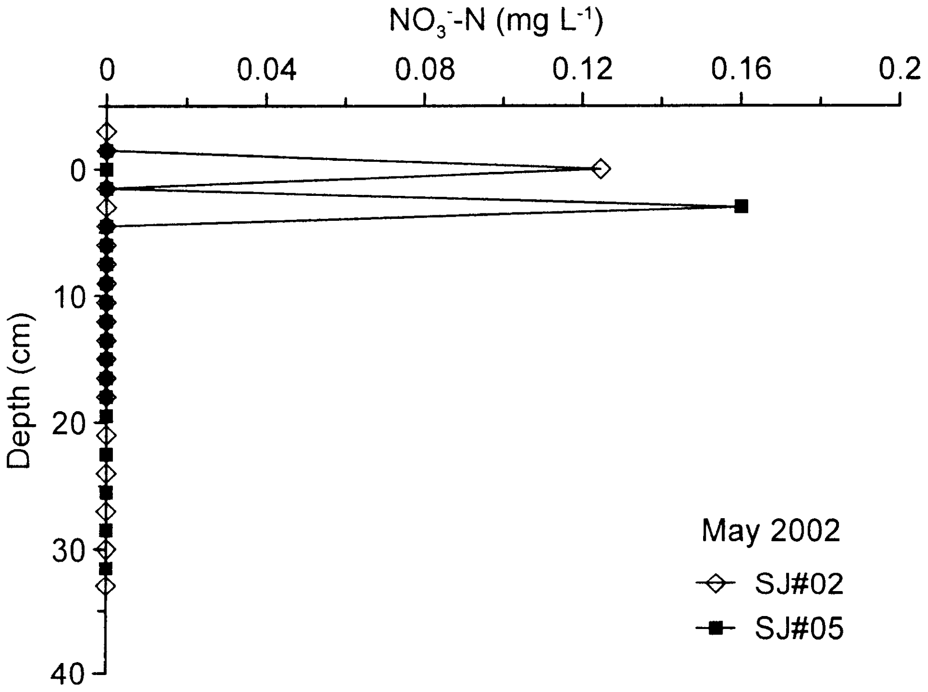


Figure 5.1. Replicate samples of nitrate-nitrogen from the control site, SJ. Samples are from May 2002 and analyzed by IC.

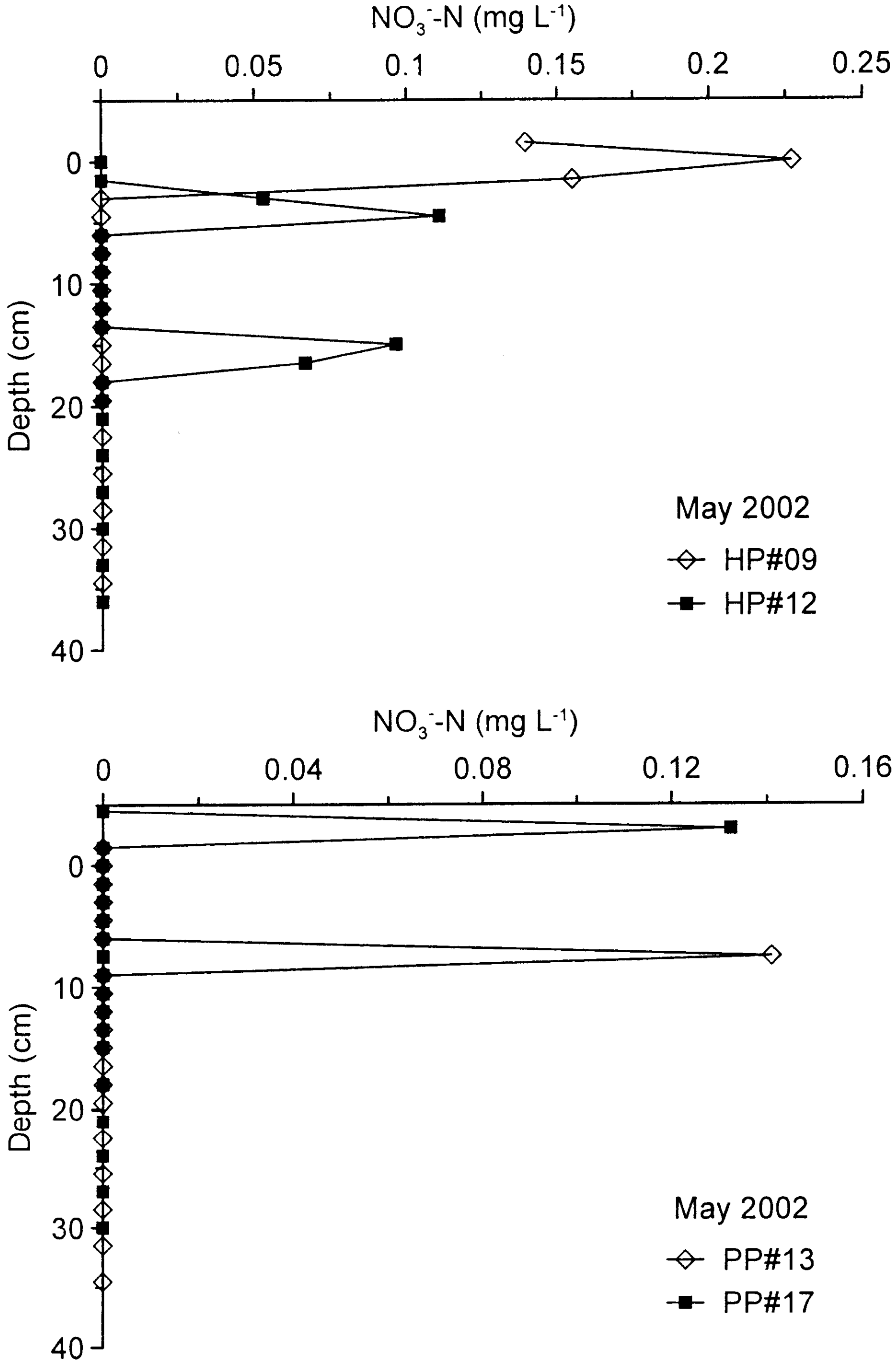


Figure 5.2. Replicate samples of nitrate-nitrogen from the two contaminated sites, HP and PP. Samples are from May 2002 and analyzed by IC.

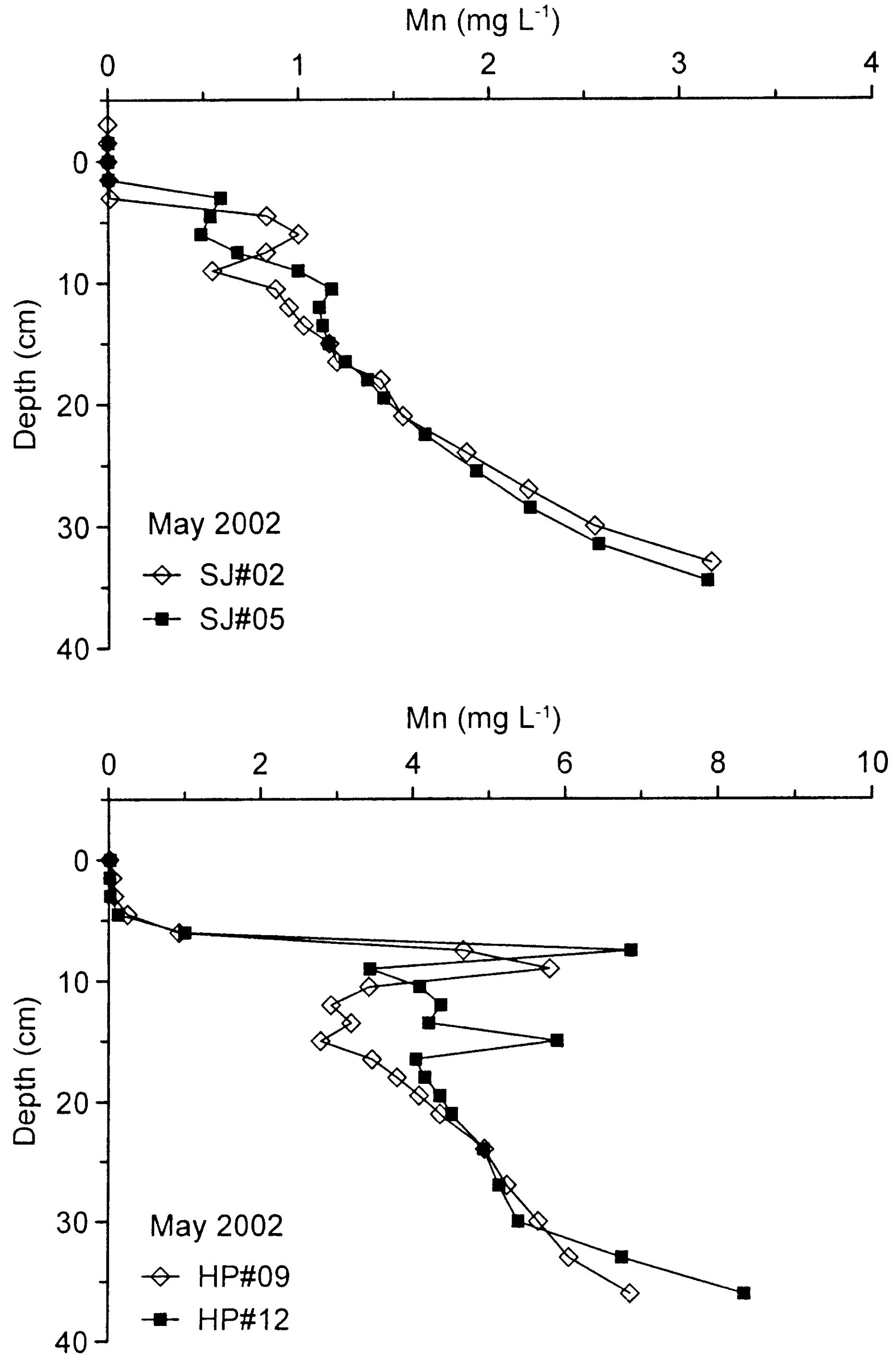


Figure 5.3. Replicate samples of Mn from the control site, SJ and the contaminated, HP. Samples are from May 2002 and analyzed by ICP-AES.

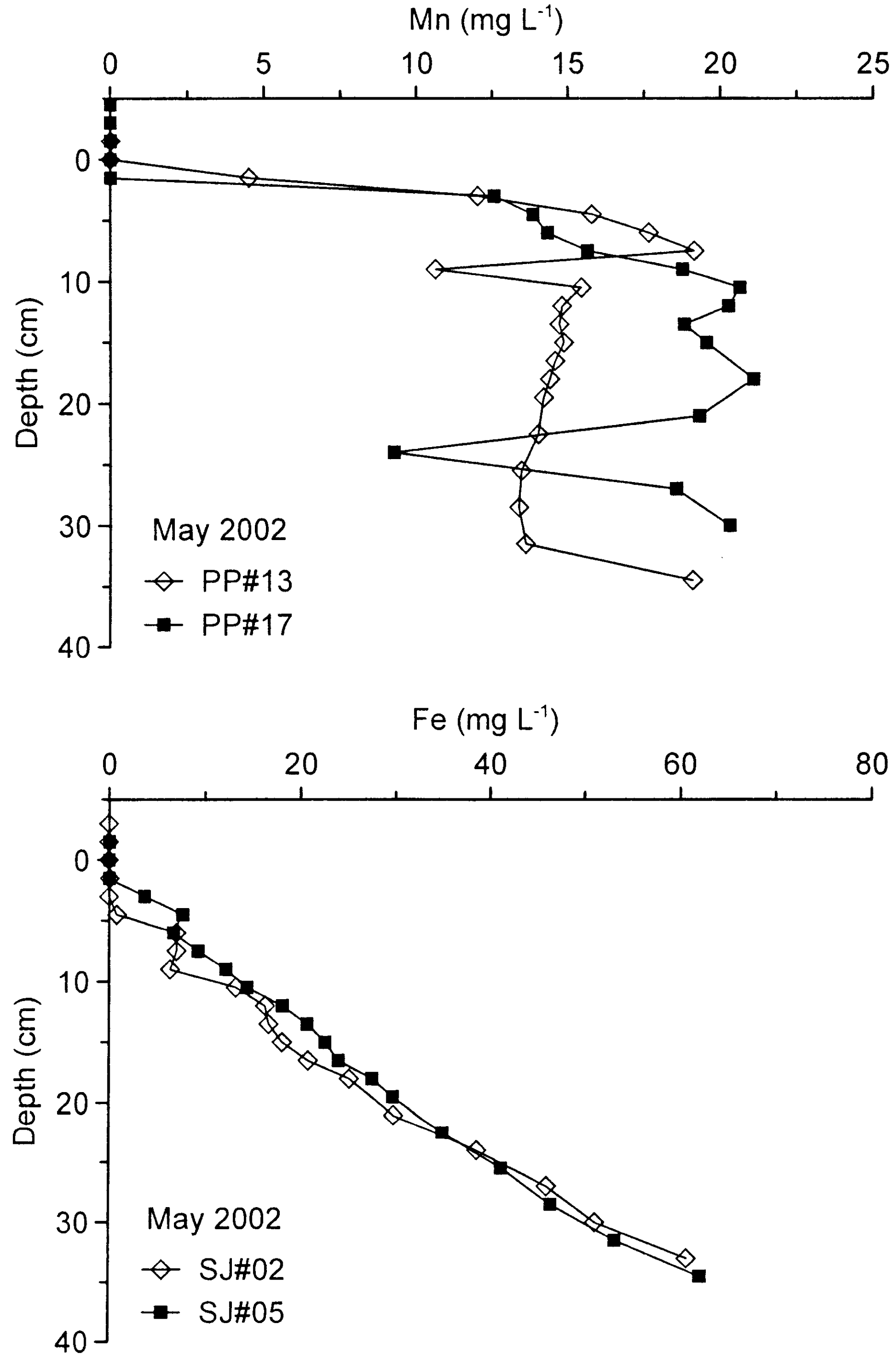
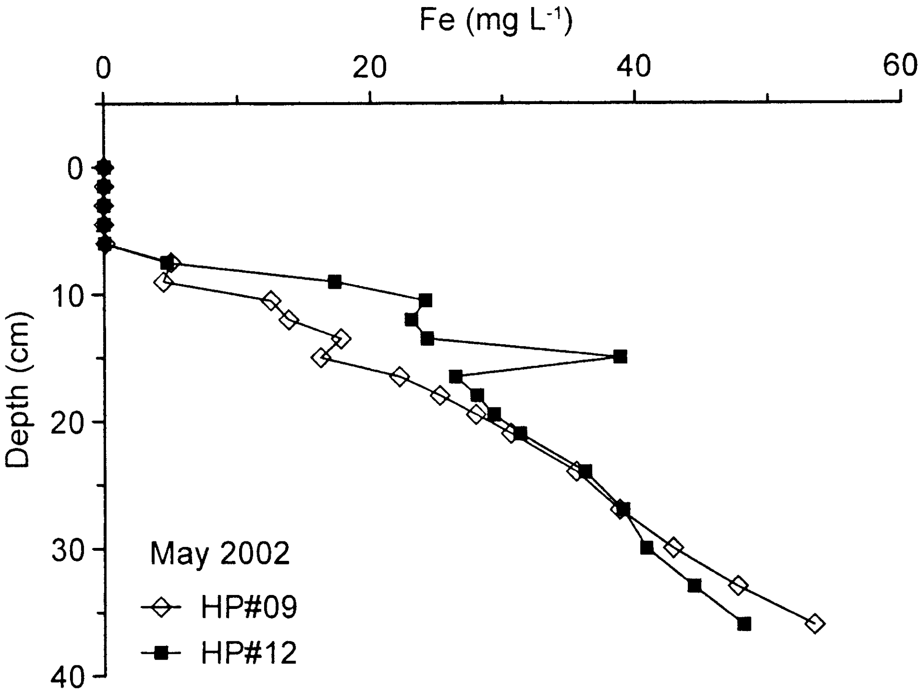


Figure 5.4. Replicate samples of Mn from one contaminated site, PP and Fe from the control site, SJ. Samples are from May 2002 and analyzed by ICP-AES.



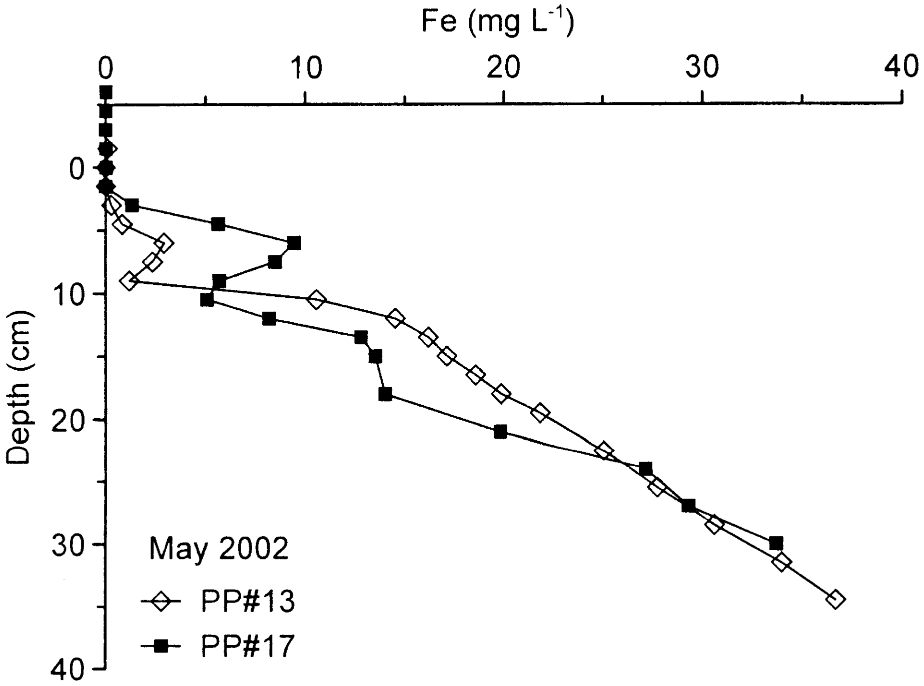


Figure 5.5. Replicate samples of Fe from the two contaminated sites, HP and PP. Samples are from May 2002 and analyzed by ICP-AES.

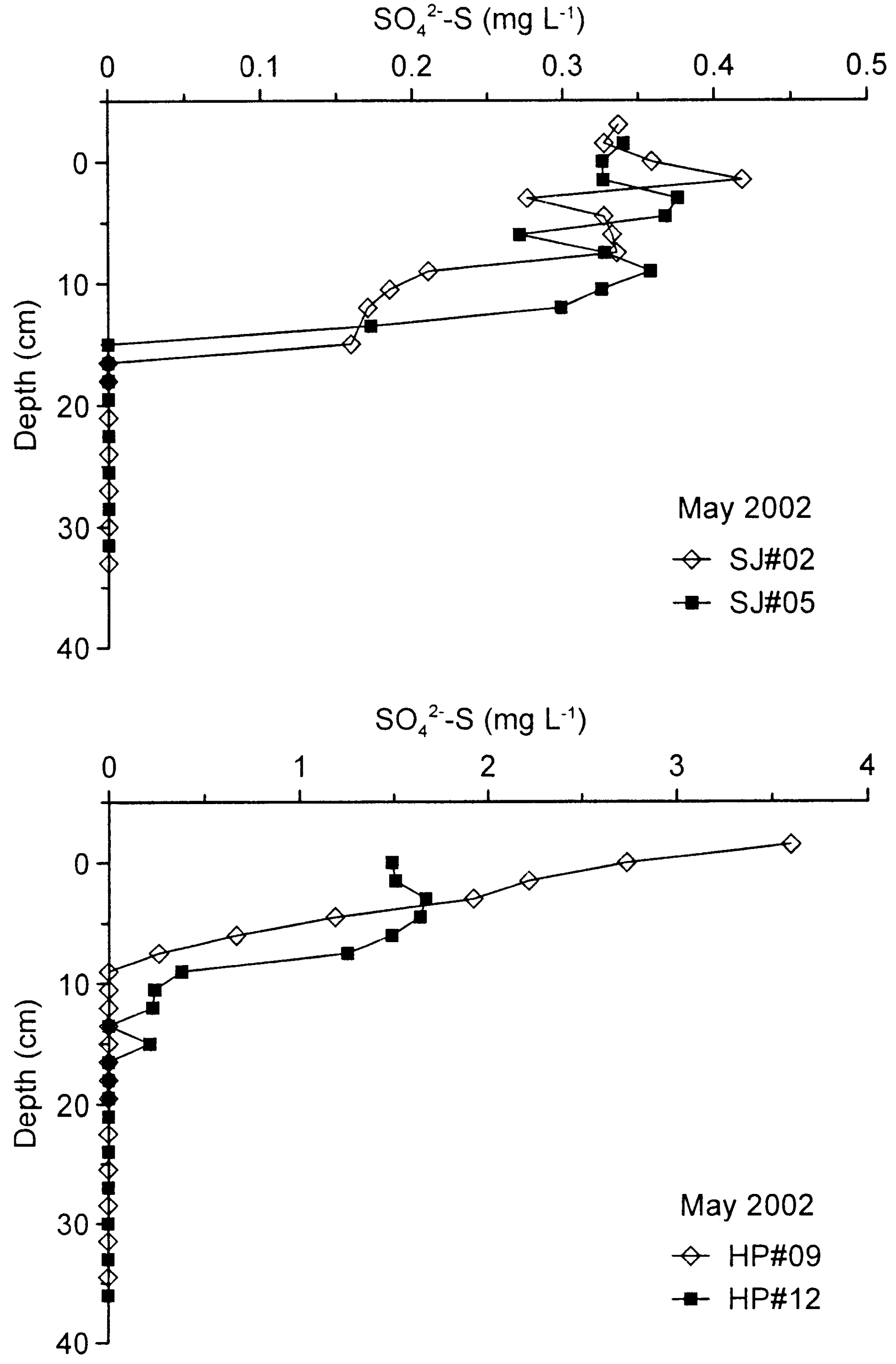


Figure 5.6. Replicate samples of Fe from the two contaminated sites, HP and PP. Samples are from May 2002 and analyzed by ICP-AES.

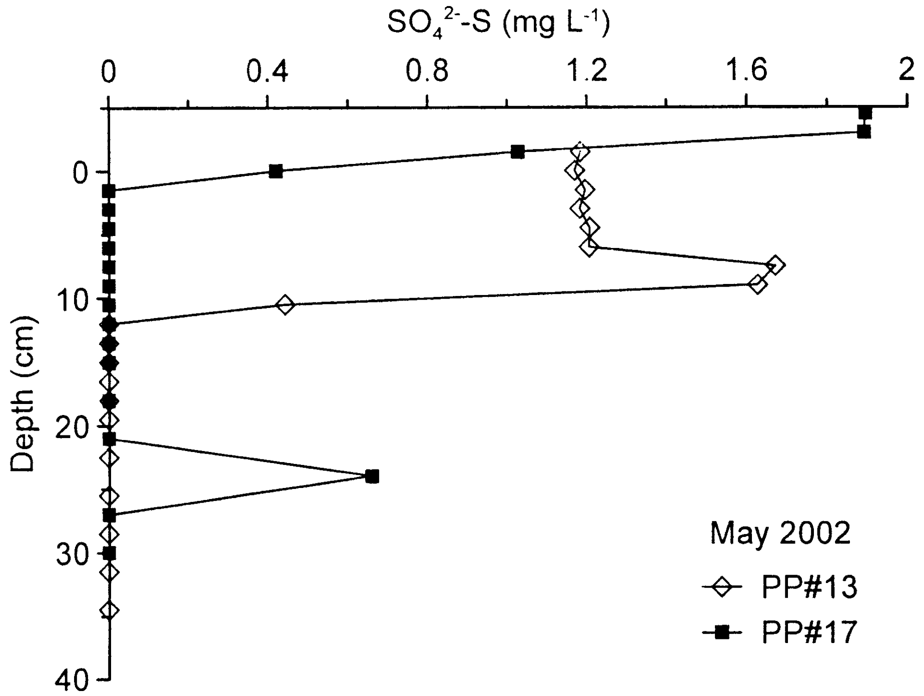


Figure 5.7. Replicate samples of Fe from the two contaminated sites, HP and PP. Samples are from May 2002 and analyzed by ICP-AES.

Redox Element Profiles, Averaged Data

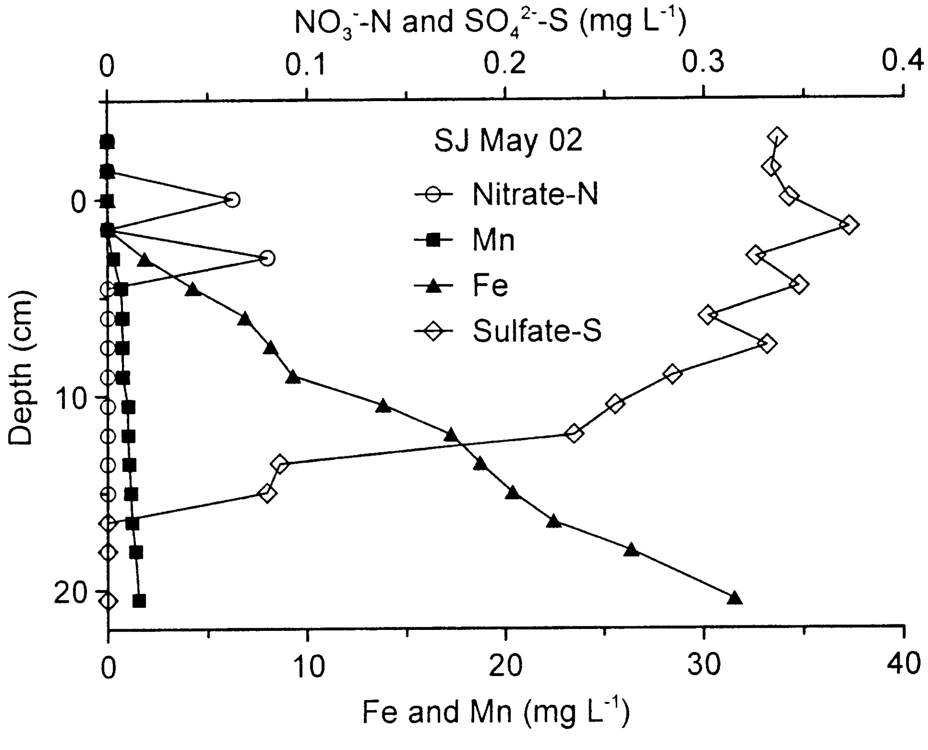
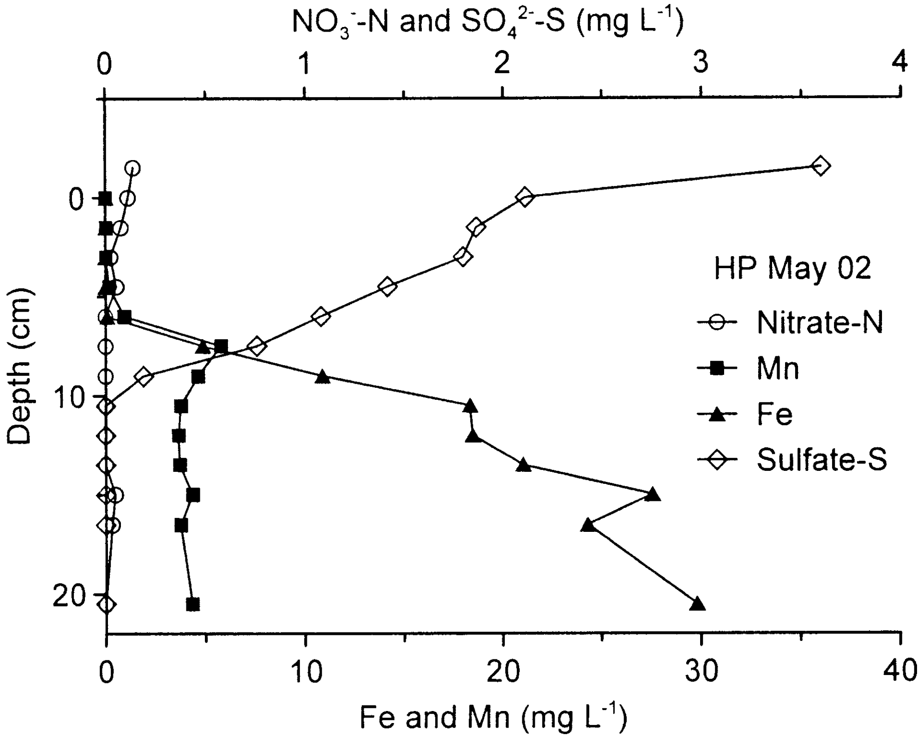


Figure 5.8. Redox profile of the control site, SJ, established from the presence or absence of TEA. The data are the average of replicate samples collected in May 2002.



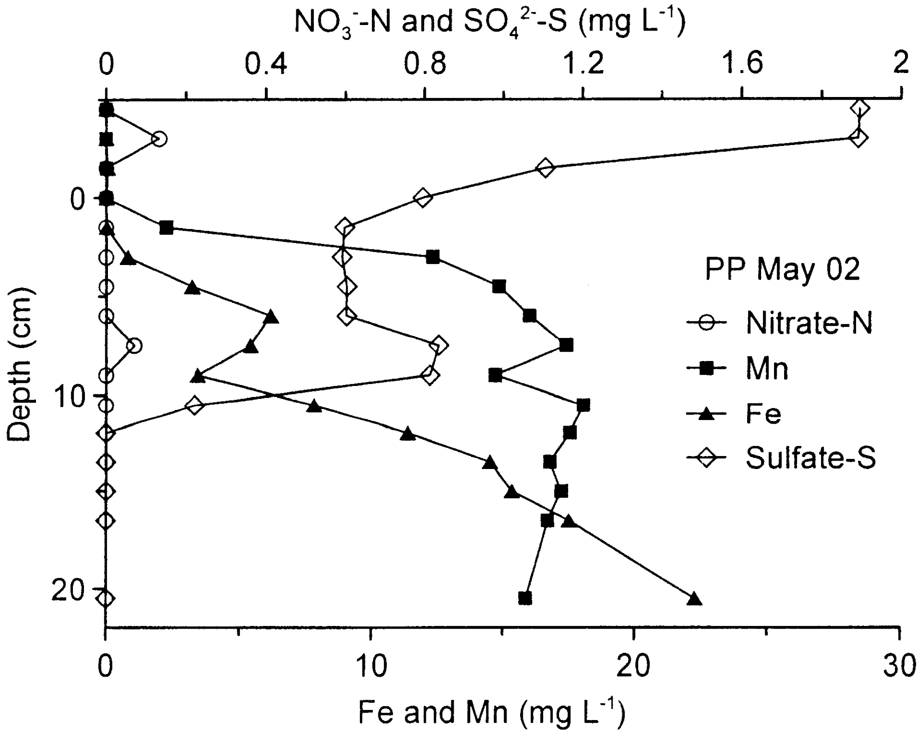
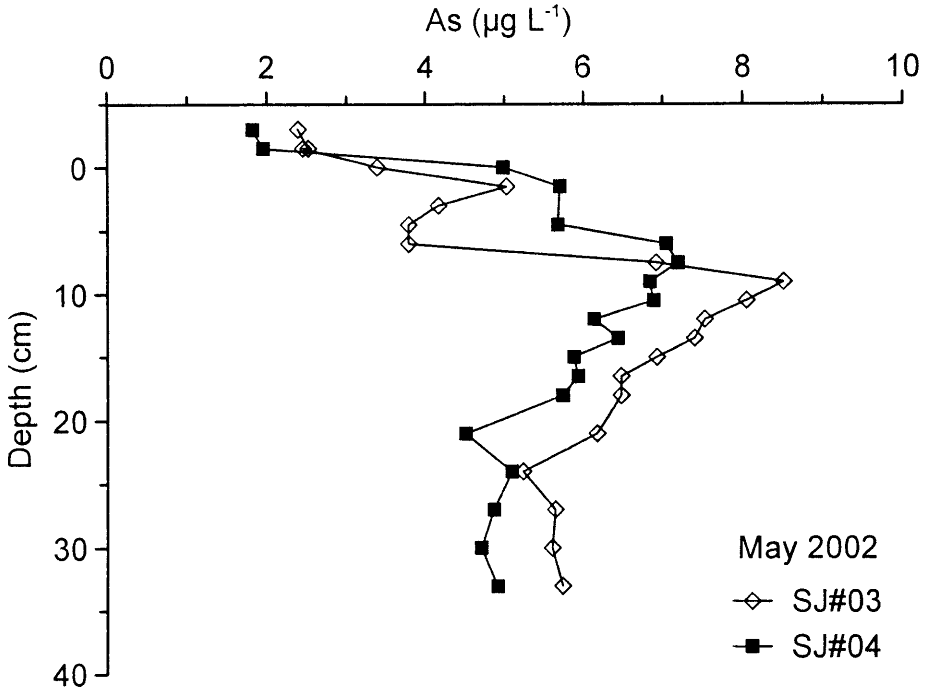


Figure 5.9. Redox profile of the two contaminated sites, HP and PP, established from the presence or absence of TEA. The data are the average of replicate samples collected in May 2002.

Dissolved Metal(loids), ICP-MS

St. Joe Site



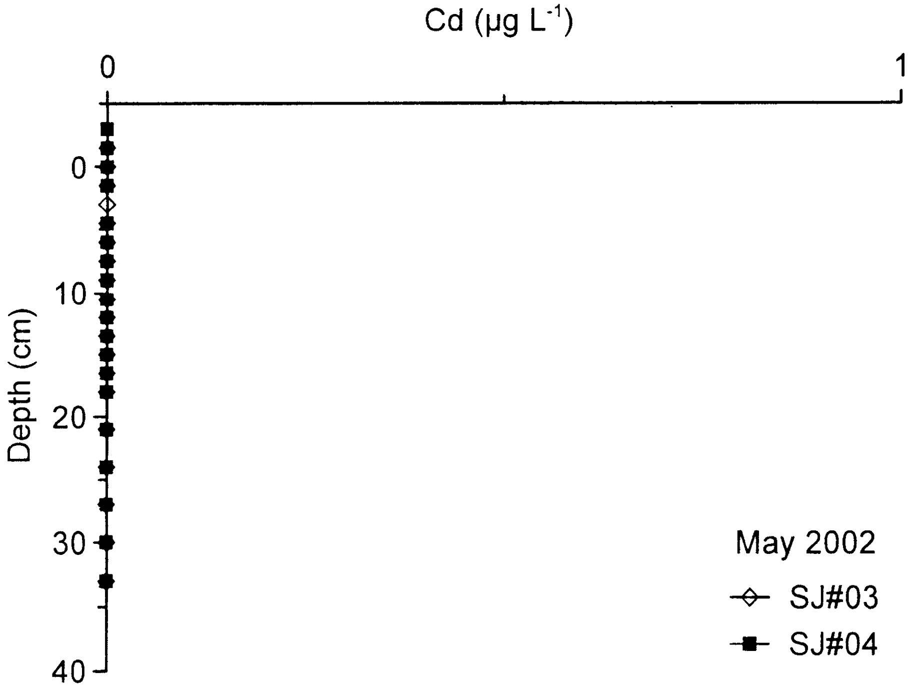


Figure 5.10. Replicate samples of As and Cd from the control site, SJ. Samples are from May 2002 and analyzed by ICP-MS.

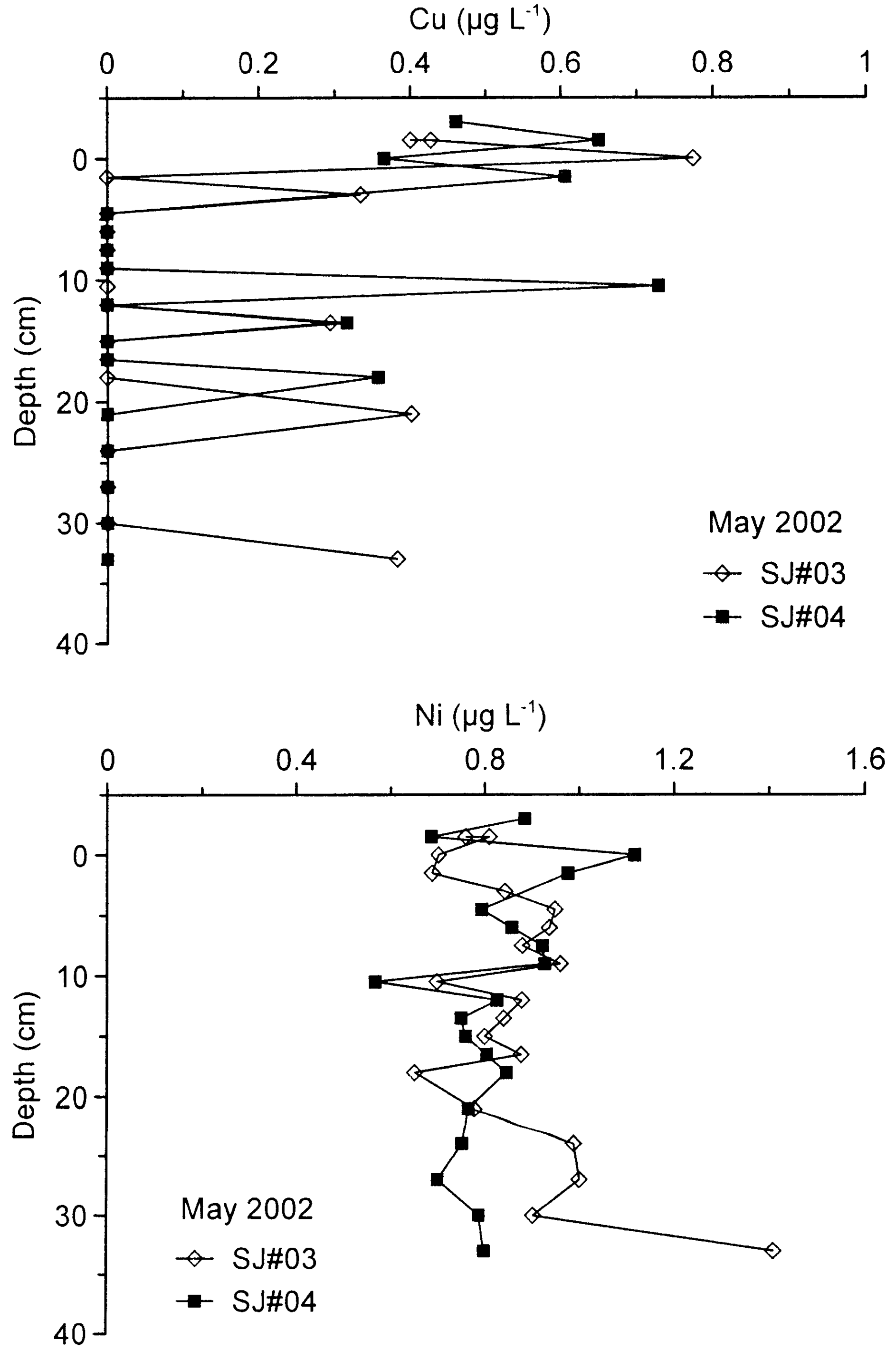
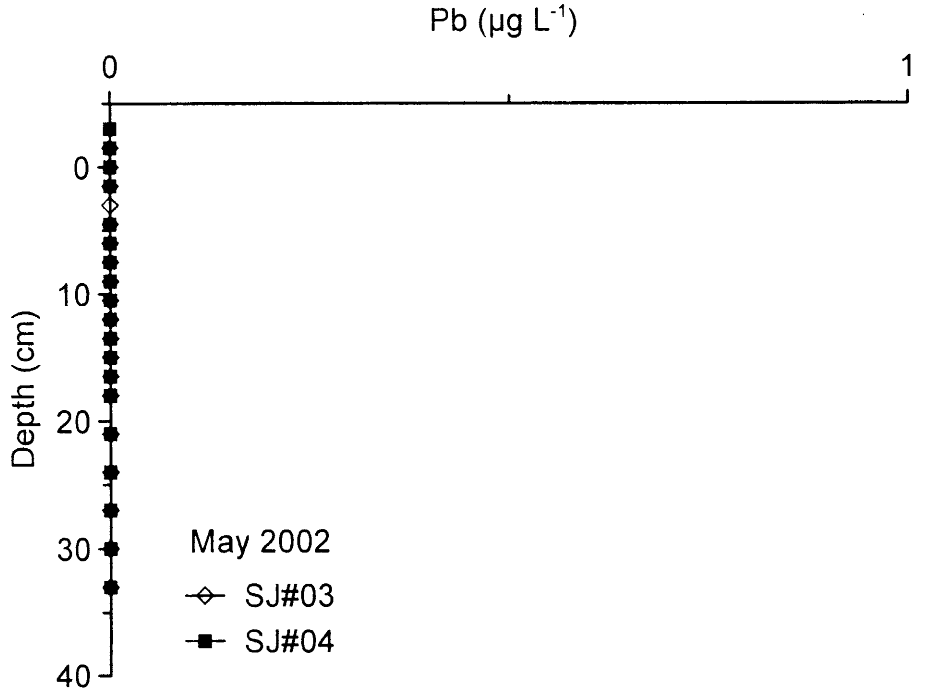


Figure 5.11. Replicate samples of Cu and Ni from the control site, SJ. Samples are from May 2002 and analyzed by ICP-MS.



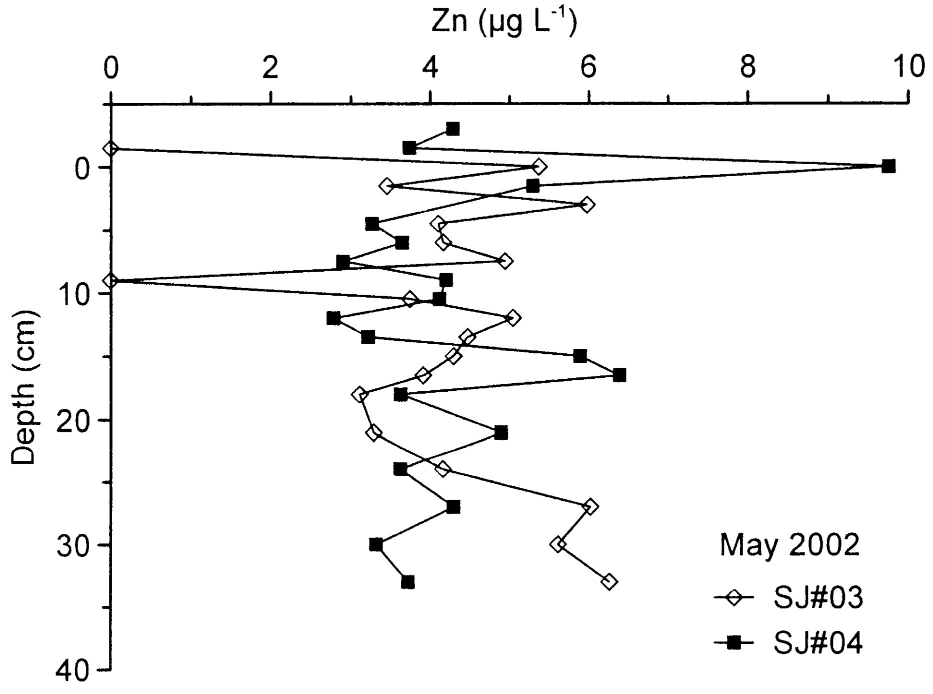


Figure 5.12. Replicate samples of Pb and Zn from the control site, SJ. Samples are from May 2002 and analyzed by ICP-MS.

Harlow Point Site

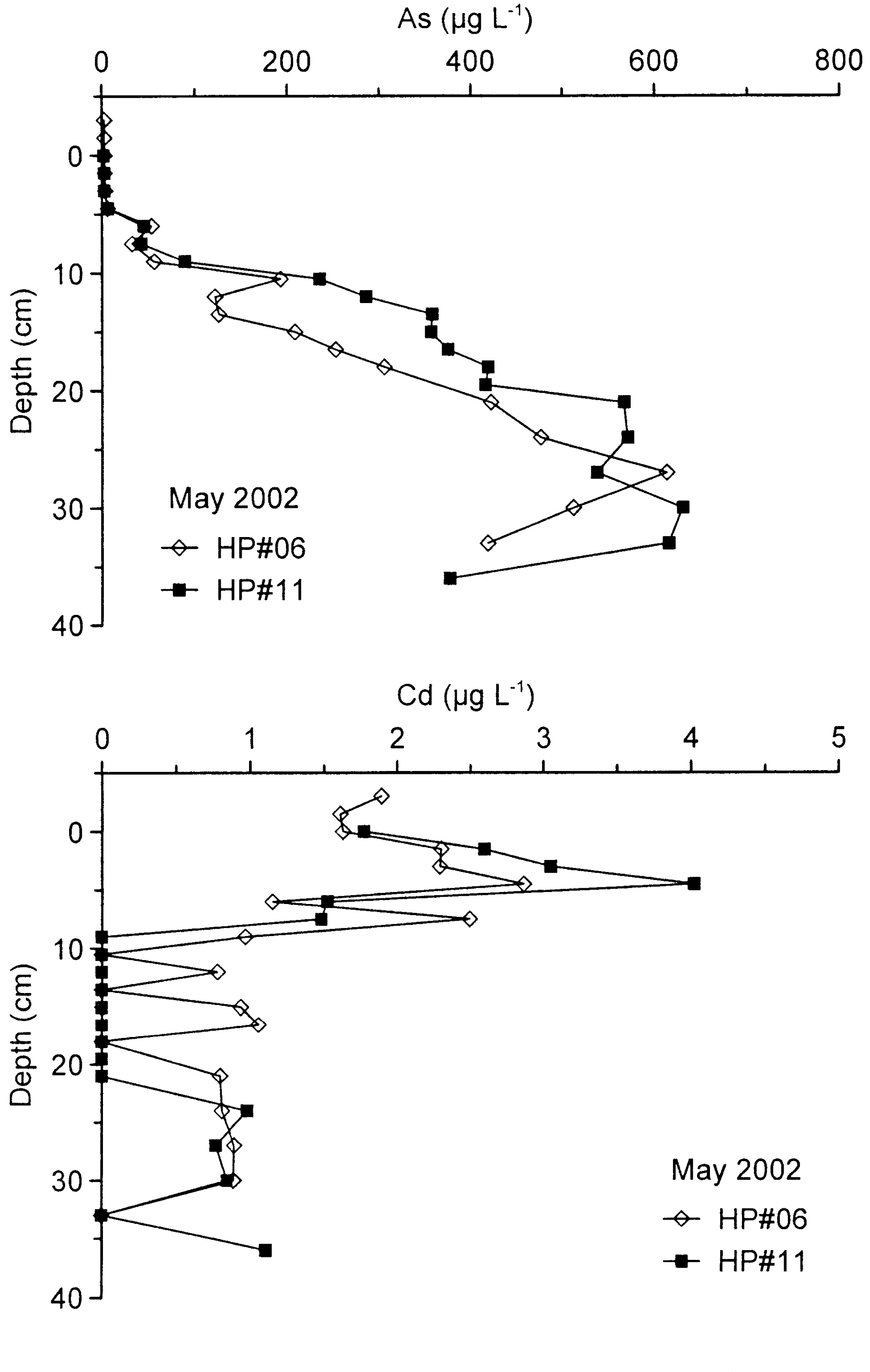


Figure 5.13. Replicate samples of As and Cd from one contaminated site, HP. Samples are from May 2002 and analyzed by ICP-MS.

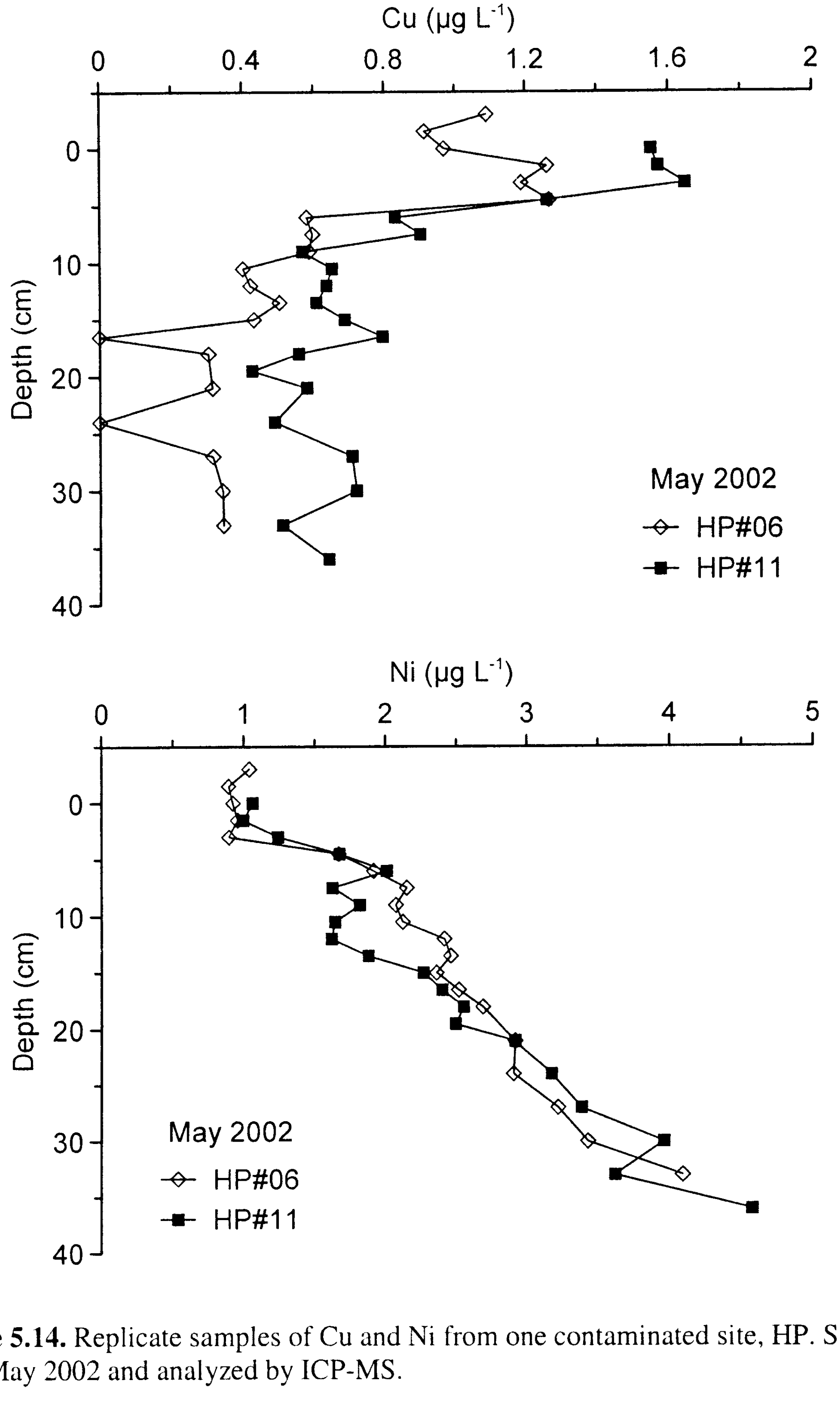


Figure 5.14. Replicate samples of Cu and Ni from one contaminated site, HP. Samples are from May 2002 and analyzed by ICP-MS.

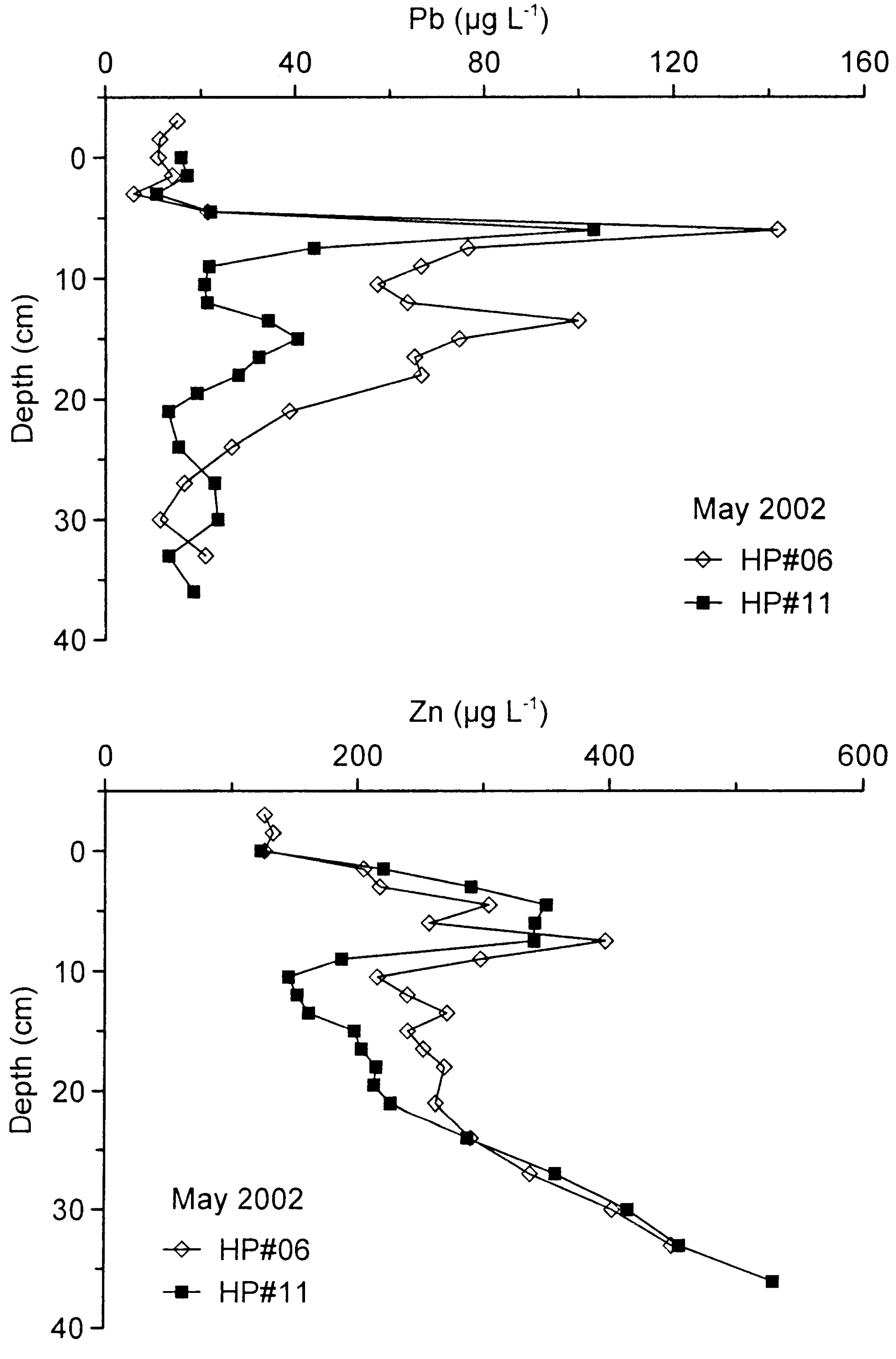
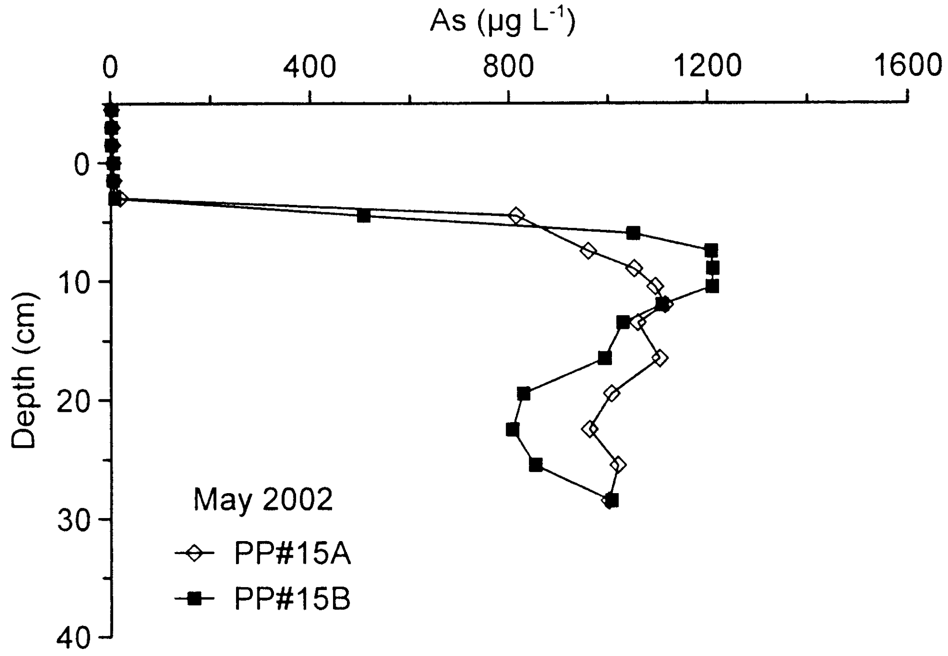


Figure 5.15. Replicate samples of Cu and Ni from one contaminated site, HP. Samples are from May 2002 and analyzed by ICP-MS.

Peaceful Point Site



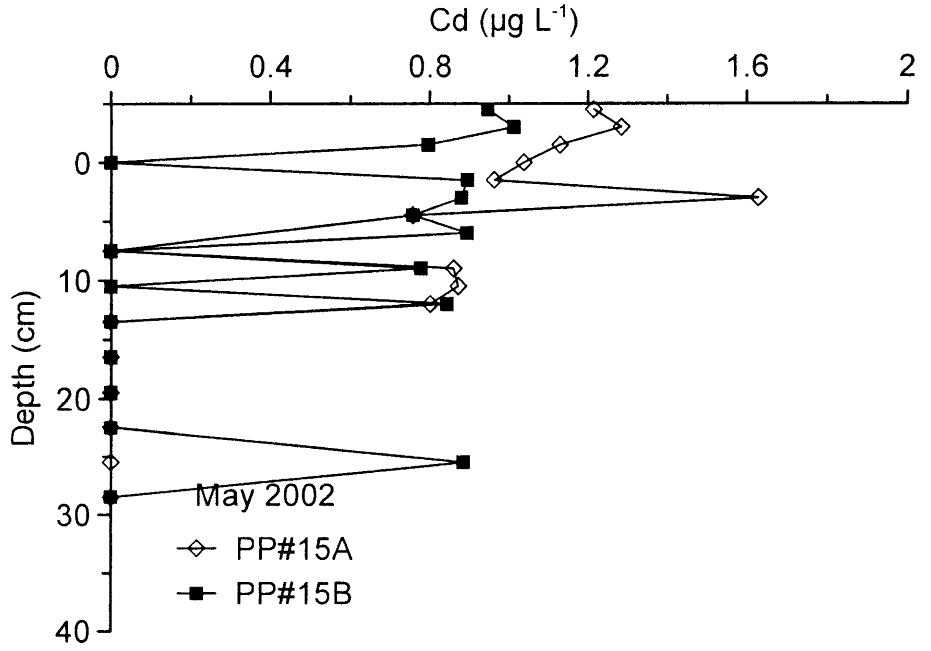


Figure 5.16. Replicate samples of As and Cd from one contaminated site, PP. Samples are from May 2002 and analyzed by ICP-MS.

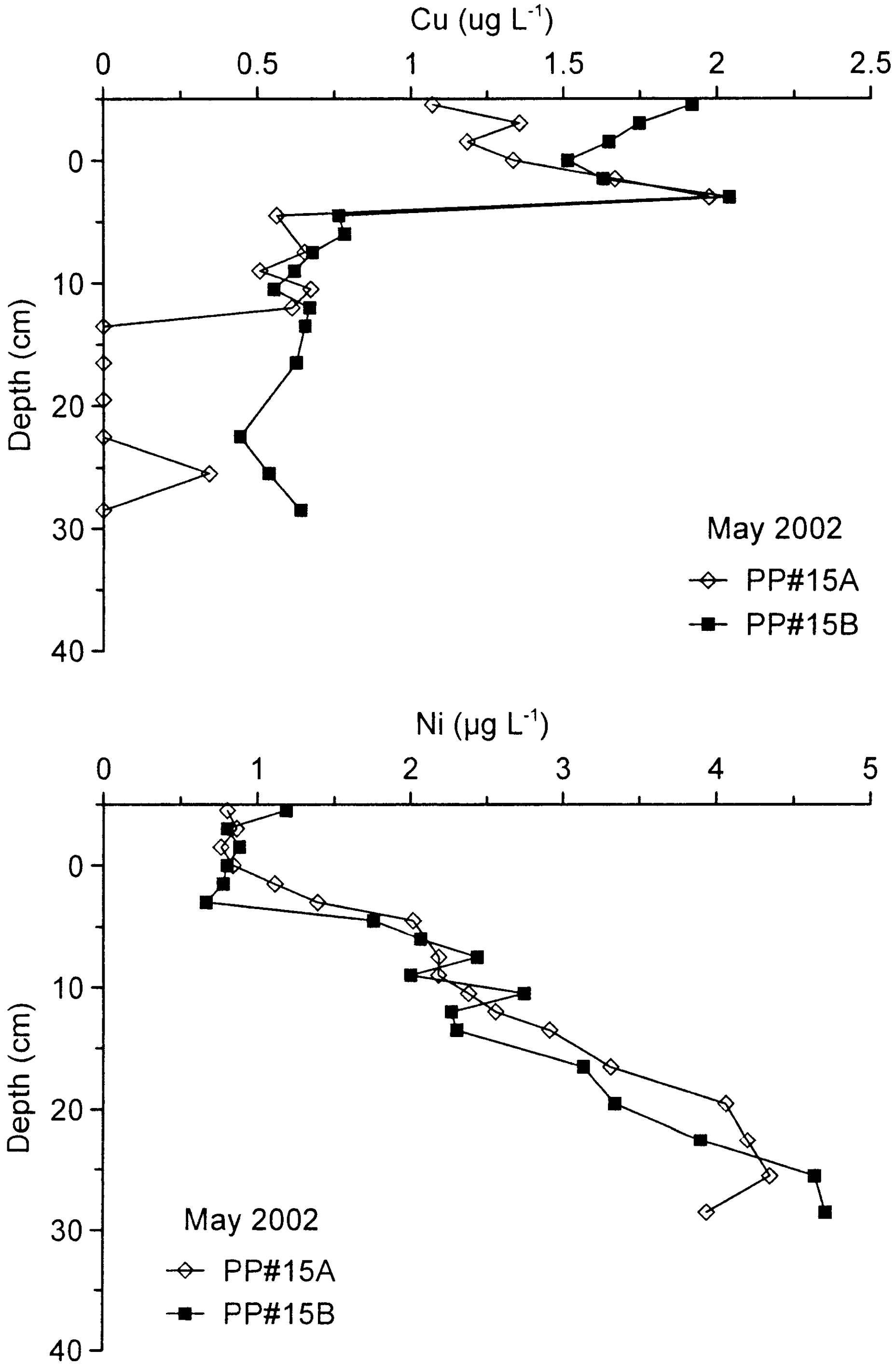
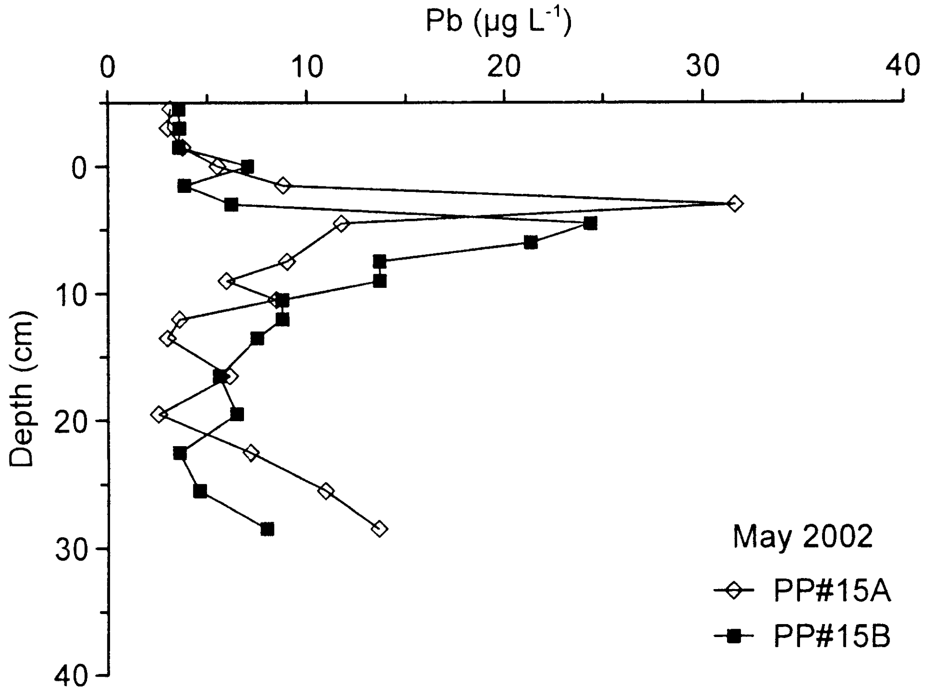


Figure 5.17. Replicate samples of Cu and Ni from one contaminated site, PP. Samples are from May 2002 and analyzed by ICP-MS.



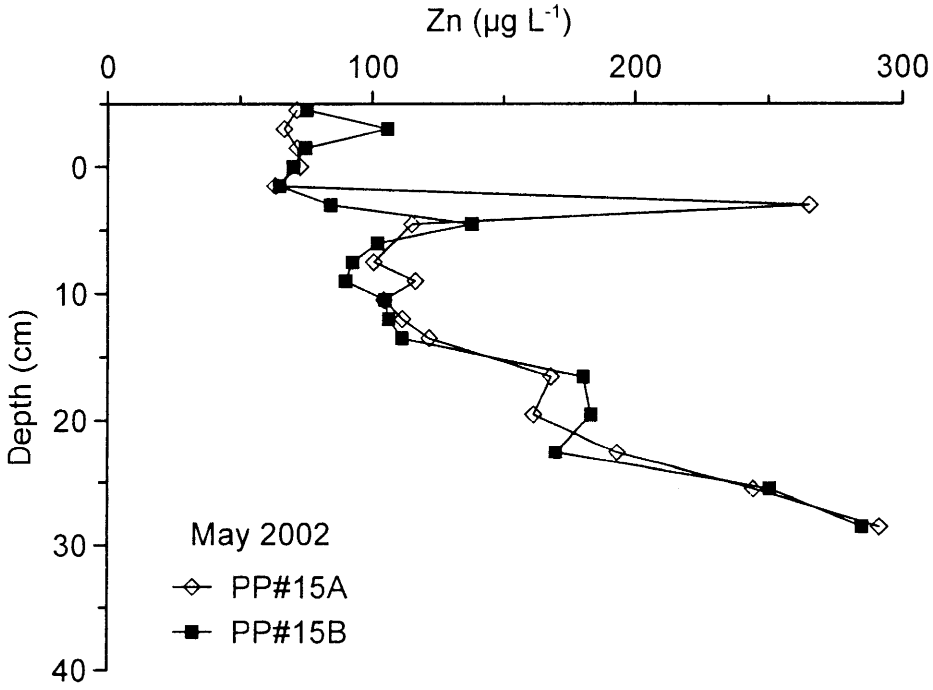


Figure 5.18. Replicate samples of Cu and Ni from one contaminated site, PP. Samples are from May 2002 and analyzed by ICP-MS.

FIGURES FOR SCHLEPP POND

Redox Elements

Replicates of Redox Elements

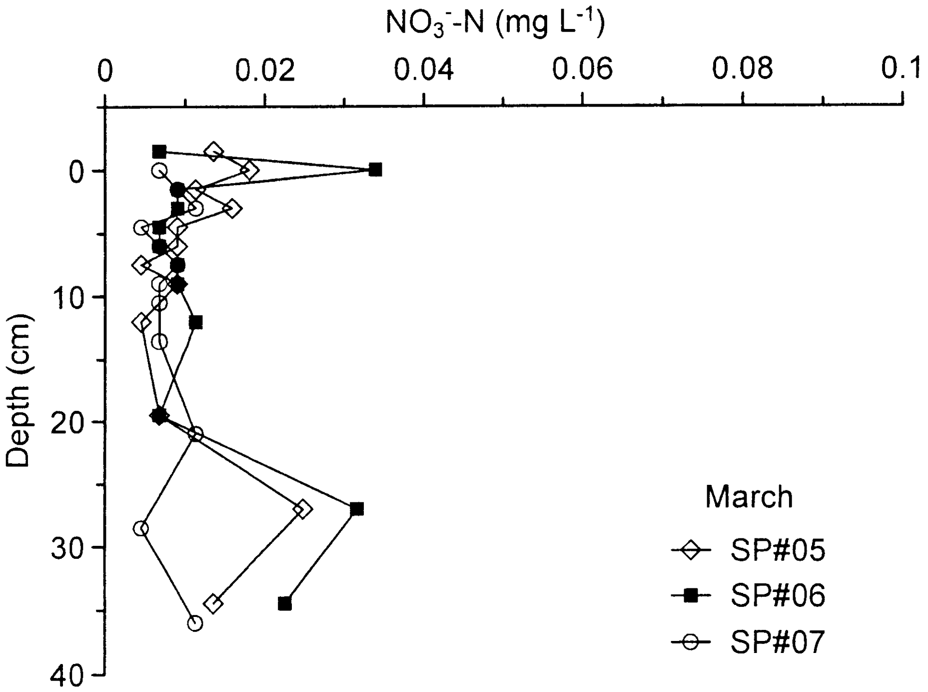


Figure 5.19. Triplicate samples of nitrate-nitrogen from the March, 2004 deployment in Schlepp Pond.

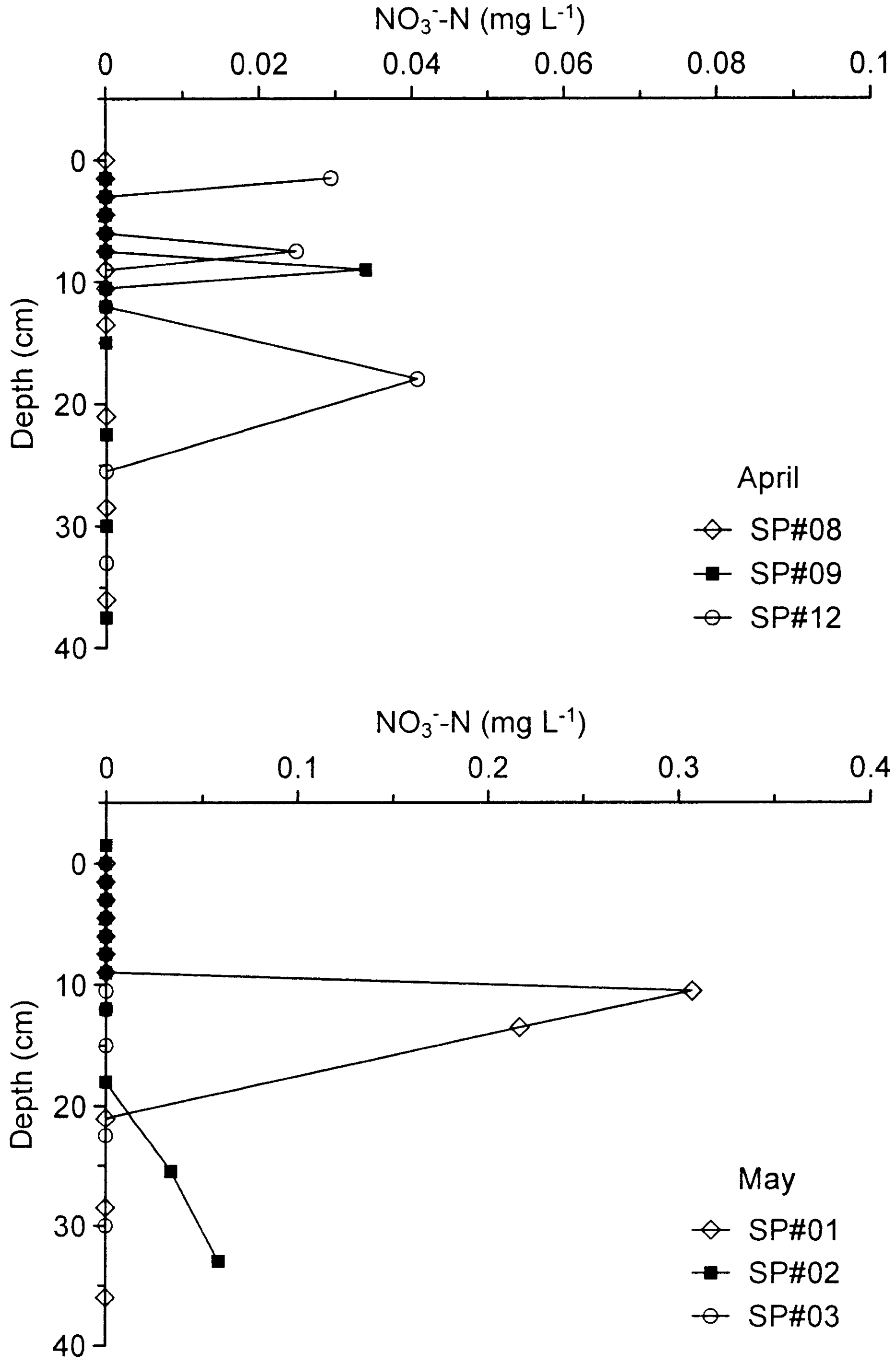
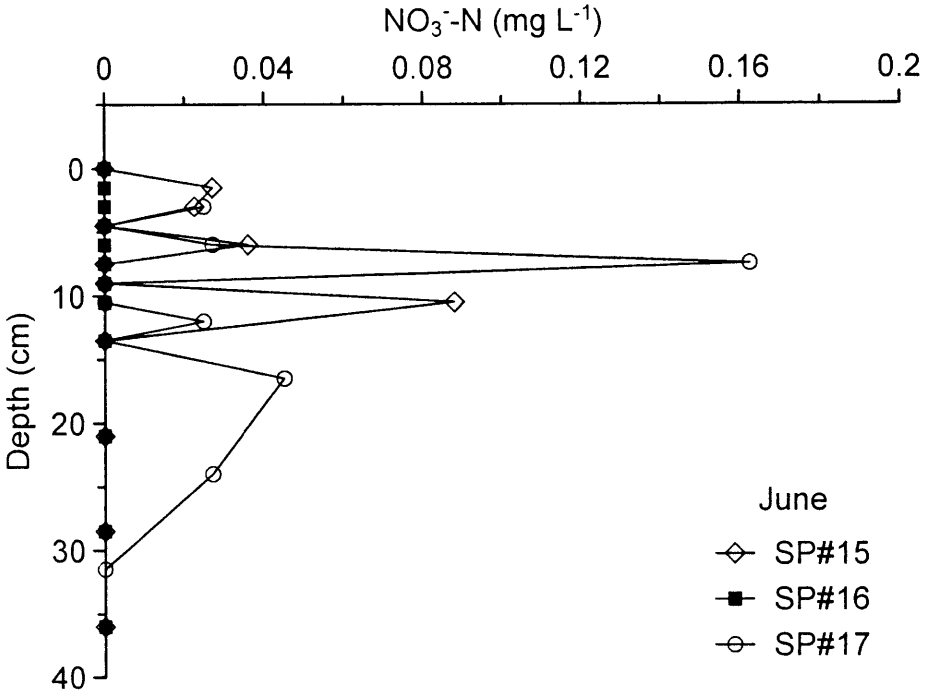


Figure 5.20. Triplicate samples of nitrate-nitrogen from the April and May, 2004 deployments in Schlepp Pond.



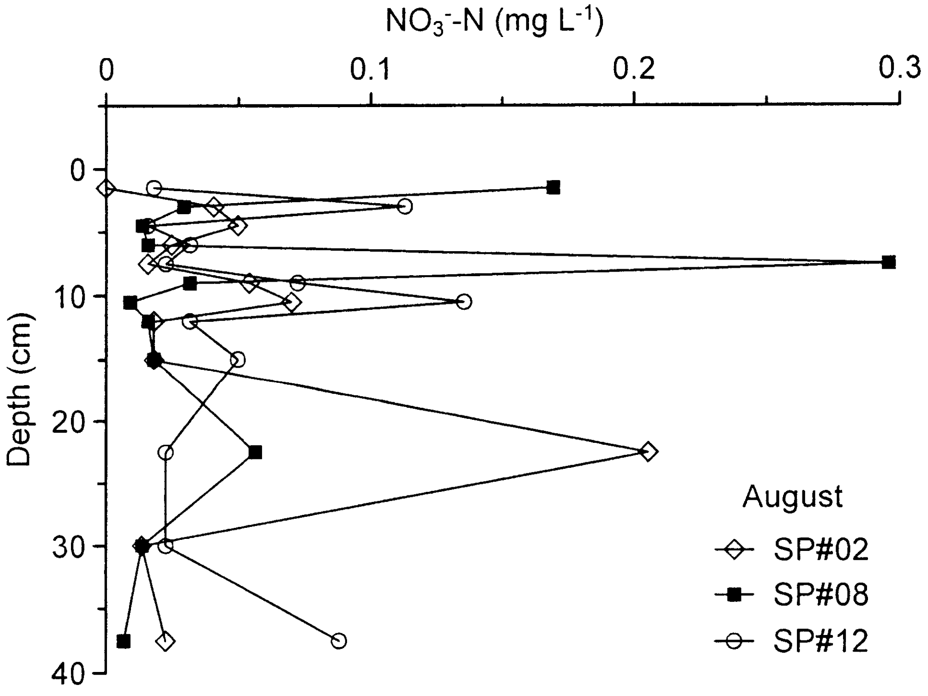


Figure 5.21. Triplicate samples of nitrate-nitrogen from the June and August, 2004 deployments in Schlepp Pond.

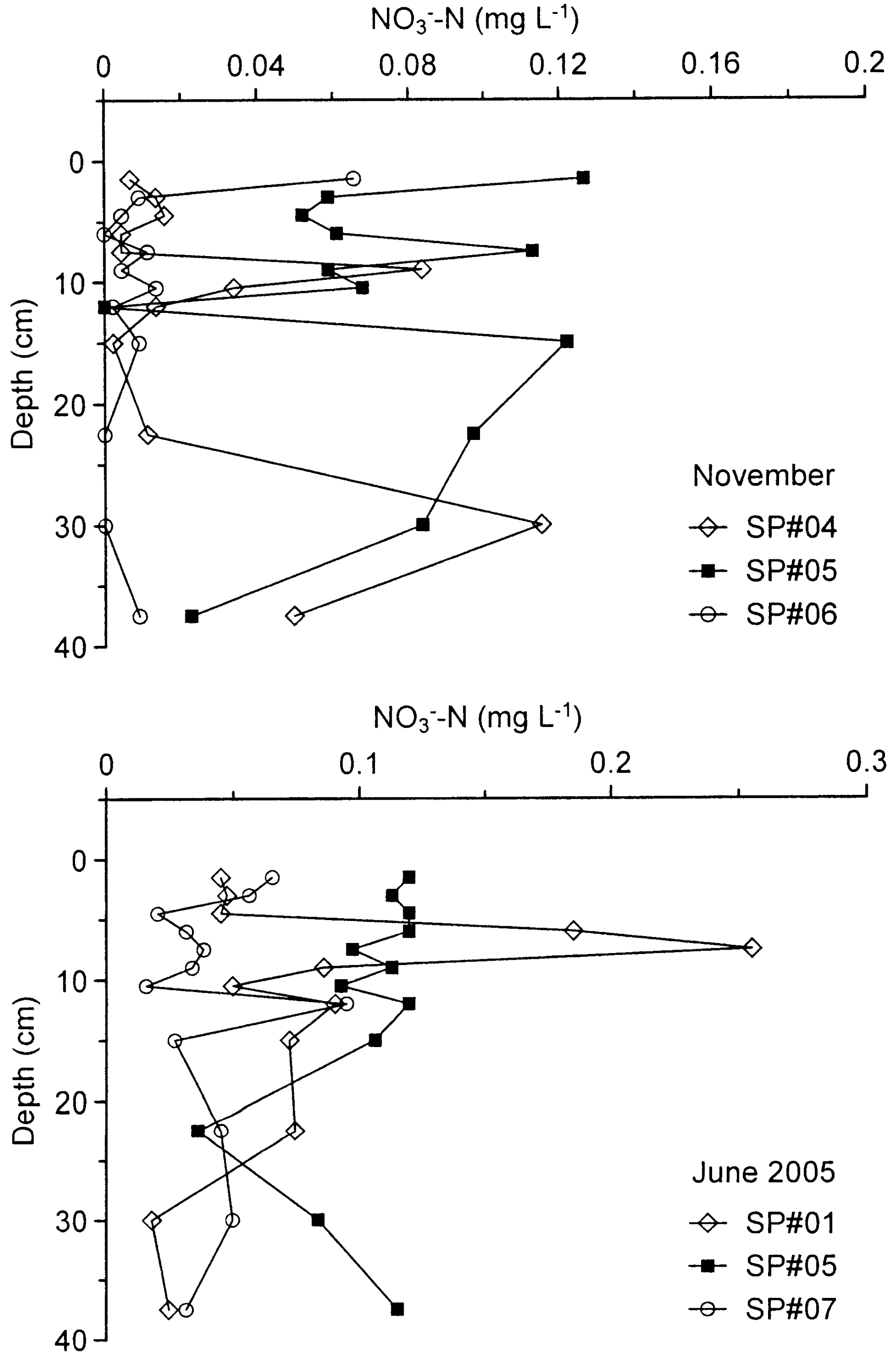
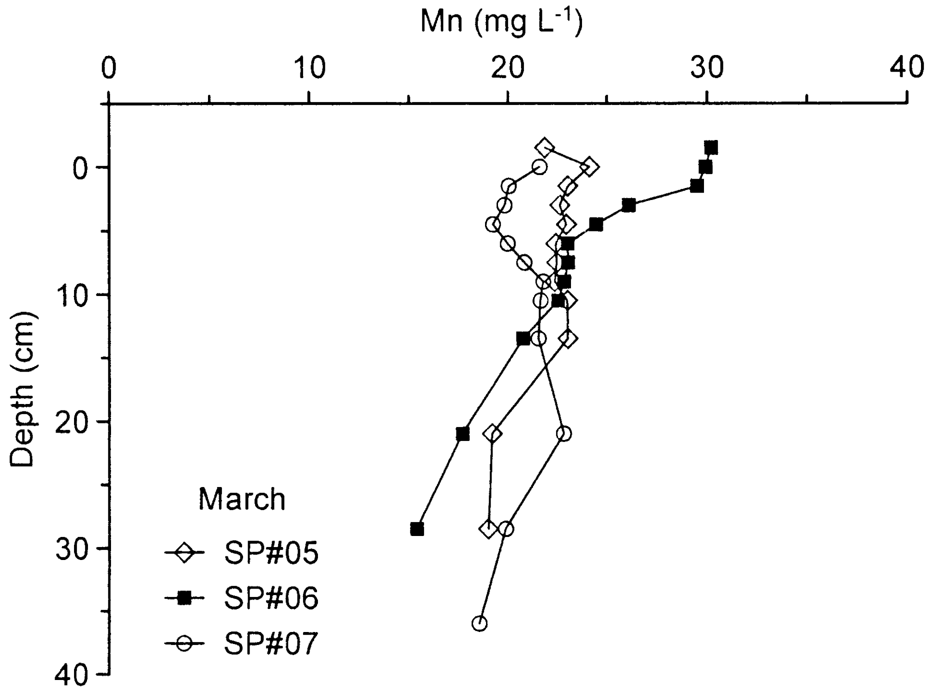


Figure 5.22. Triplicate samples of nitrate-nitrogen from the November 2004 and June 2005 deployment in Schlepp Pond.



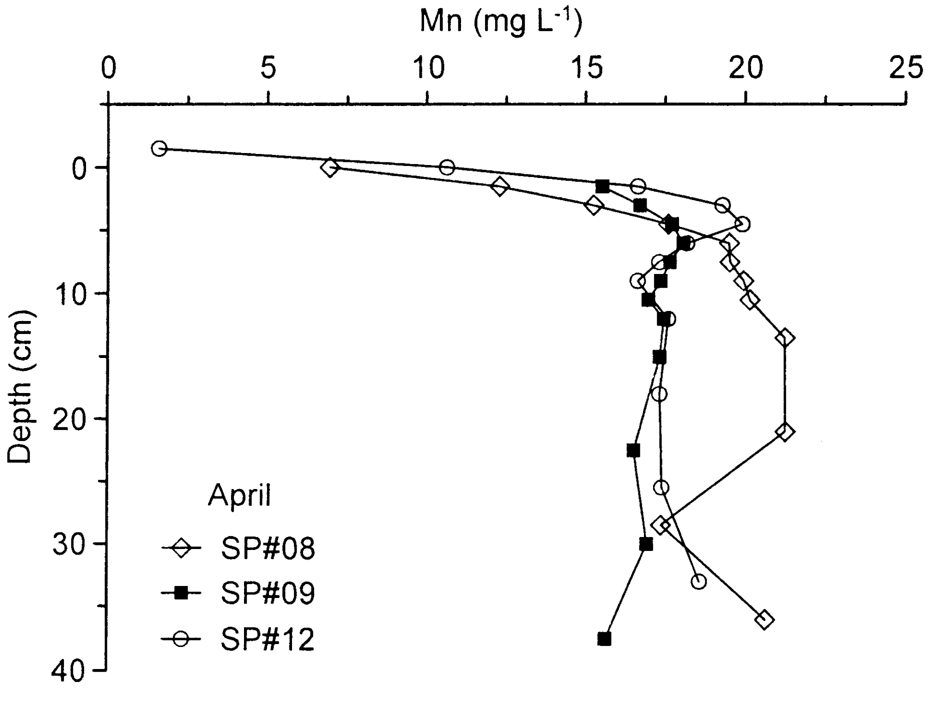


Figure 0.23. Triplicate samples of Mn from the March and April, 2004 deployment in Schlepp Pond.

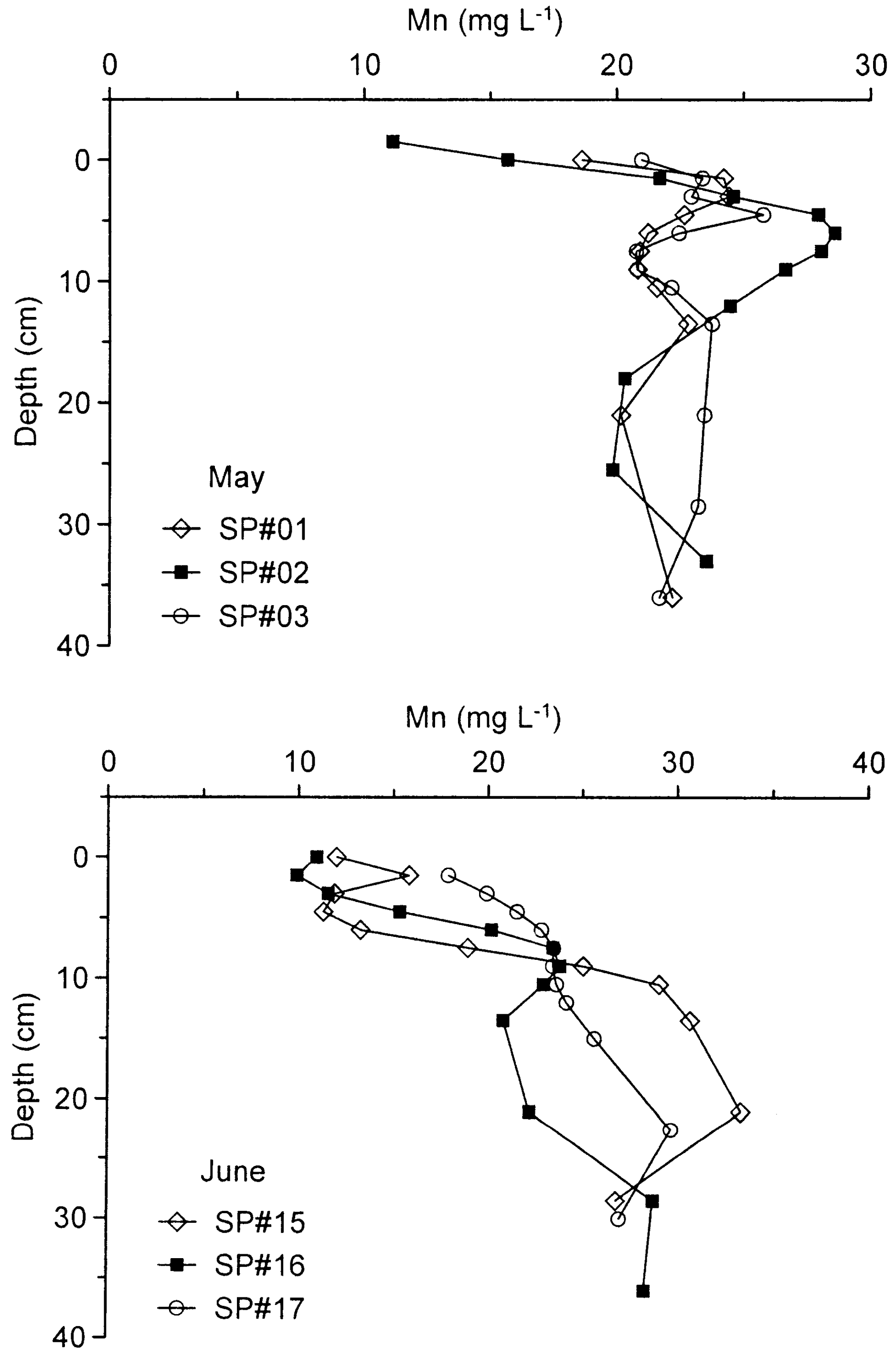


Figure 5.24. Triplicate samples of Mn from the May and June, 2004 deployment in Schlepp Pond.

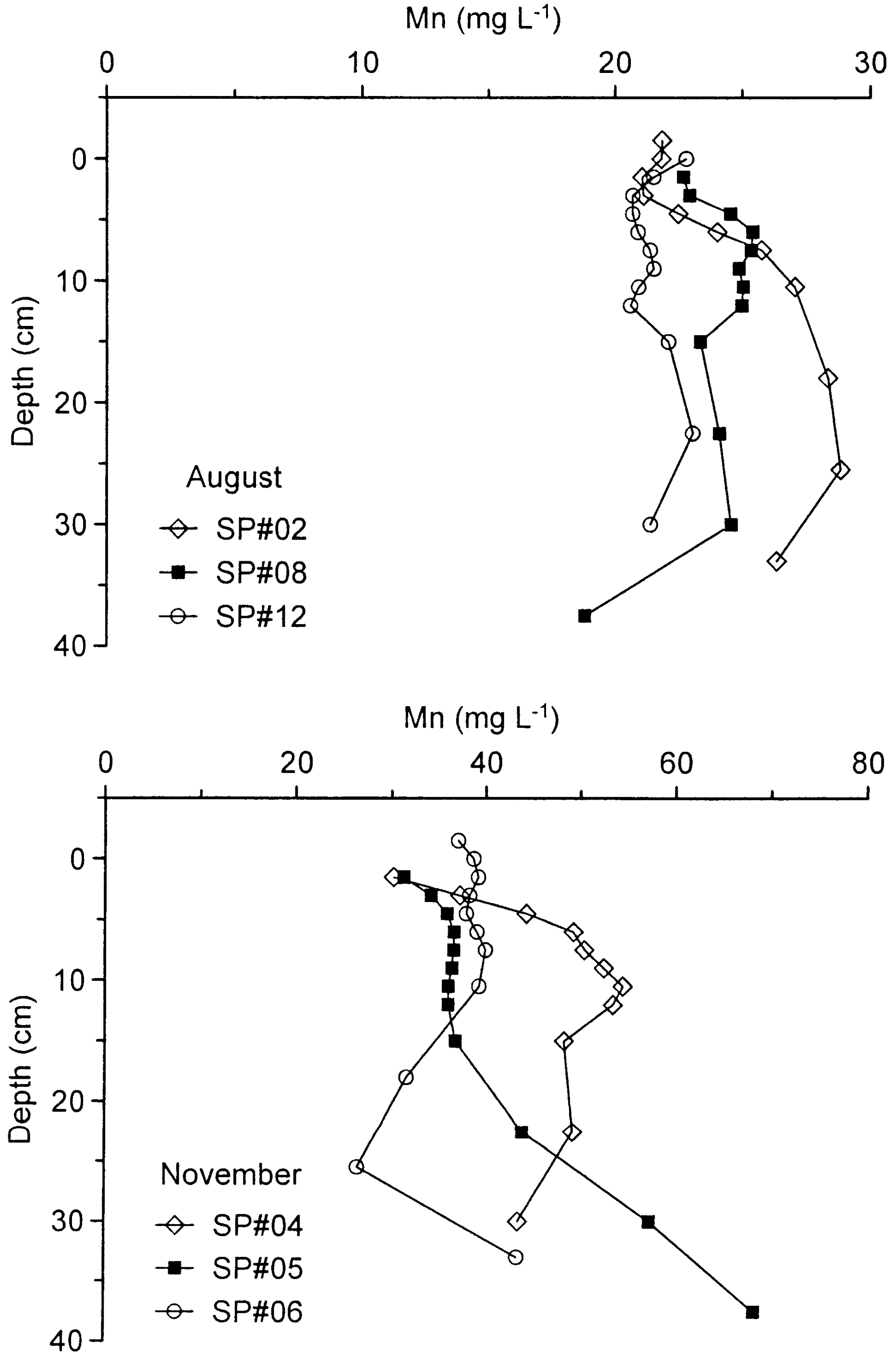


Figure 5.25. Triplicate samples of Mn from the August and November, 2004 deployment in Schlepp Pond.

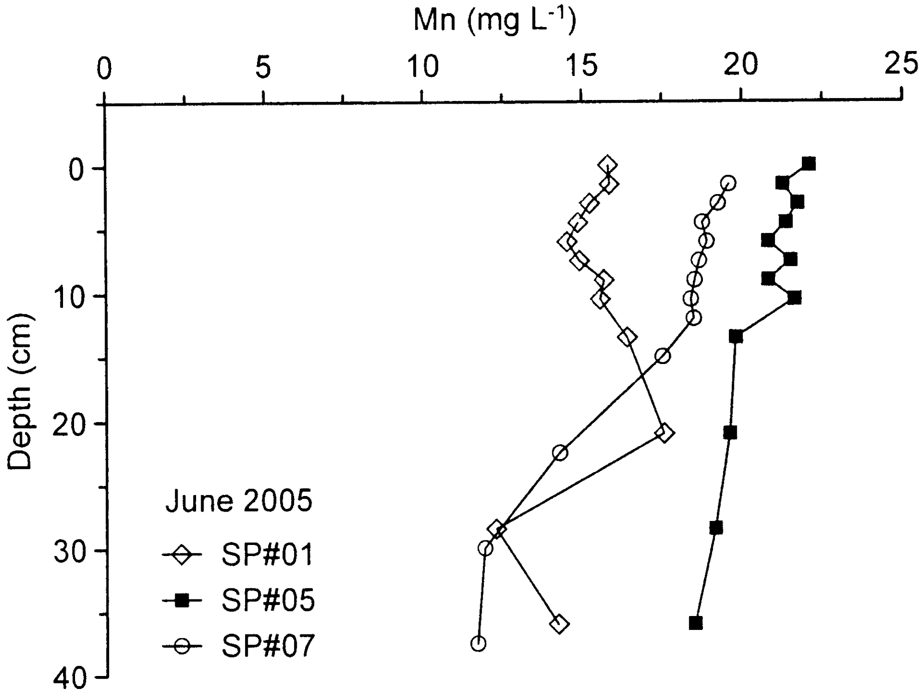


Figure 5.26. Triplicate samples of Mn from the June, 2005 deployment in Schlepp Pond.

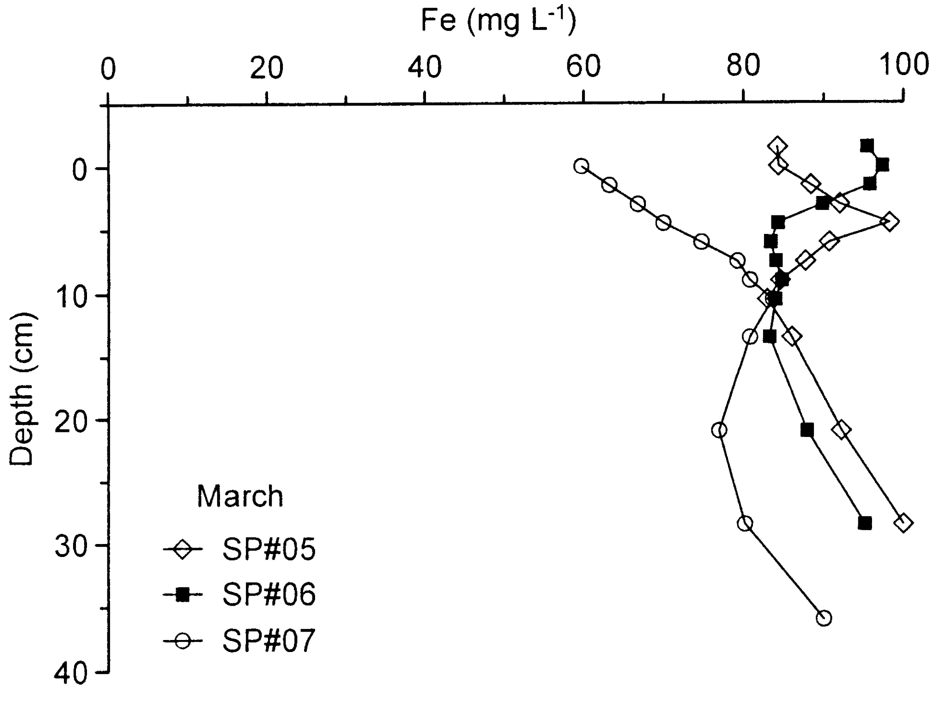


Figure 5.27. Triplicate samples of Fe from the March, 2004 deployment in Schlepp Pond.

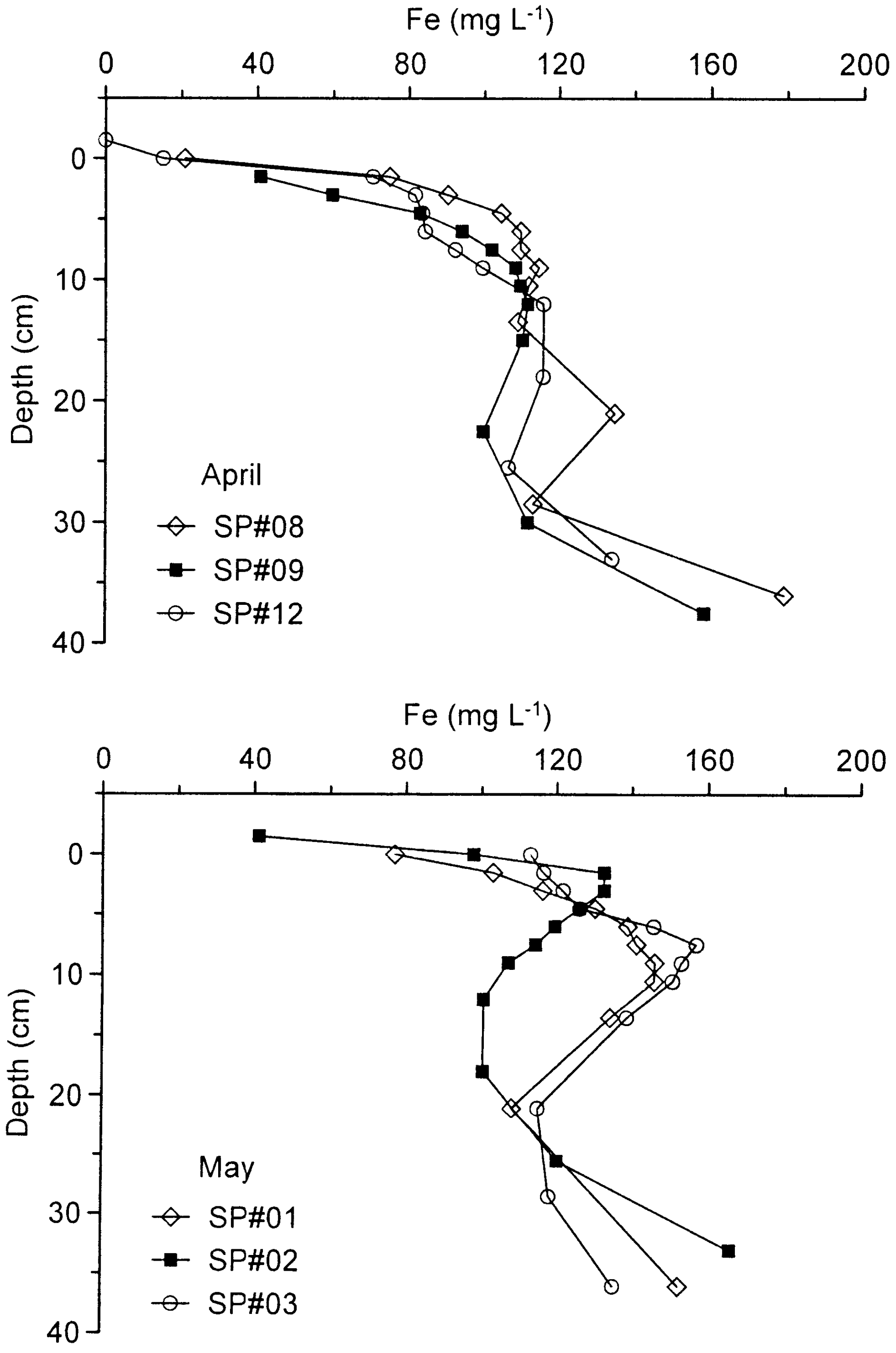


Figure 5.28. Triplicate samples of Fe from the April and May, 2004 deployments in Schlepp Pond.

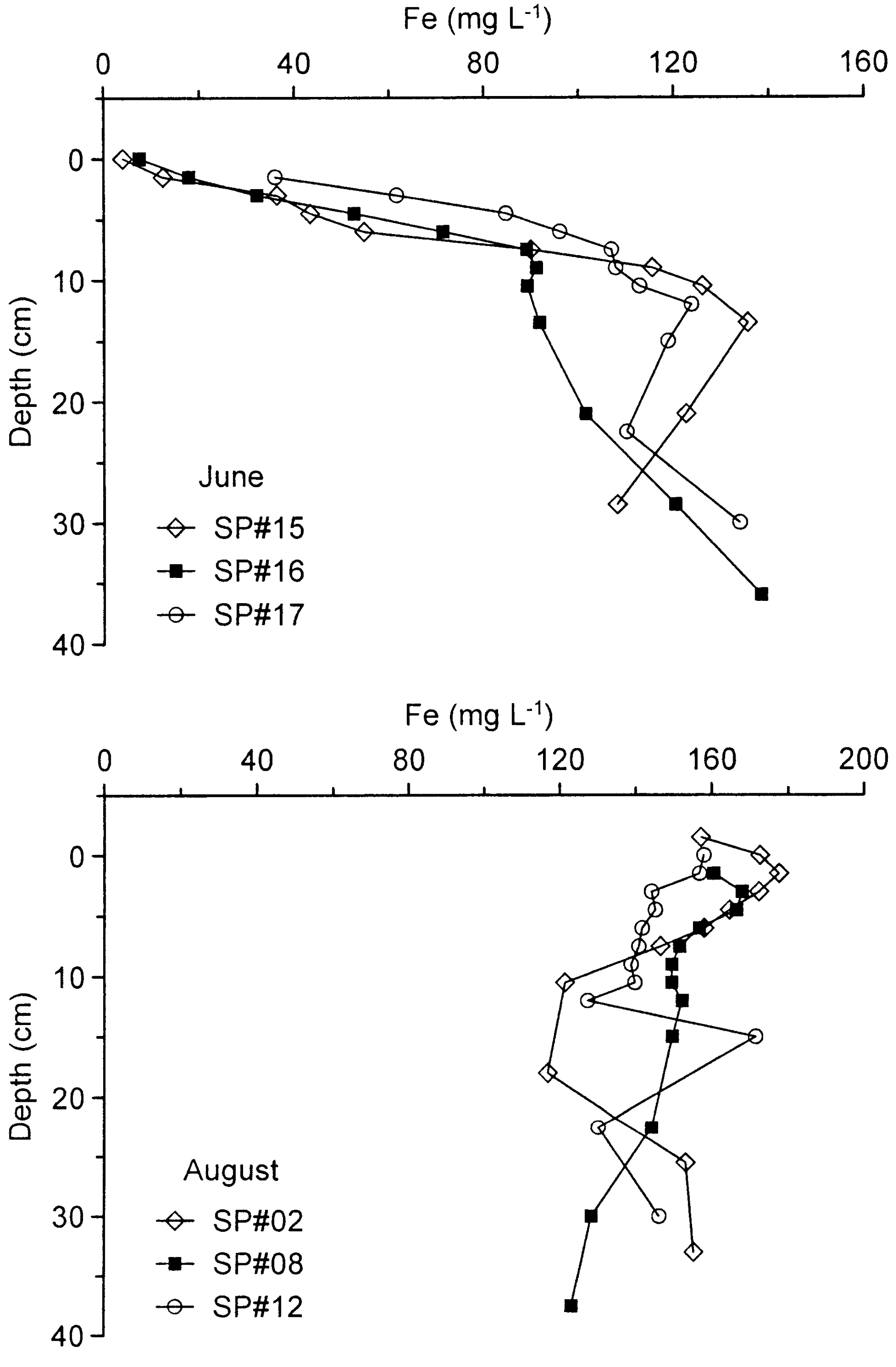


Figure 5.29. Triplicate samples of Fe from the June and August, 2004 deployments in Schlepp Pond.

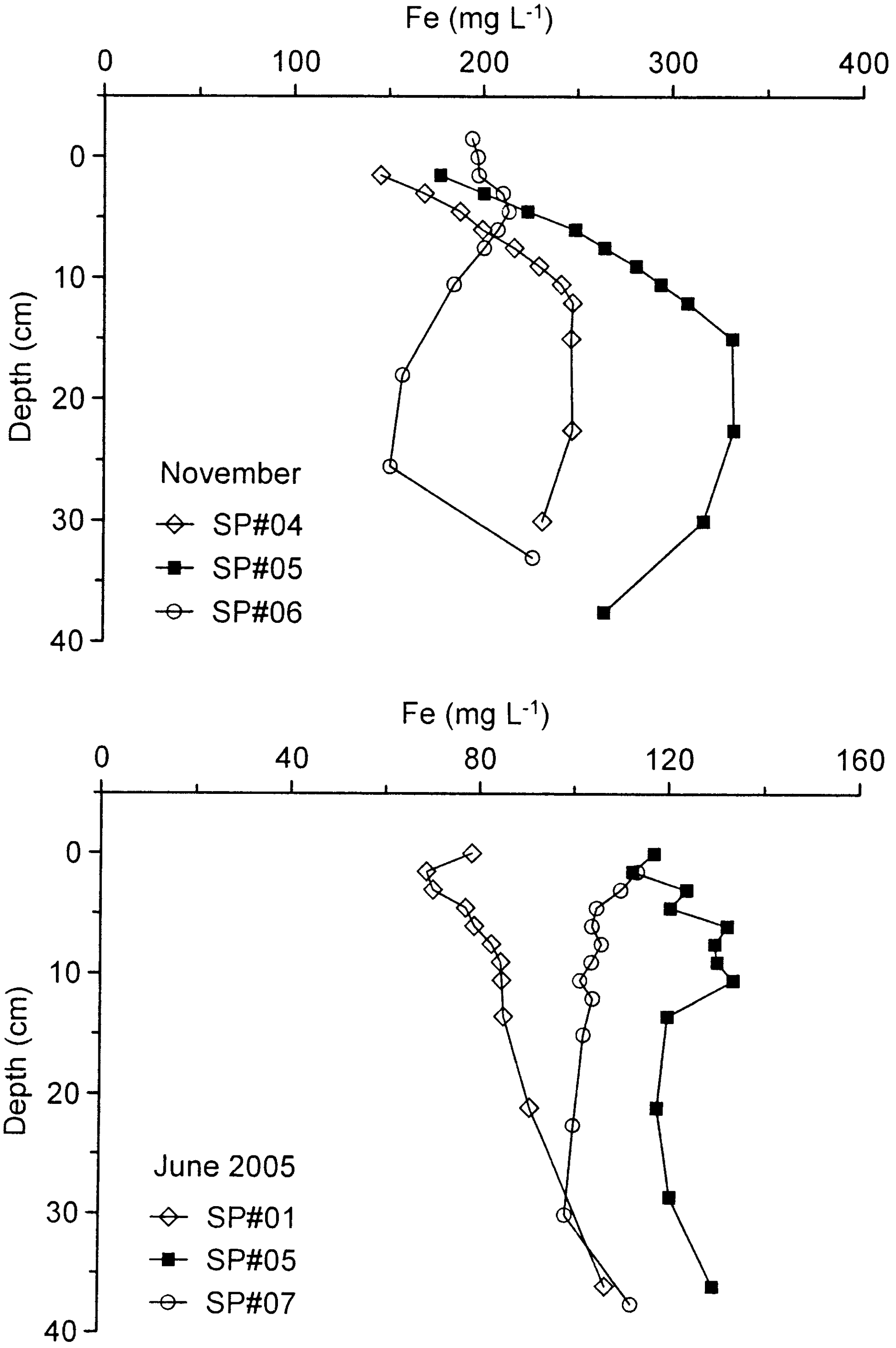
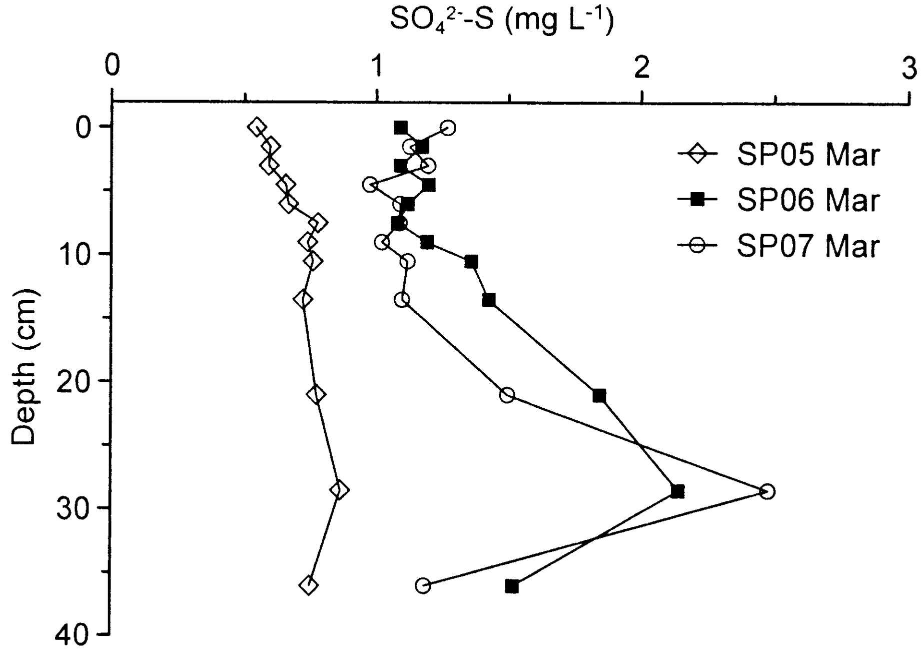


Figure 5.30. Triplicate samples of Fe from the November, 2004 and June, 2005 deployments in Schlepp Pond.



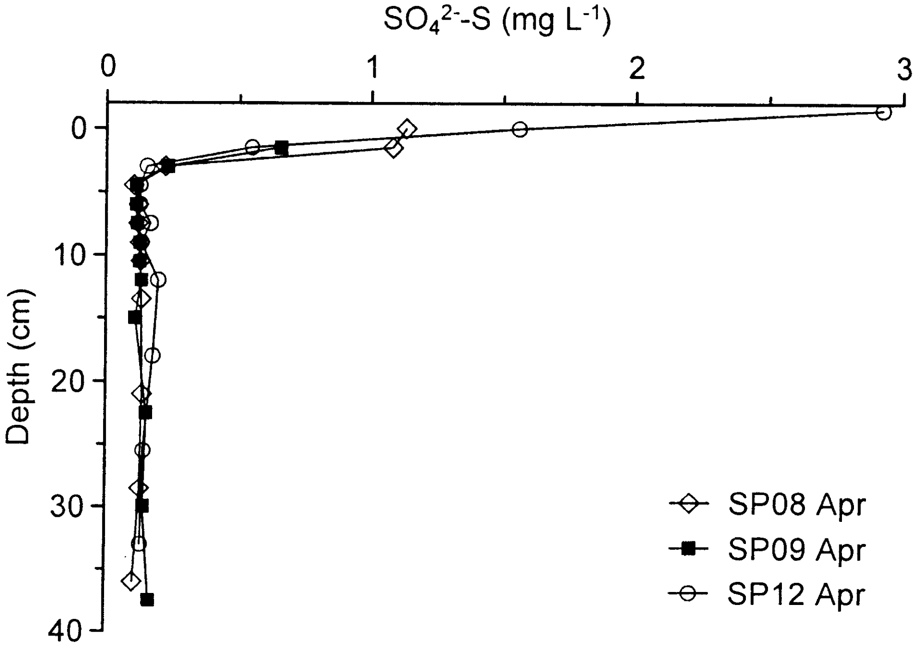


Figure 5.31. Triplicate samples of sulfate-sulfur from the March and April, 2004 deployments in Schlepp Pond.

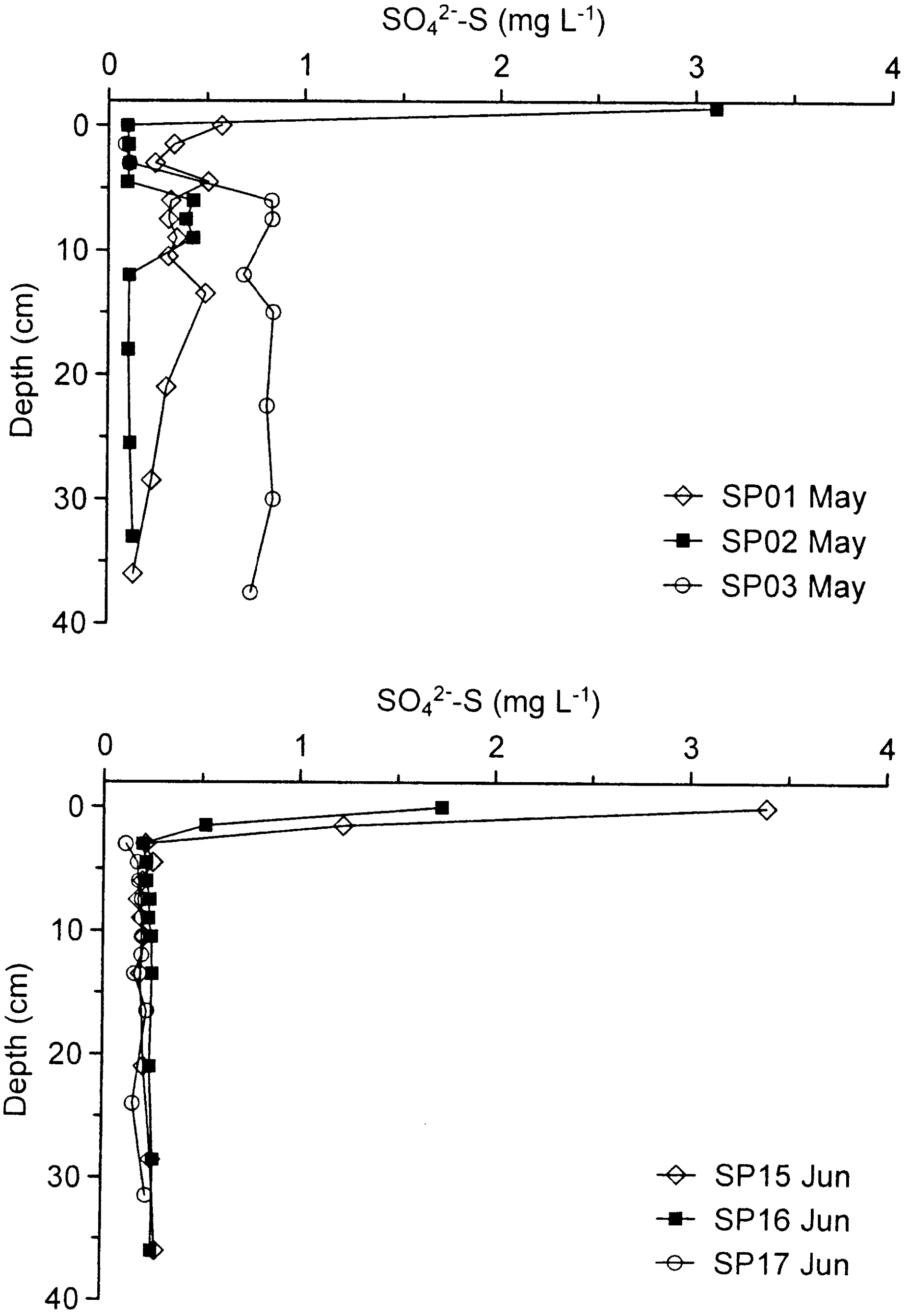
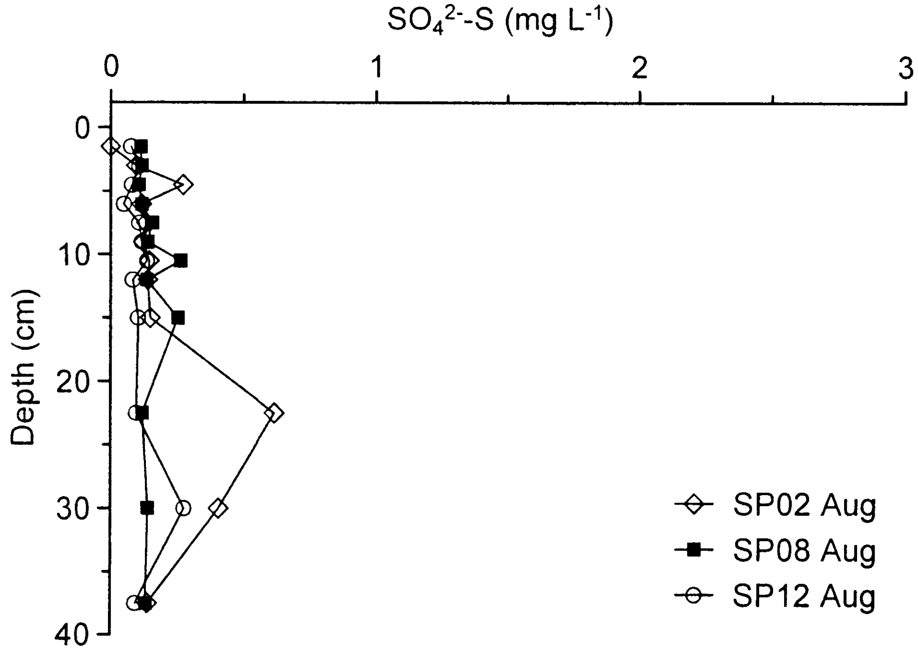


Figure 5.32. Triplicate samples of sulfate-sulfur from the May and June, 2004 deployments in Schlepp Pond.



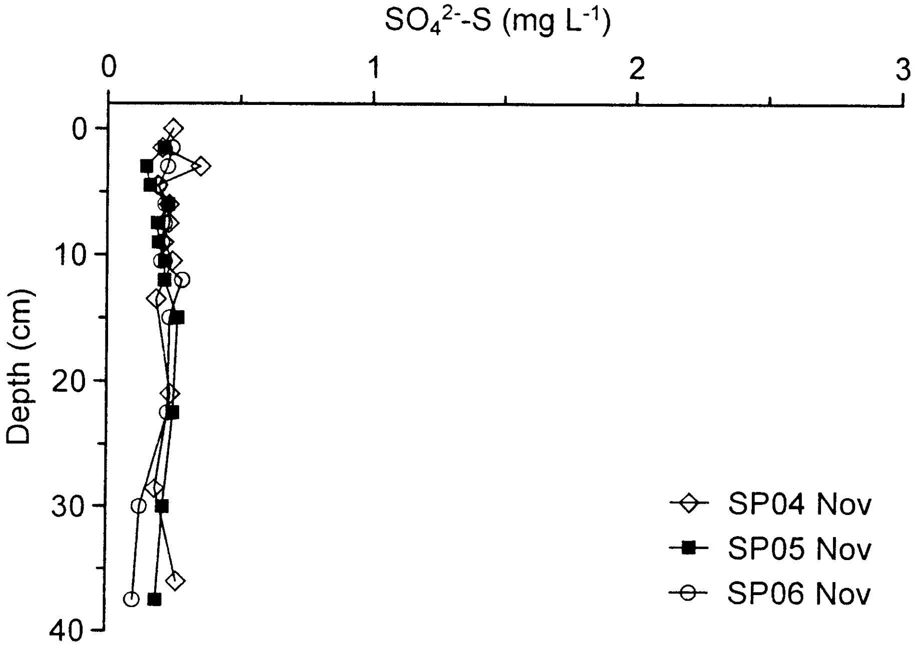


Figure 5.33. Triplicate samples of sulfate-sulfur from the August and November, 2004 deployments in Schlepp Pond.

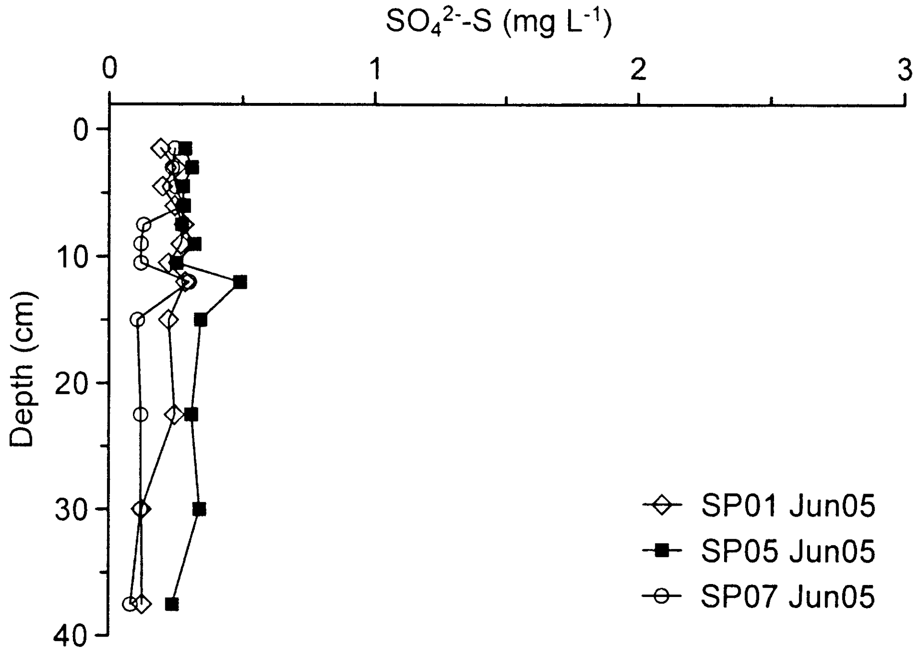


Figure 5.34. Triplicate samples of sulfate-sulfur from the June, 2005 deployment in Schlepp Pond.

Redox Element Profiles, Averaged Data

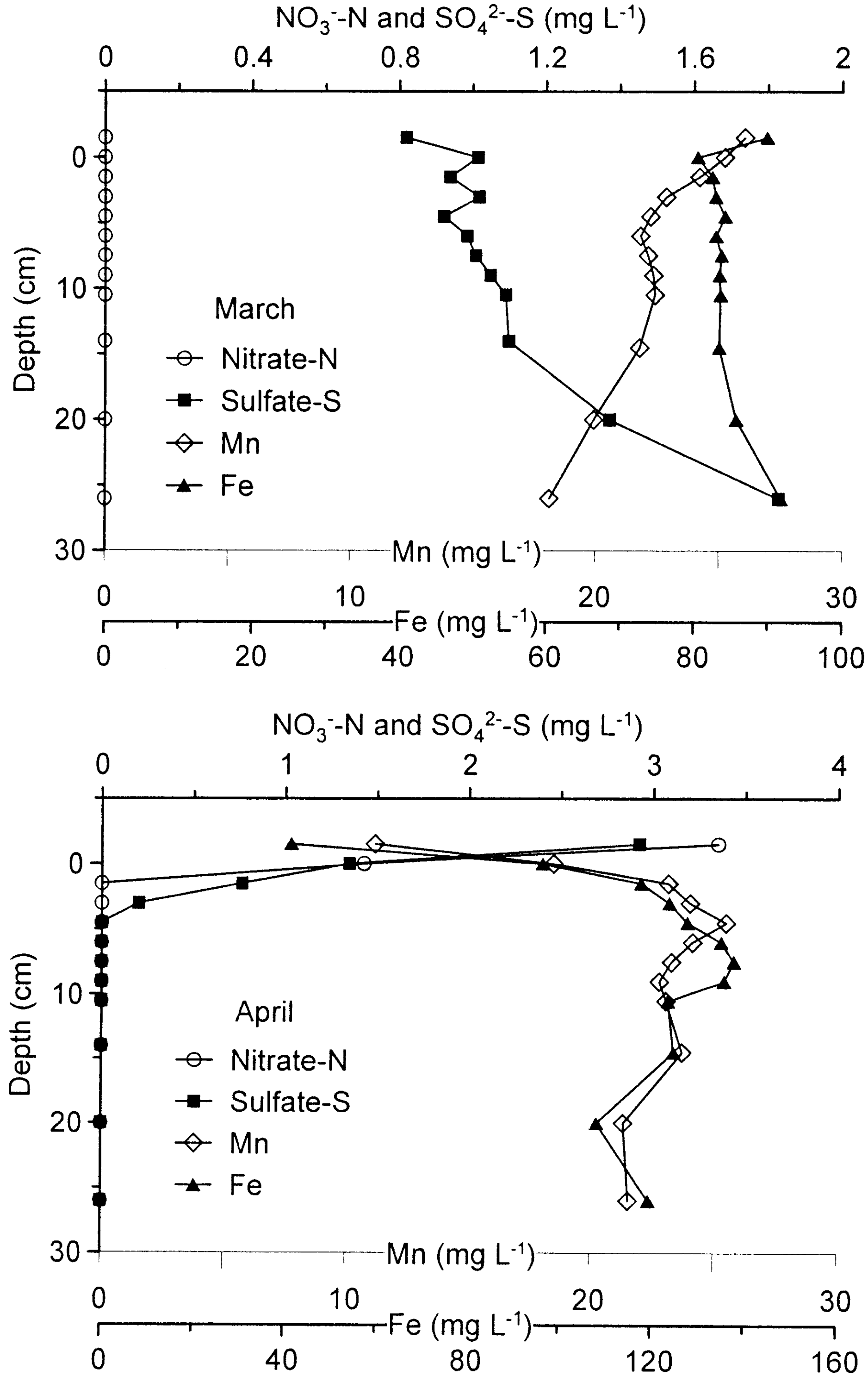


Figure 5.35. Redox profiles from the March and April, 2004 deployments in Schlepp Pond. The data are the average of triplicate samples with reduction potential determined by presence or absence of TEA.

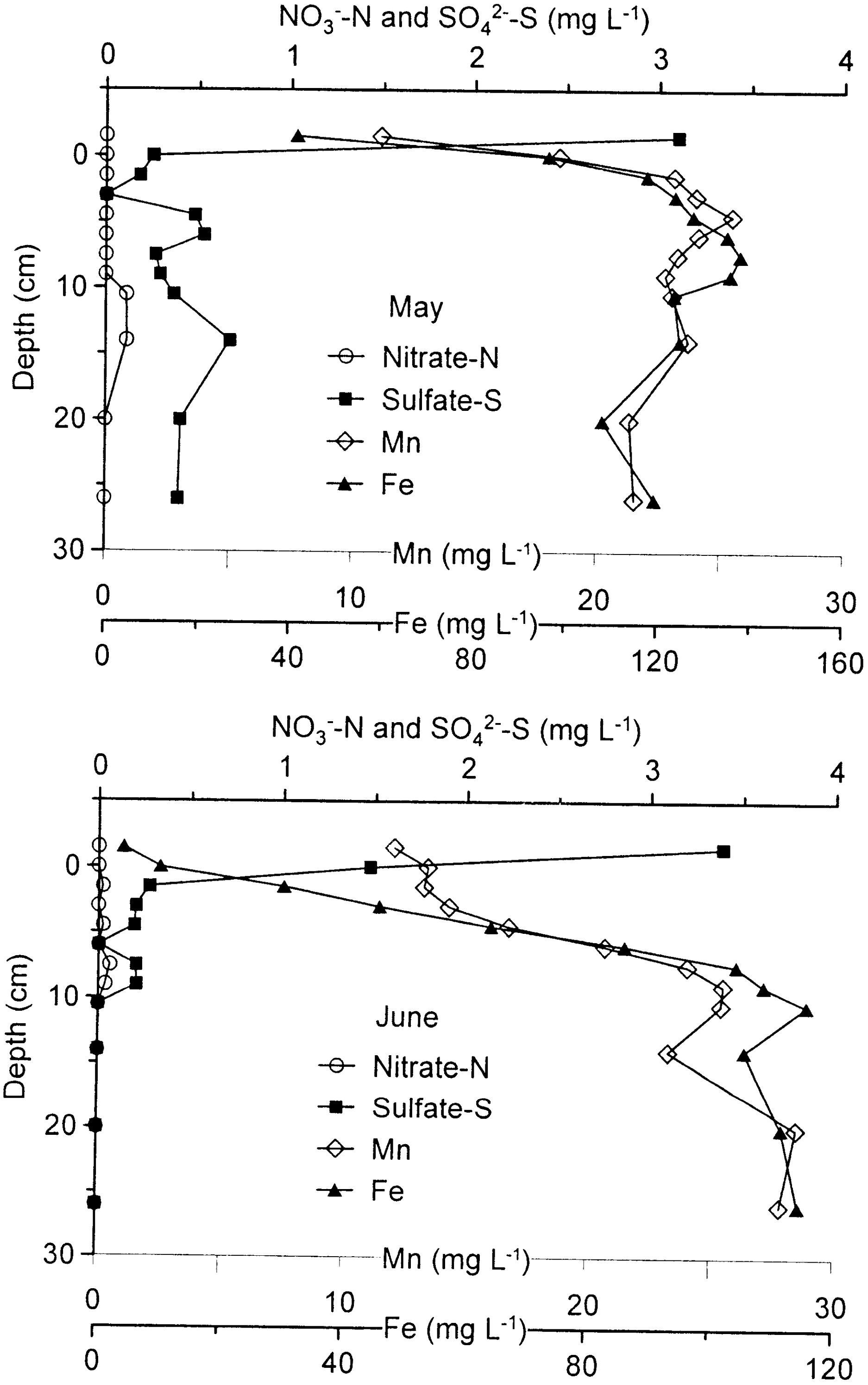


Figure 5.36. Redox profiles from the May and June, 2004 deployments in Schlepp Pond. The data are the average of triplicate samples with reduction potential determined by presence or absence of TEA.

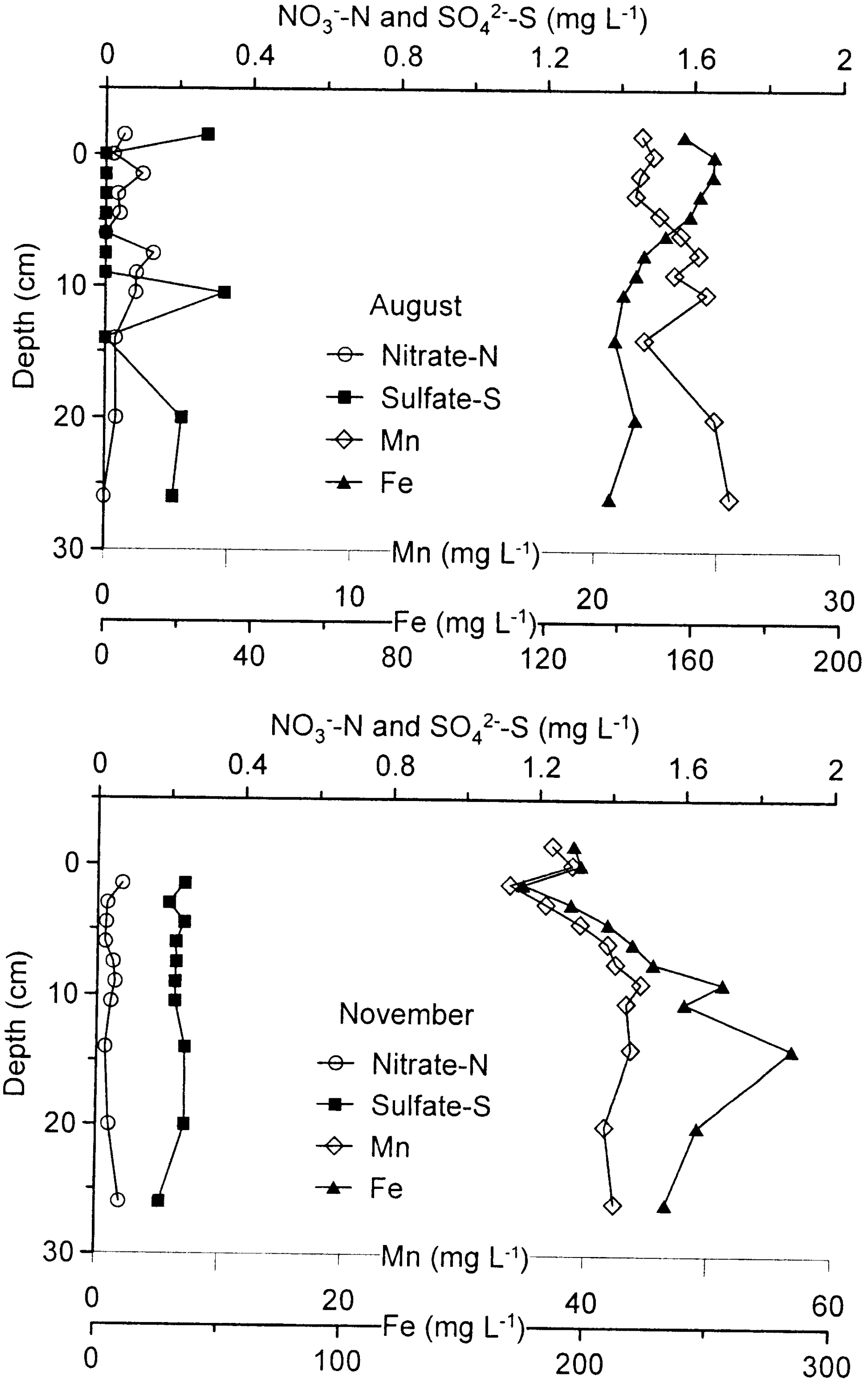


Figure 5.37. Redox profiles from the August and November, 2004 deployments in Schlepp Pond. The data are the average of triplicate samples with reduction potential determined by presence or absence of TEA.

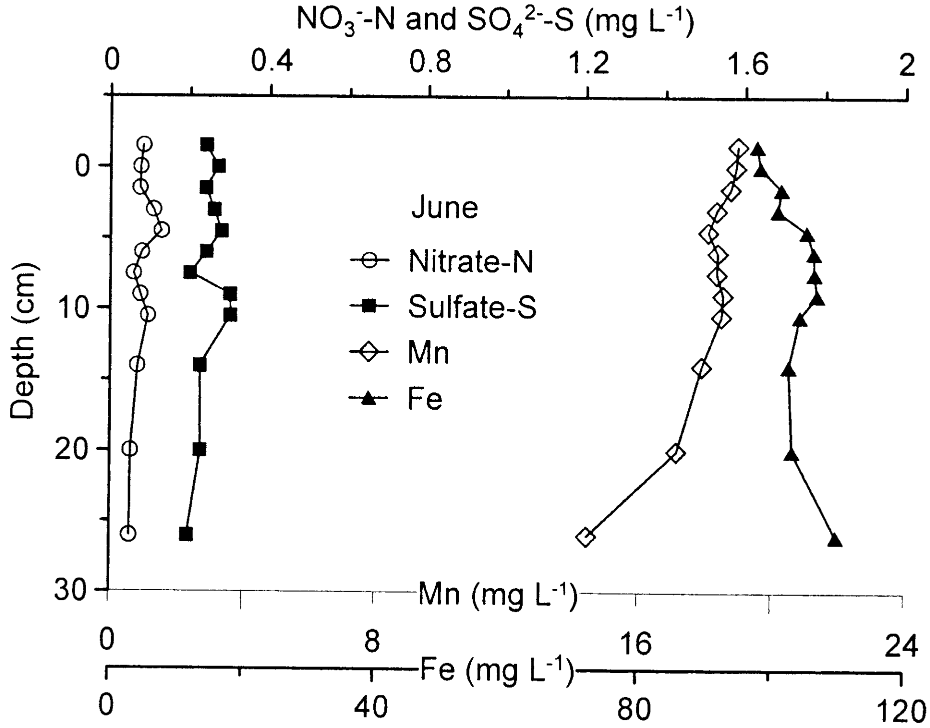
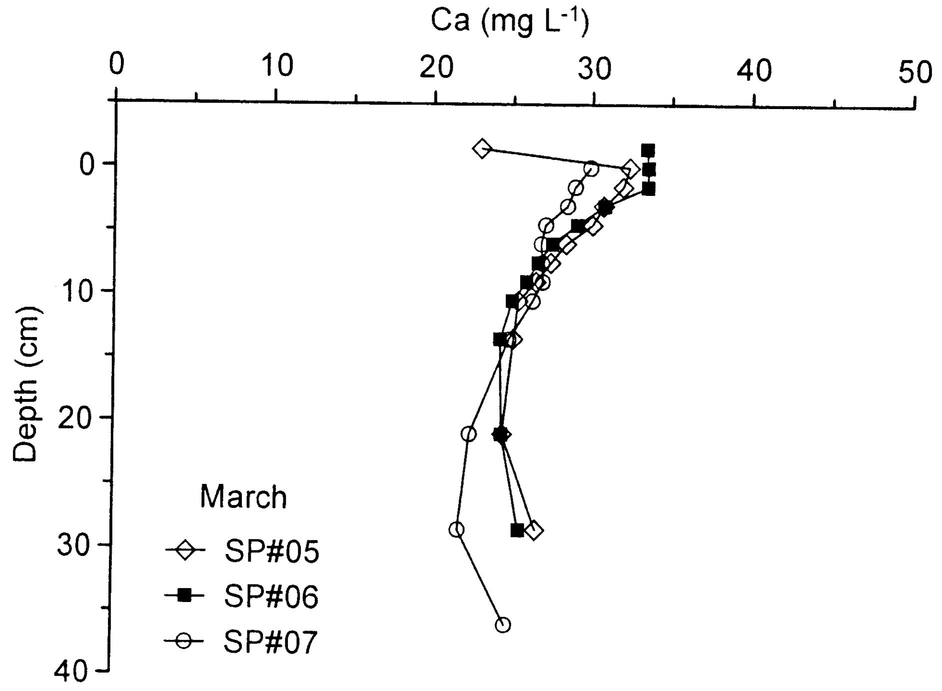


Figure 5.38. Redox profile from the June, 2005 deployment in Schlepp Pond. The data are the average of triplicate samples with reduction potential determined by presence or absence of TEA.

Dissolved Constituents Schlepp Pond, ICP-AES



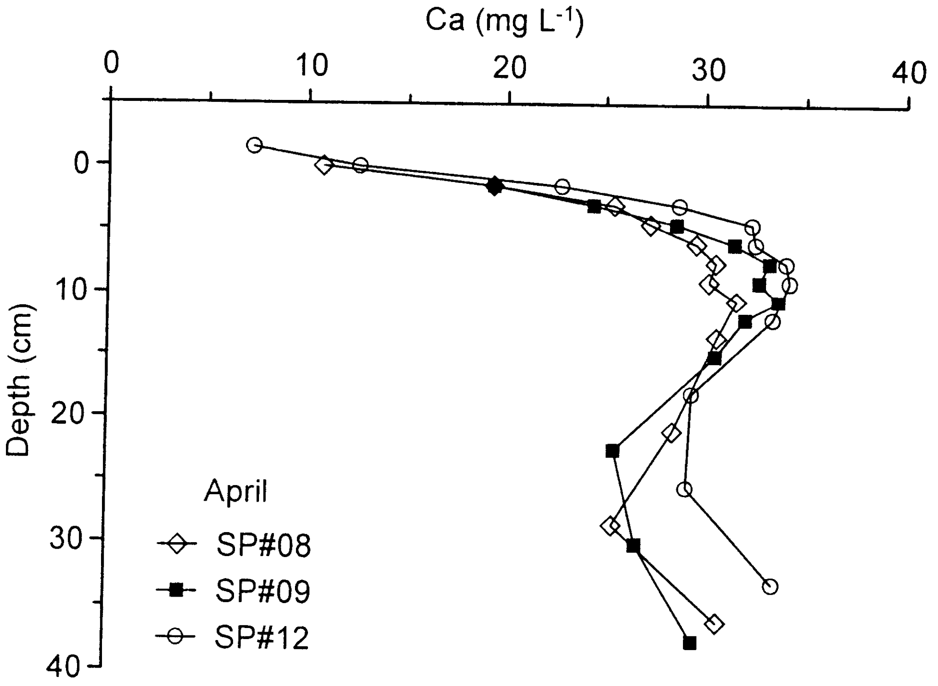


Figure 5.39. Triplicate samples of dissolved Ca in interstitial water from Schlepp Pond samples collected in March and April, 2004.

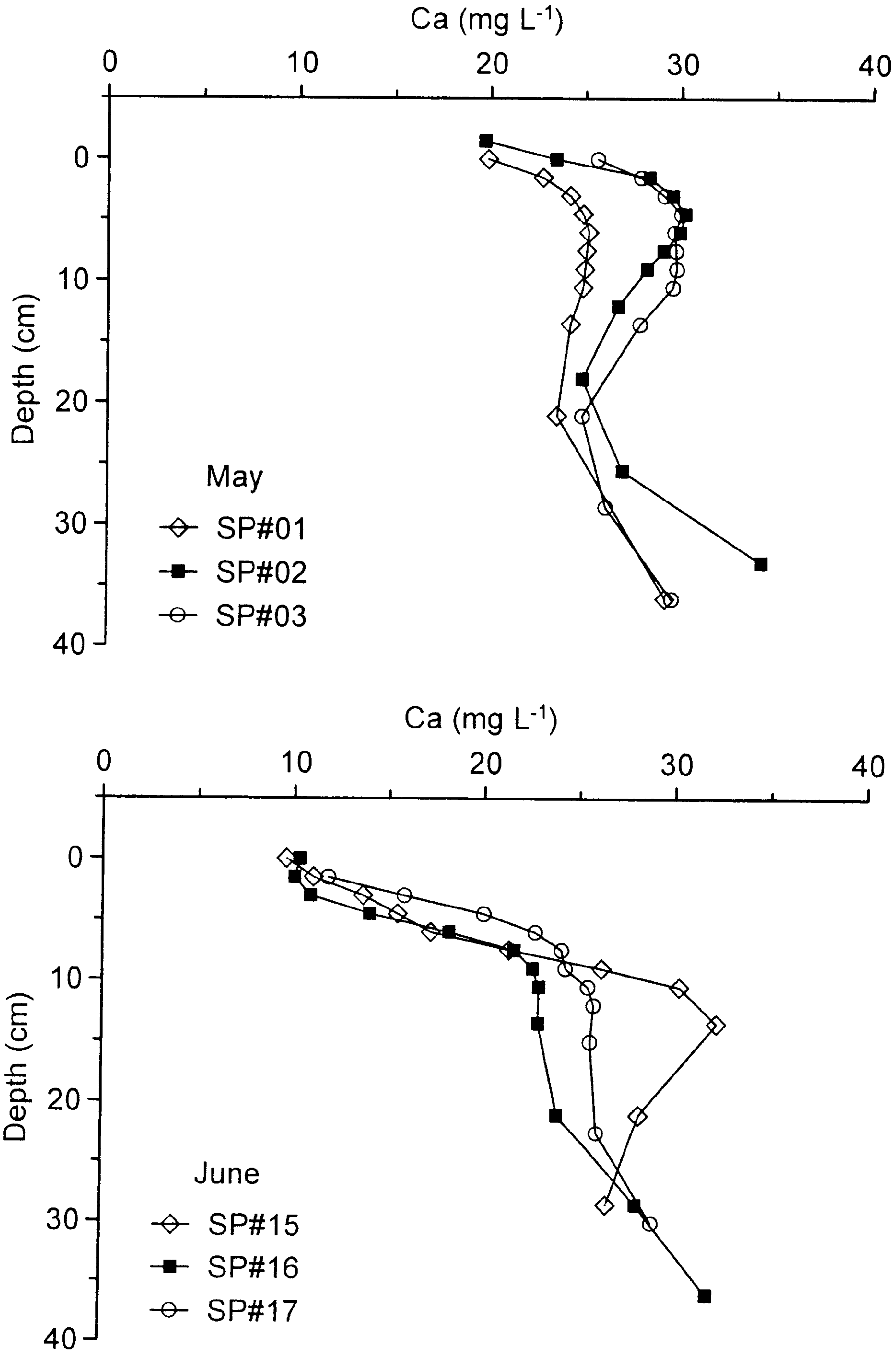


Figure 5.40. Triplicate samples of dissolved Ca in interstitial water from Schlepp Pond samples collected in May and June, 2004.

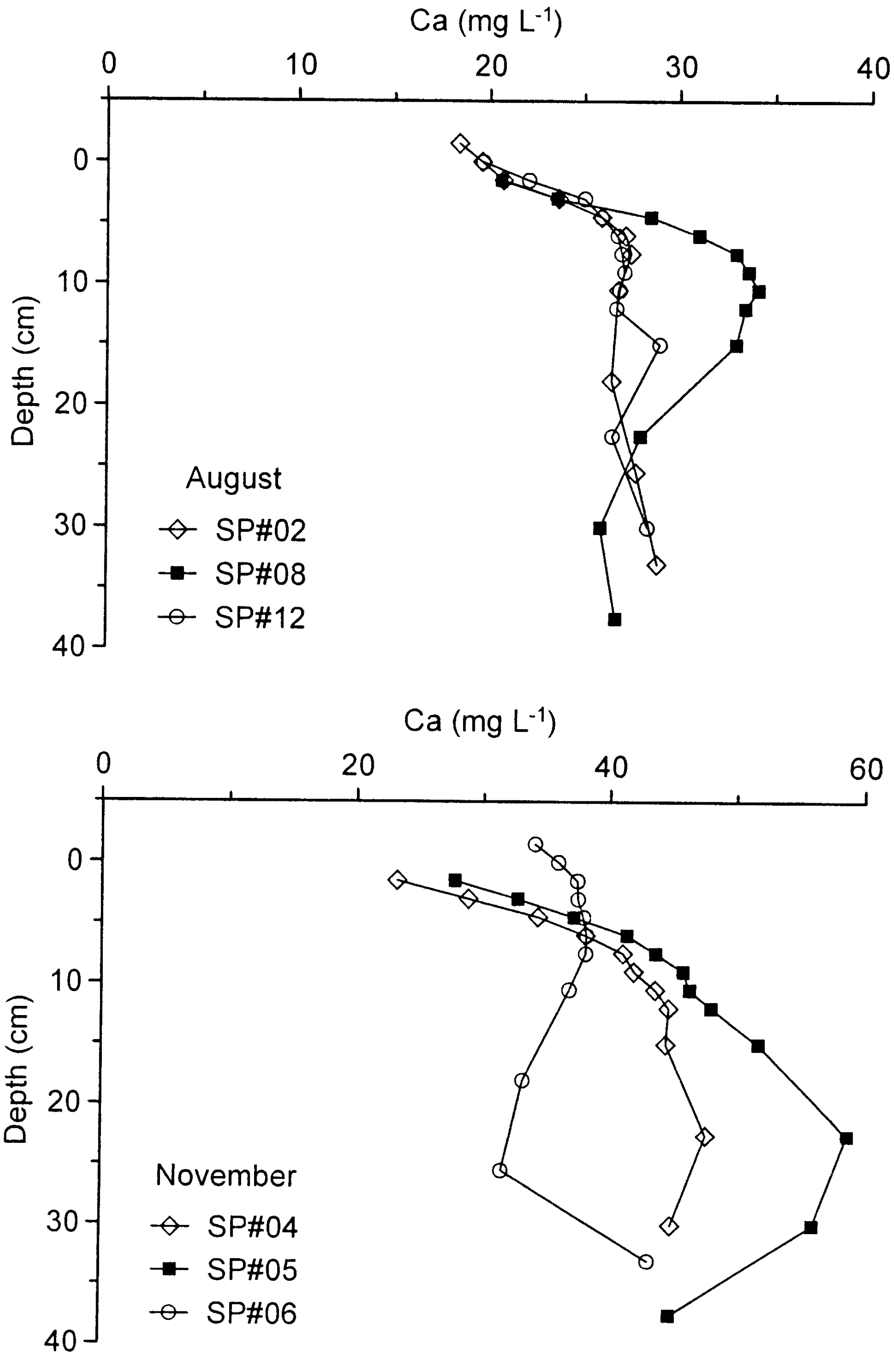


Figure 5.41. Triplicate samples of dissolved Ca in interstitial water from Schlepp Pond samples collected in August and November, 2004.

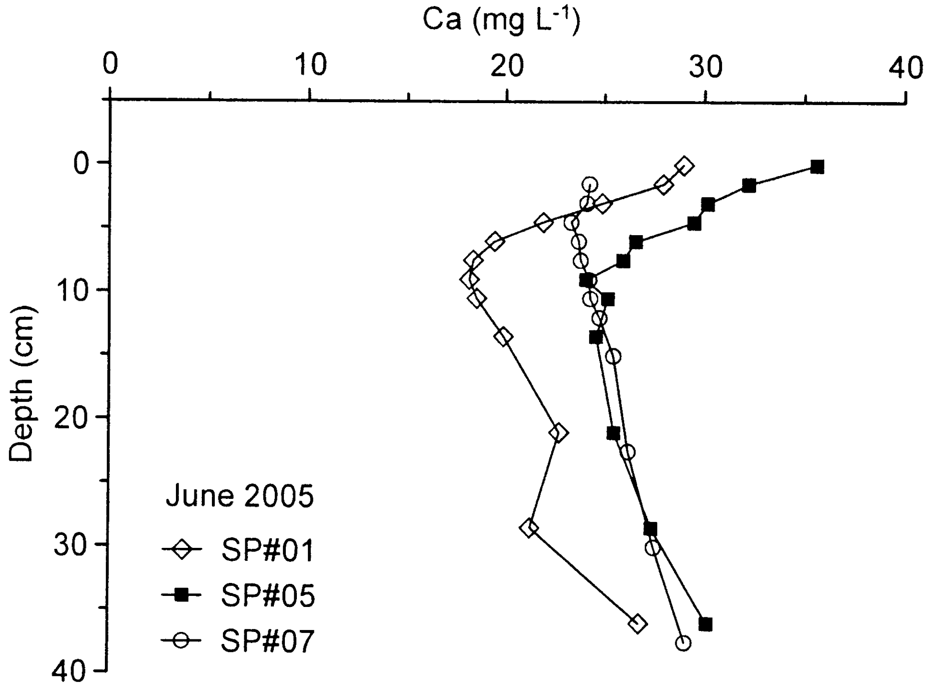


Figure 5.42. Triplicate samples of dissolved Ca in interstitial water from Schlepp Pond samples collected in June 2005.

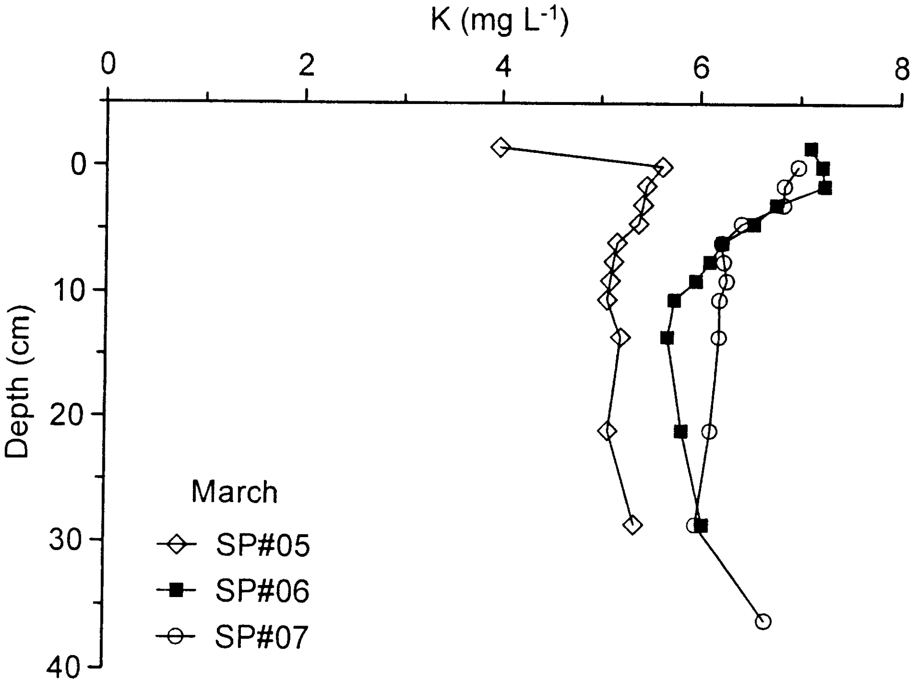


Figure 5.43. Triplicate samples of dissolved K in interstitial water from Schlepp Pond samples collected in March, 2004.

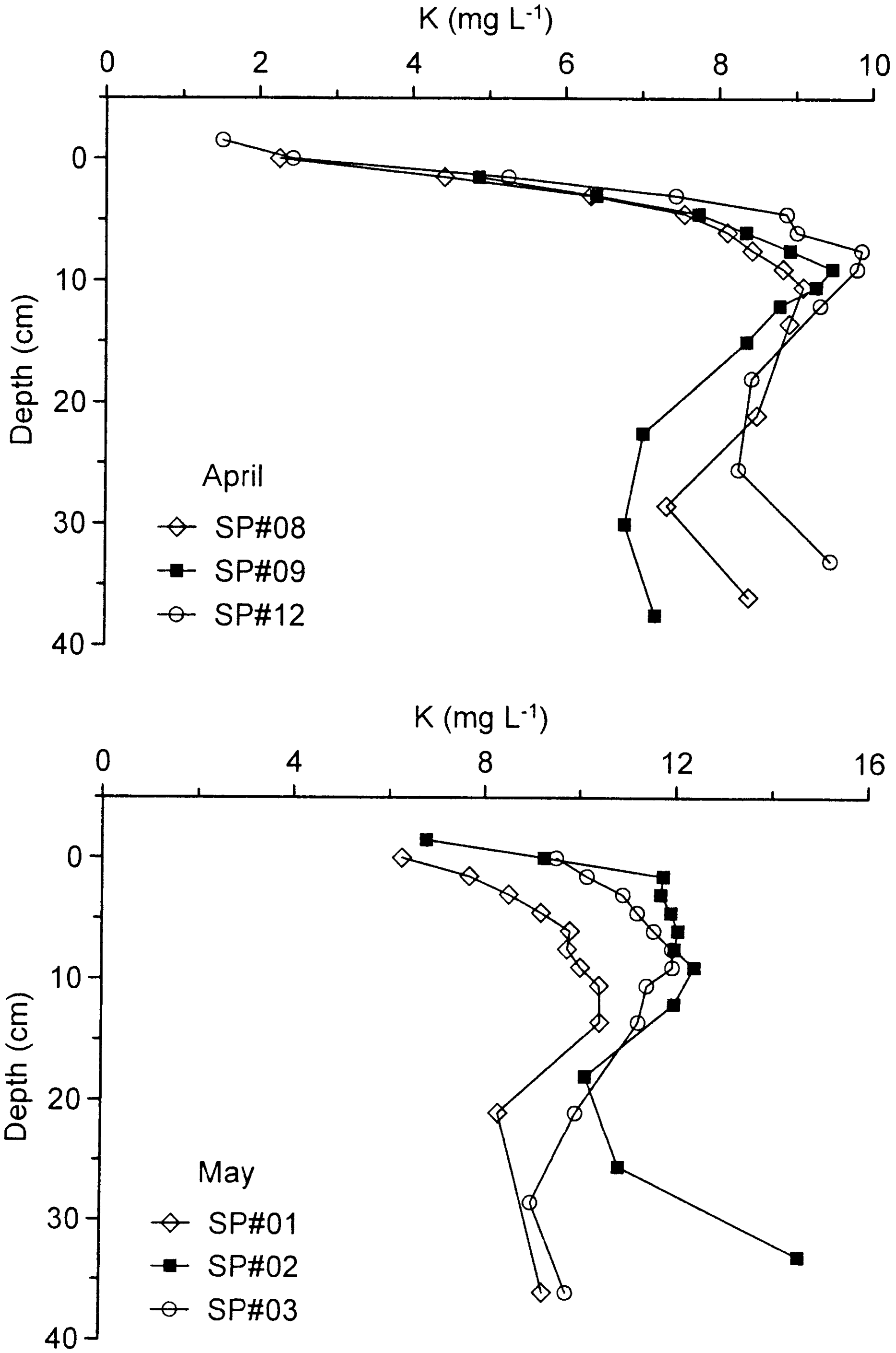


Figure 5.44. Triplicate samples of dissolved K in interstitial water from Schlepp Pond samples collected in April and May, 2004.

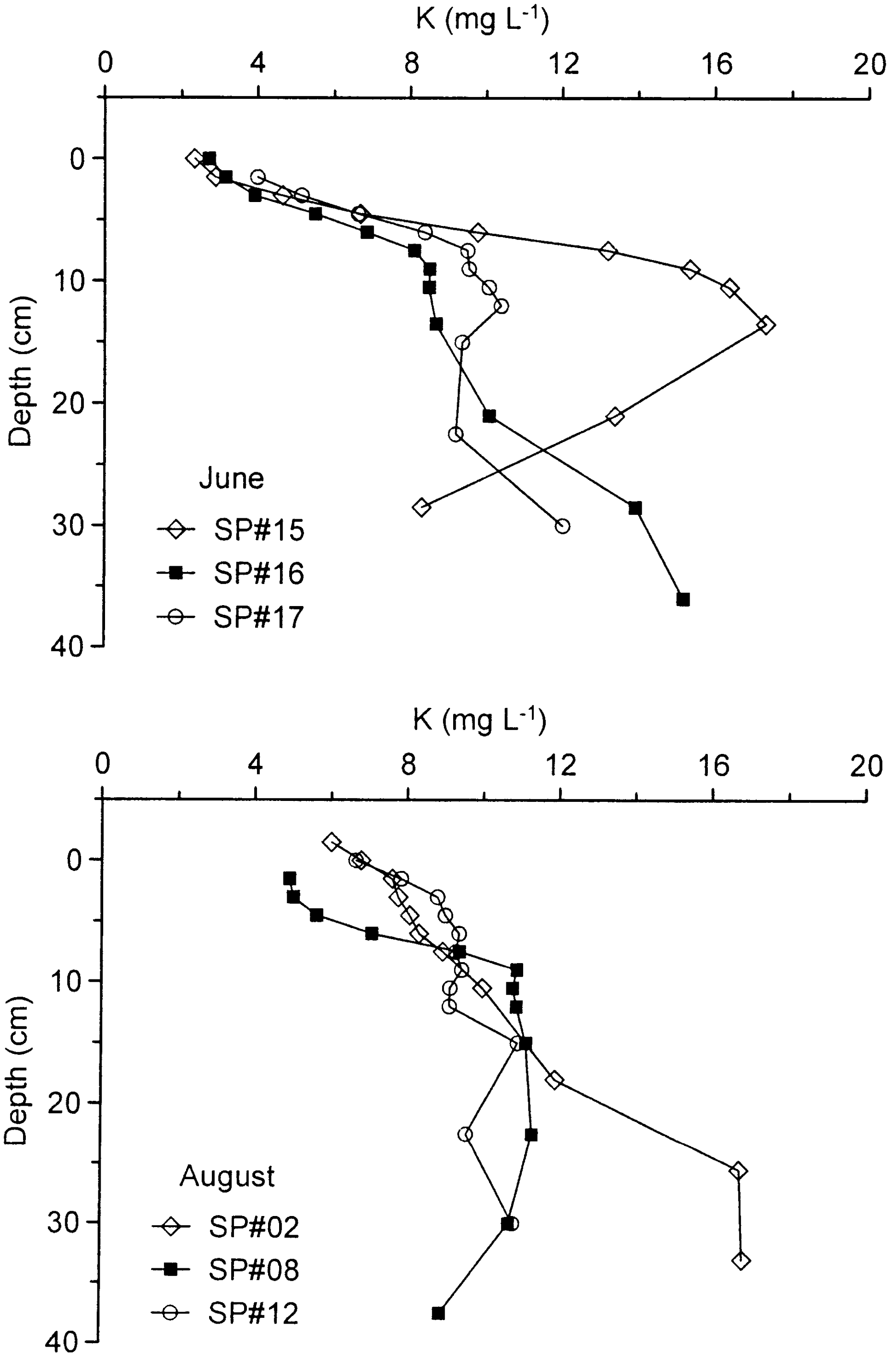


Figure 5.45. Triplicate samples of dissolved K in interstitial water from Schlepp Pond samples collected in June and August, 2004.

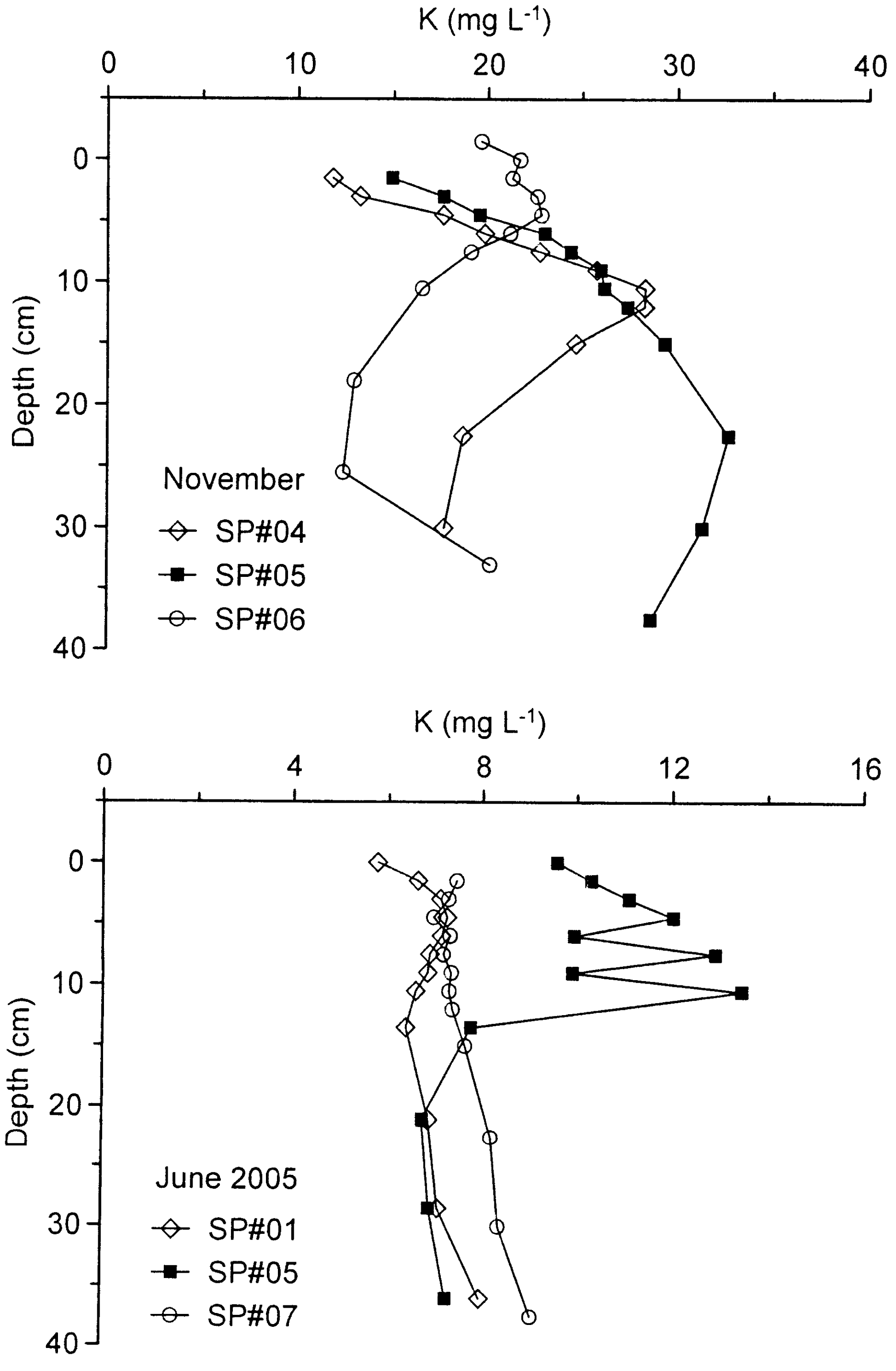
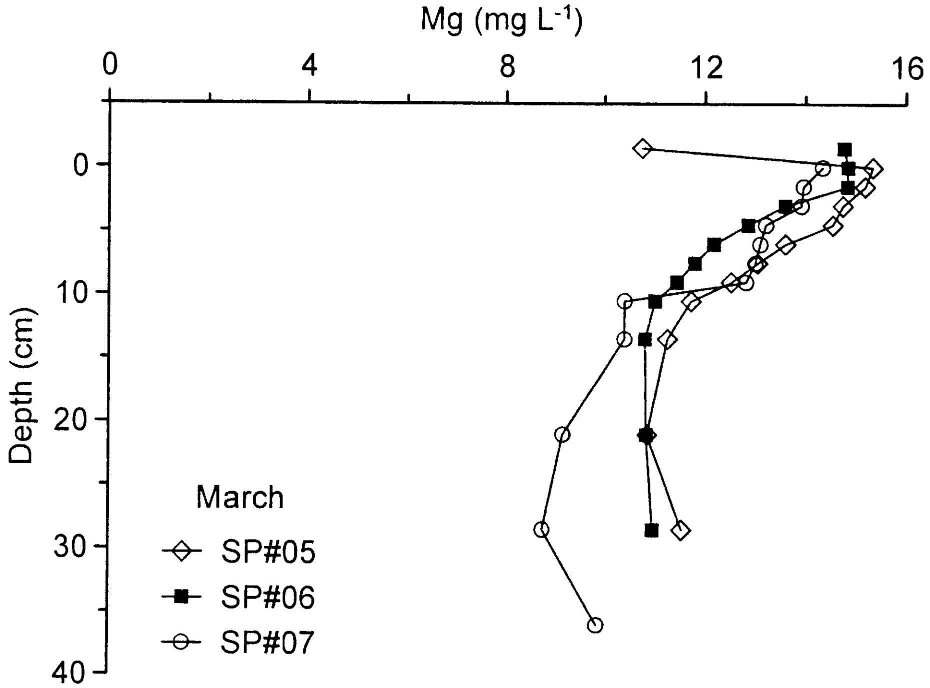


Figure 5.46. Triplicate samples of dissolved K in interstitial water from Schlepp Pond samples collected in November, 2004 and June, 2005.



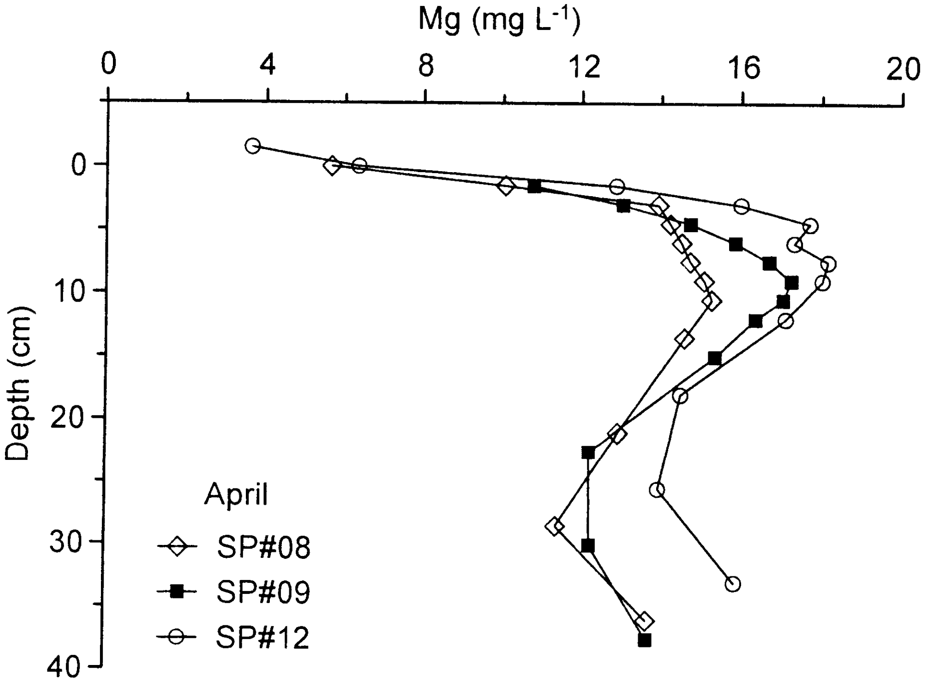


Figure 5.47. Triplicate samples of dissolved Mg in interstitial water from Schlepp Pond samples collected in March and April, 2004.

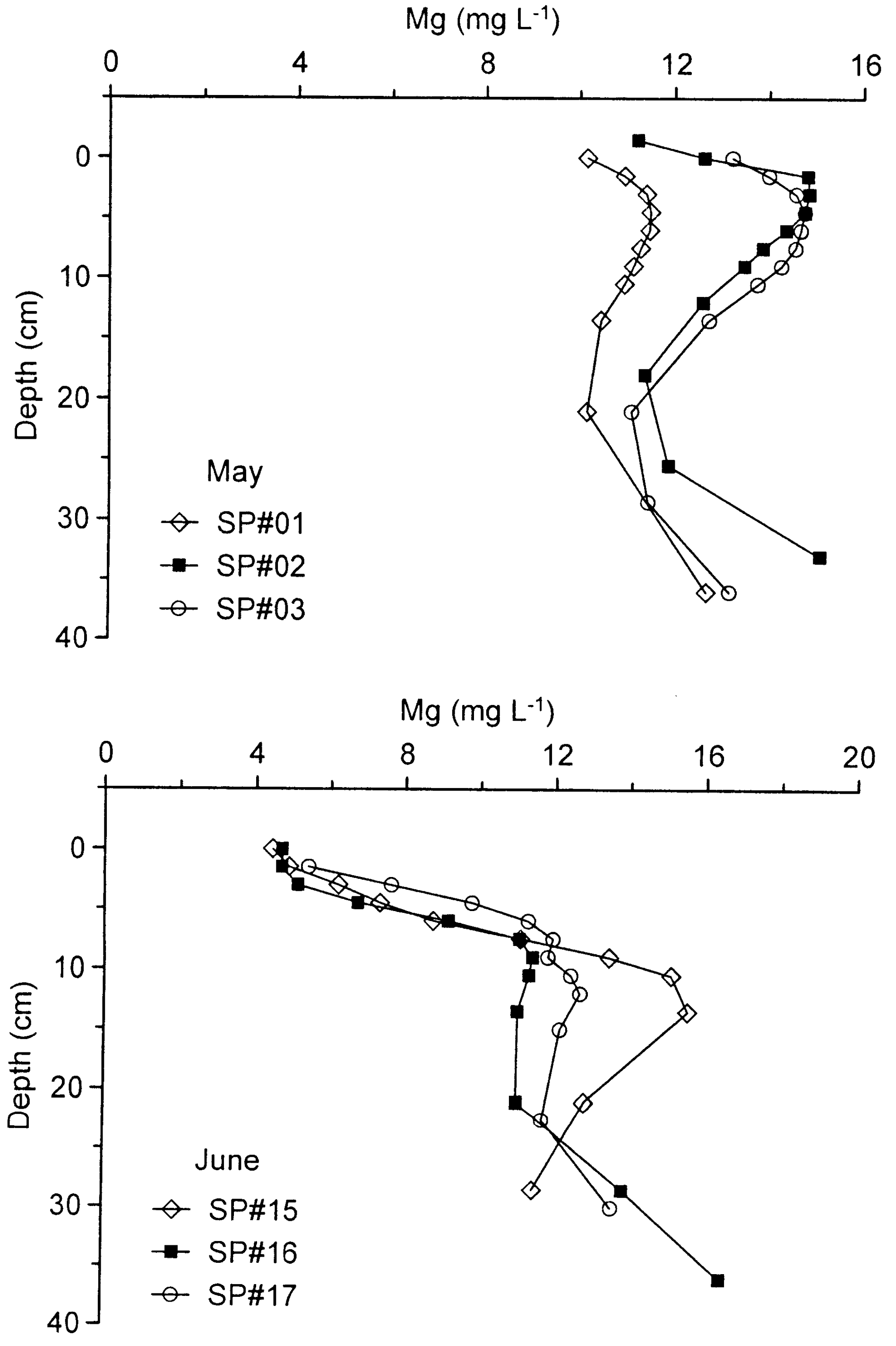


Figure 5.48. Triplicate samples of dissolved Mg in interstitial water from Schlepp Pond samples collected in May and June, 2004.

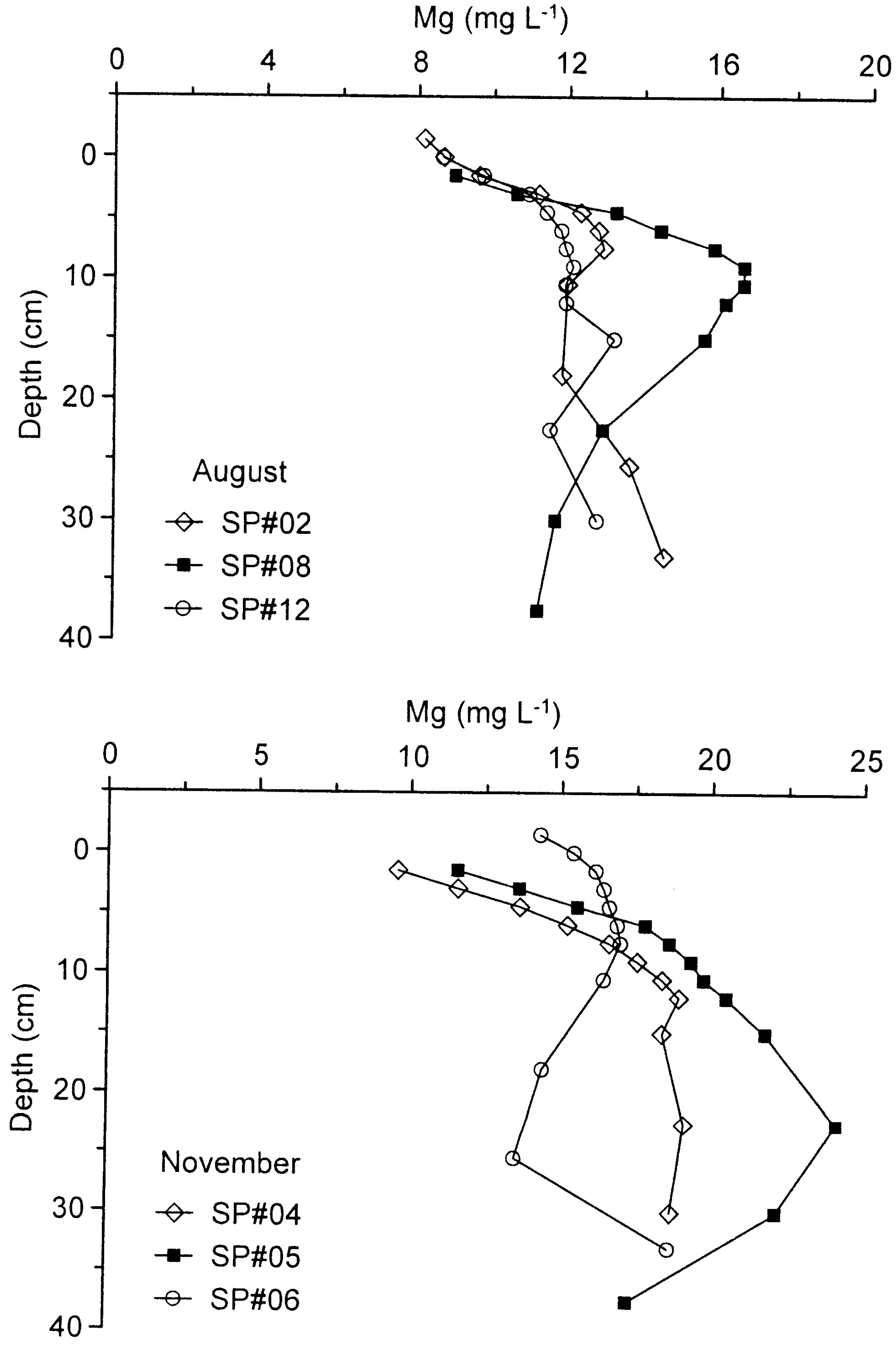


Figure 5.49. Triplicate samples of dissolved Mg in interstitial water from Schlepp Pond samples collected in August and November, 2004.

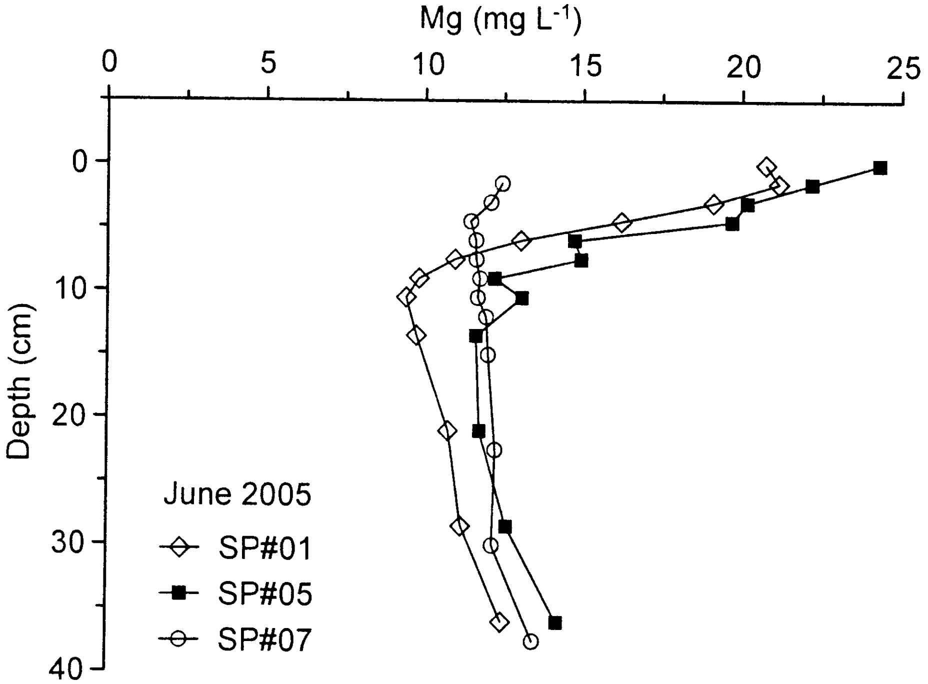


Figure 5.50. Triplicate samples of dissolved Mg in interstitial water from Schlepp Pond samples collected in June, 2005.

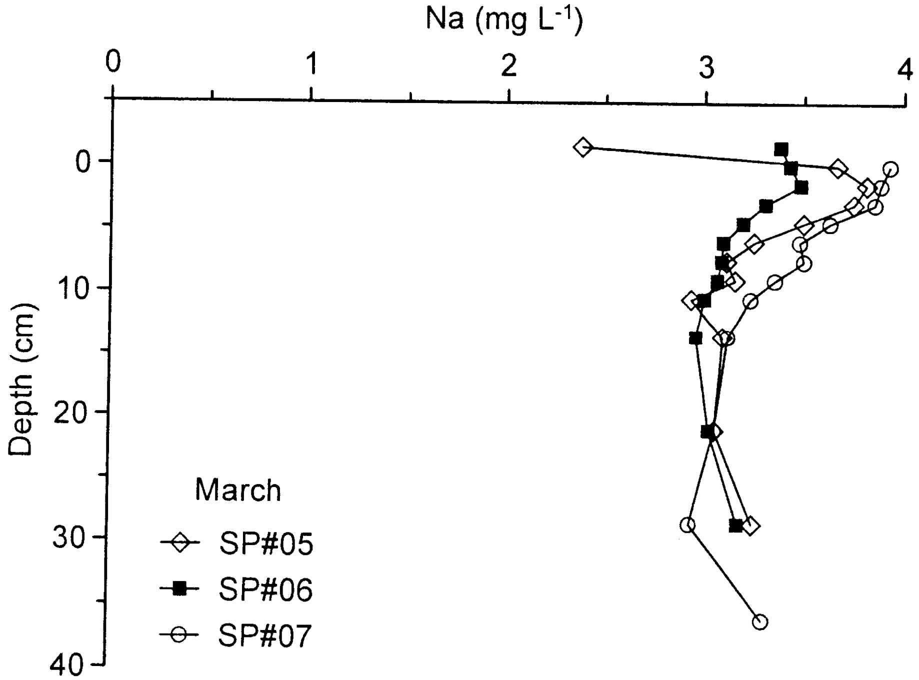


Figure 5.51. Triplicate samples of dissolved Na in interstitial water from Schlepp Pond samples collected in March, 2004.

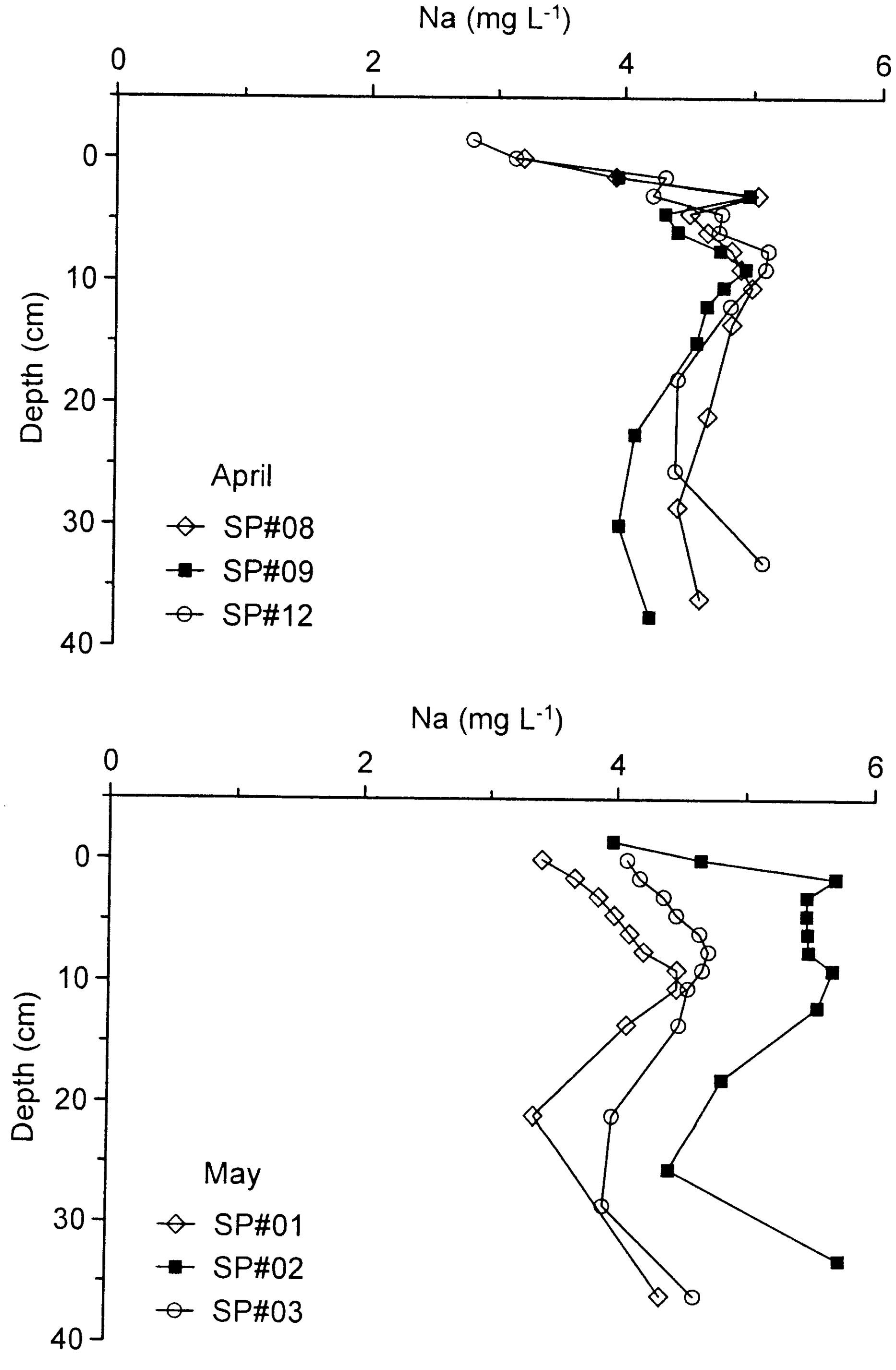


Figure 5.52. Triplicate samples of dissolved Na in interstitial water from Schlepp Pond samples collected in April and May, 2004.

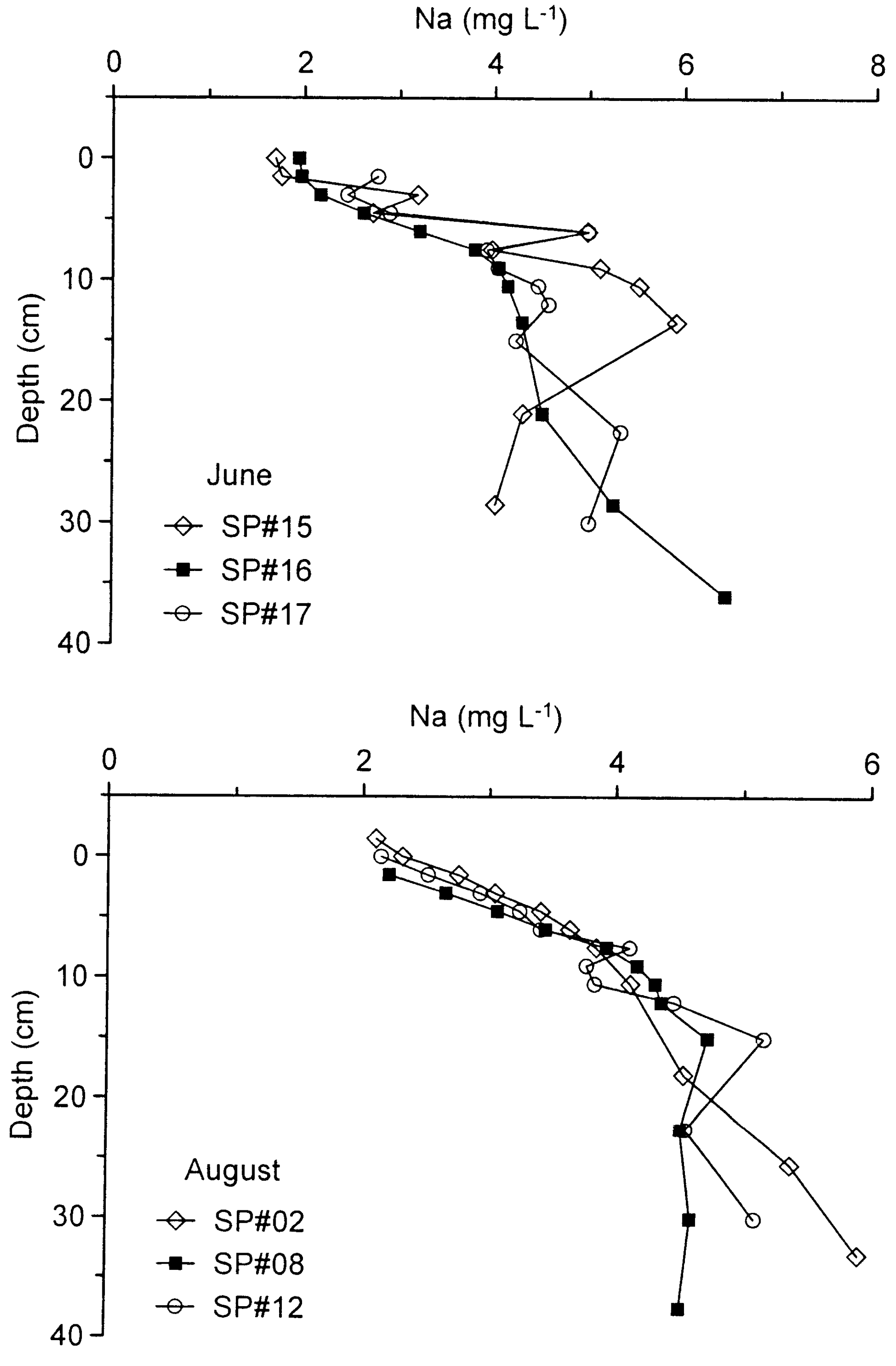
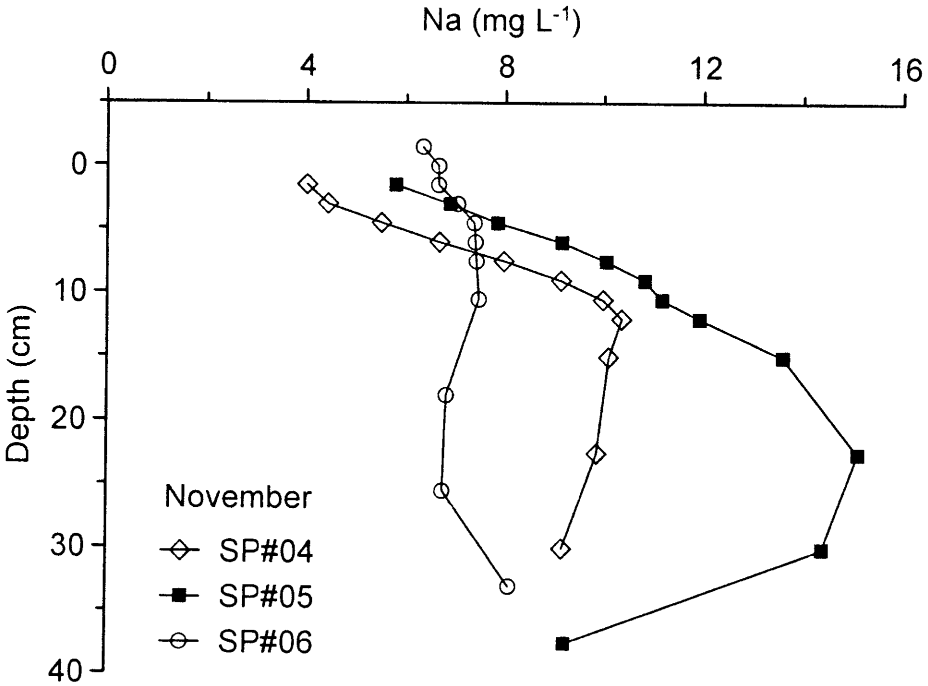


Figure 5.53. Triplicate samples of dissolved Na in interstitial water from Schlepp Pond samples collected in June and August, 2004.



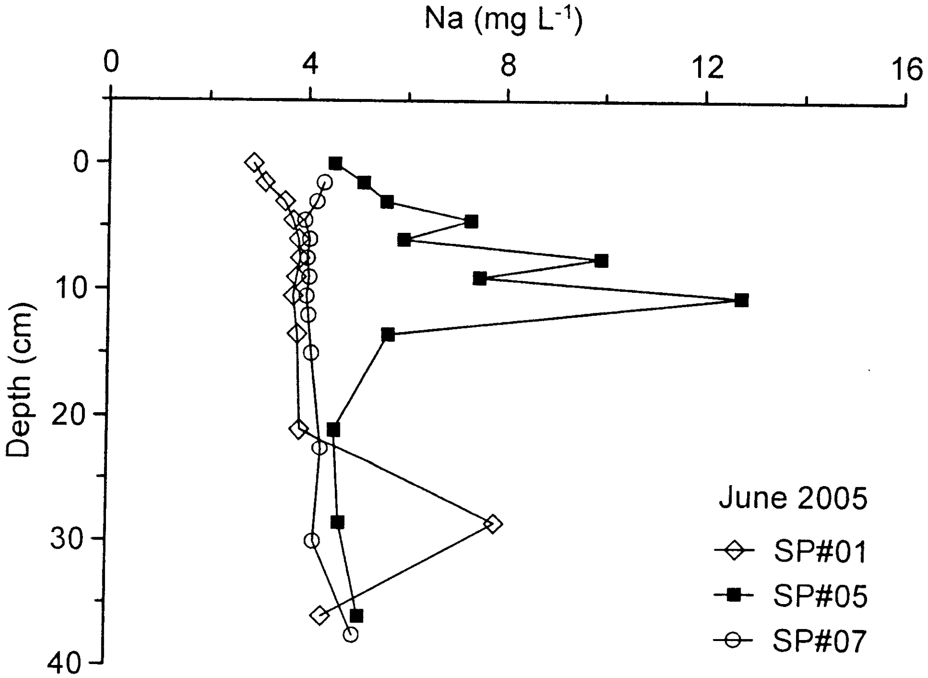


Figure 5.54. Triplicate samples of dissolved Na in interstitial water from Schlepp Pond samples collected in November, 2004 and June, 2005.

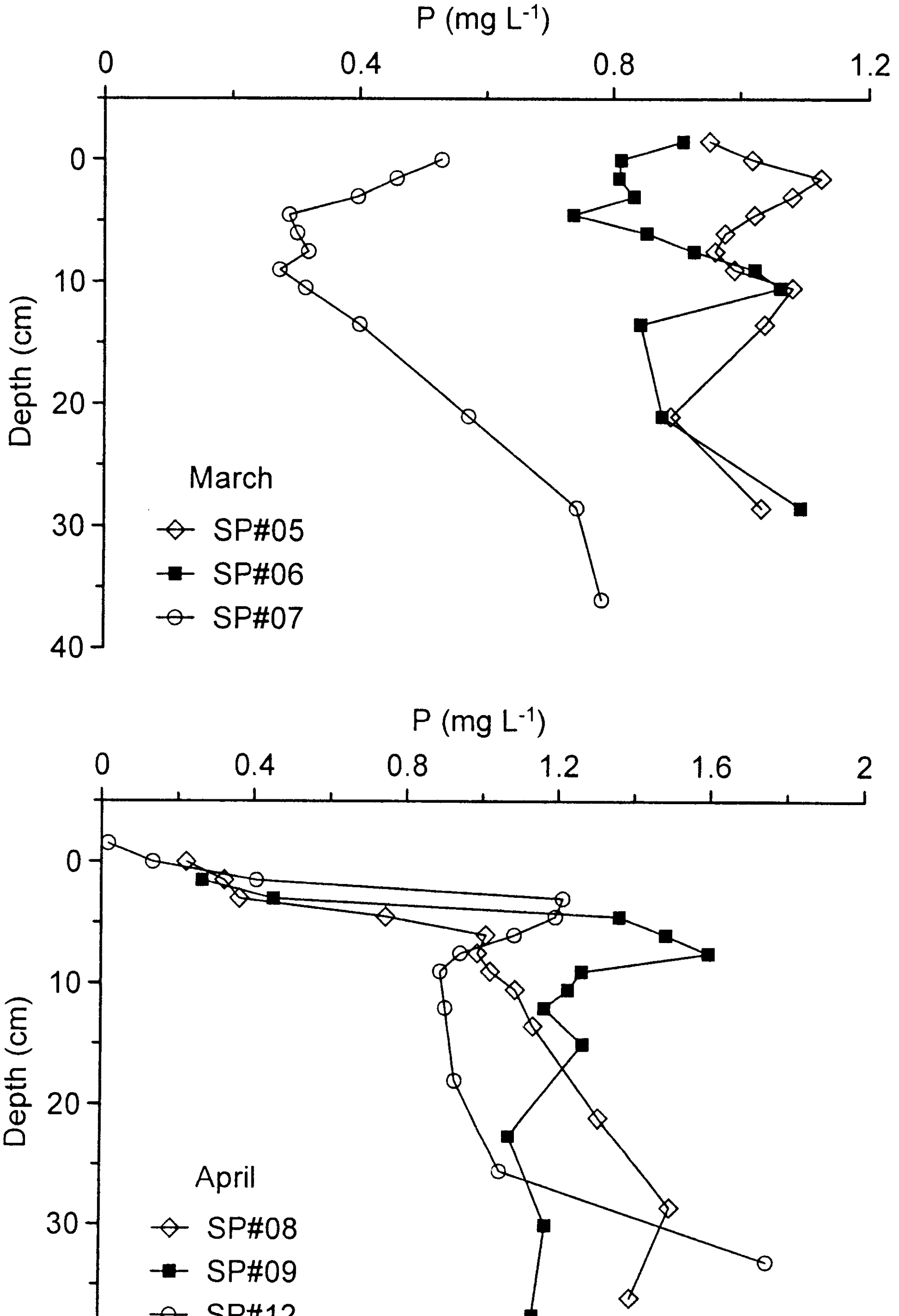


Figure 5.55. Triplicate samples of dissolved P in interstitial water from Schlepp Pond samples collected in March and April, 2004.

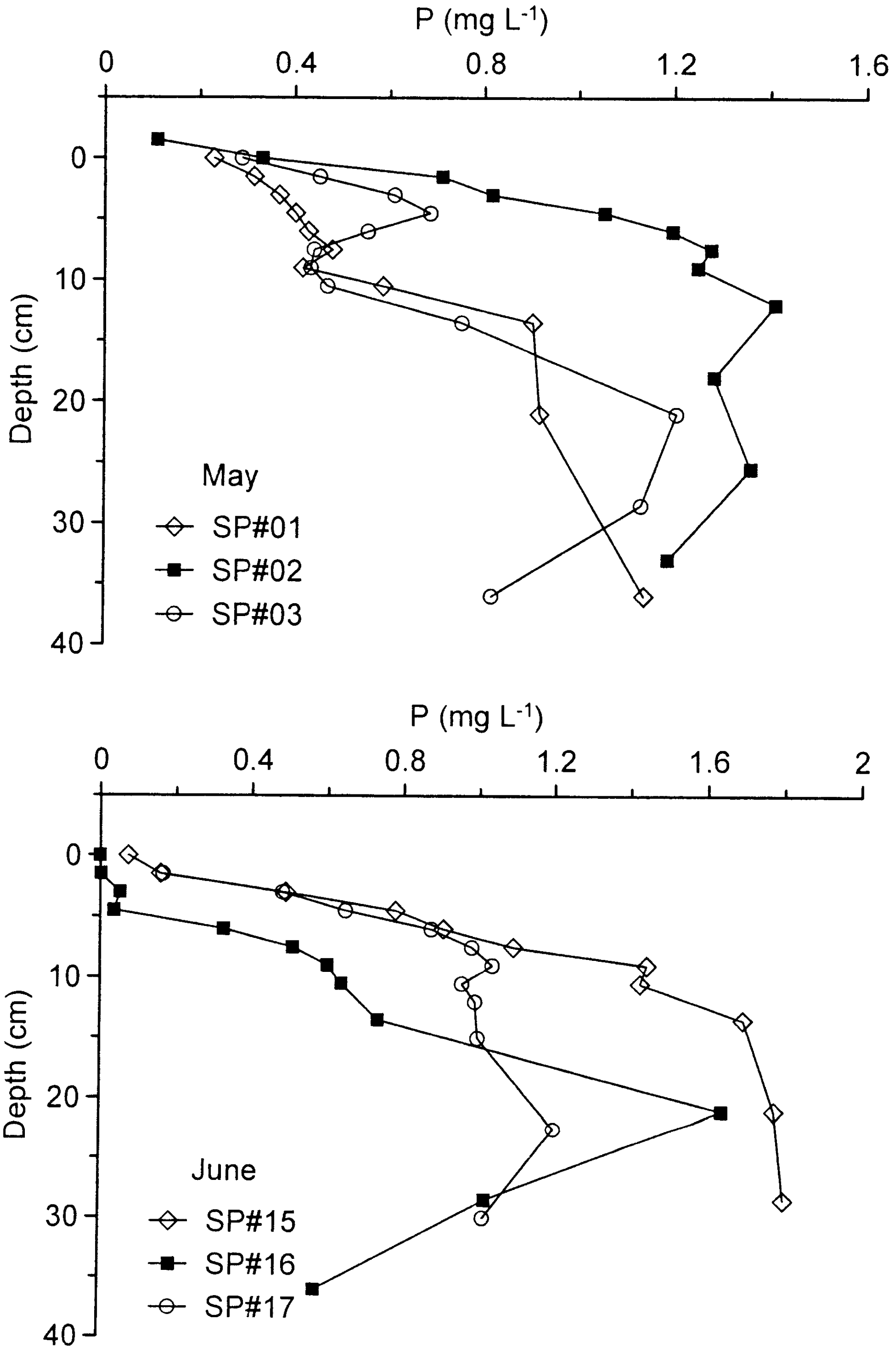


Figure 5.56. Triplicate samples of dissolved P in interstitial water from Schlepp Pond samples collected in May and June, 2004.

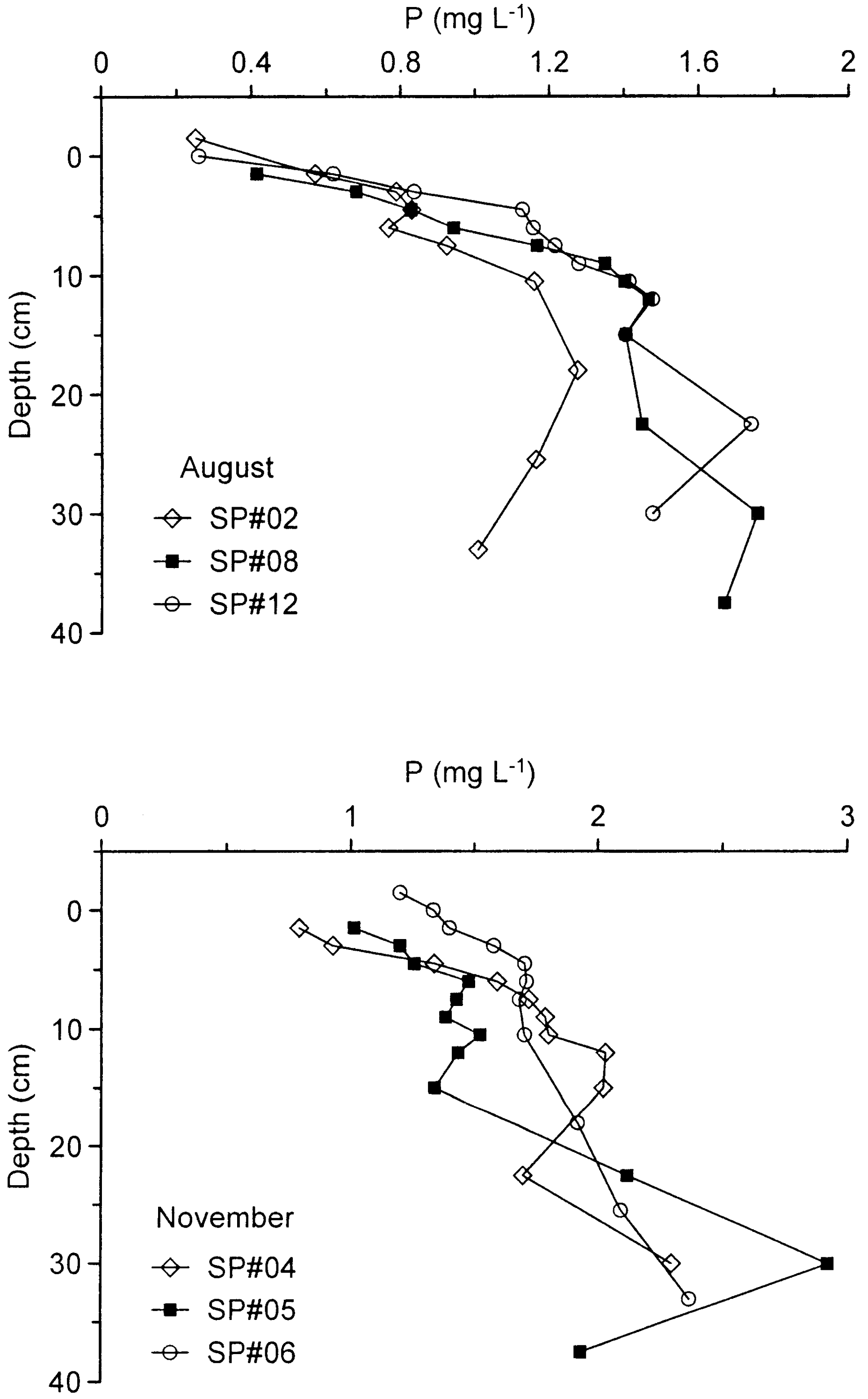


Figure 5.57. Triplicate samples of dissolved P in interstitial water from Schlepp Pond samples collected in August and November, 2004.

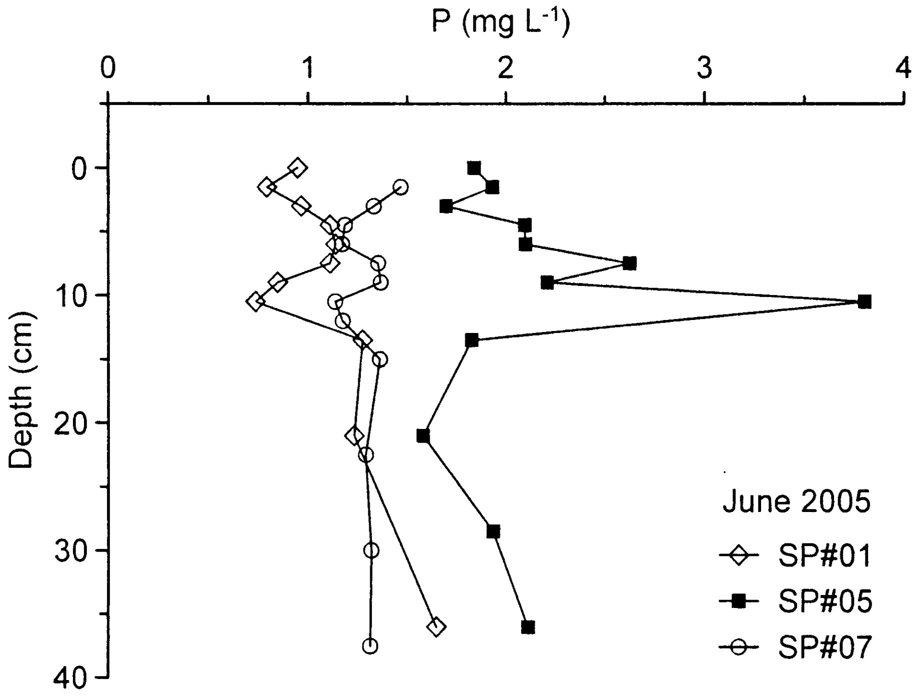


Figure 5.58. Triplicate samples of dissolved P in interstitial water from Schlepp Pond samples collected in June, 2005.

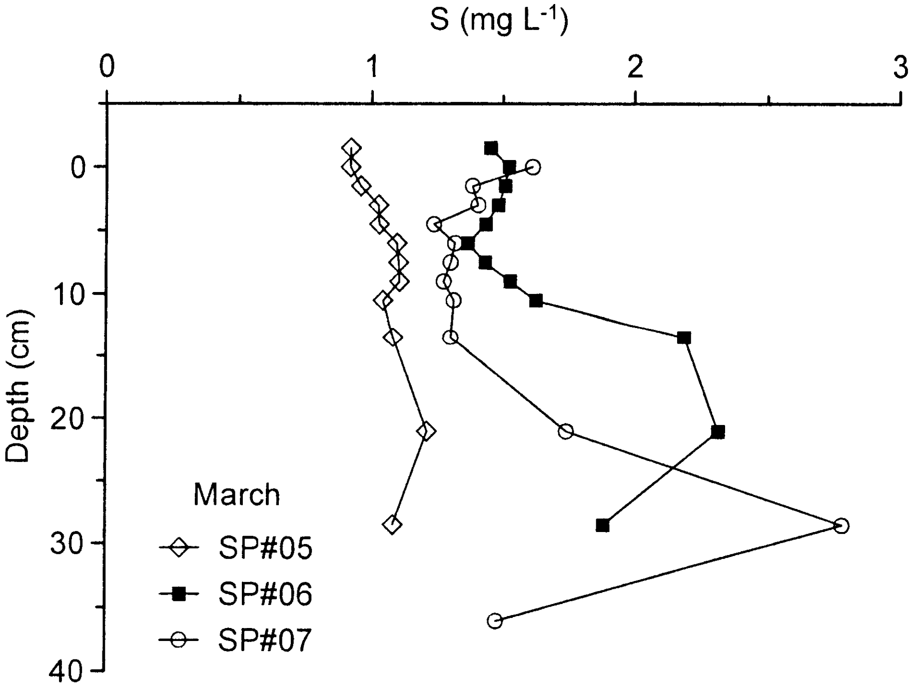


Figure 5.59. Triplicate samples of dissolved S in interstitial water from Schlepp Pond samples collected in March, 2004.

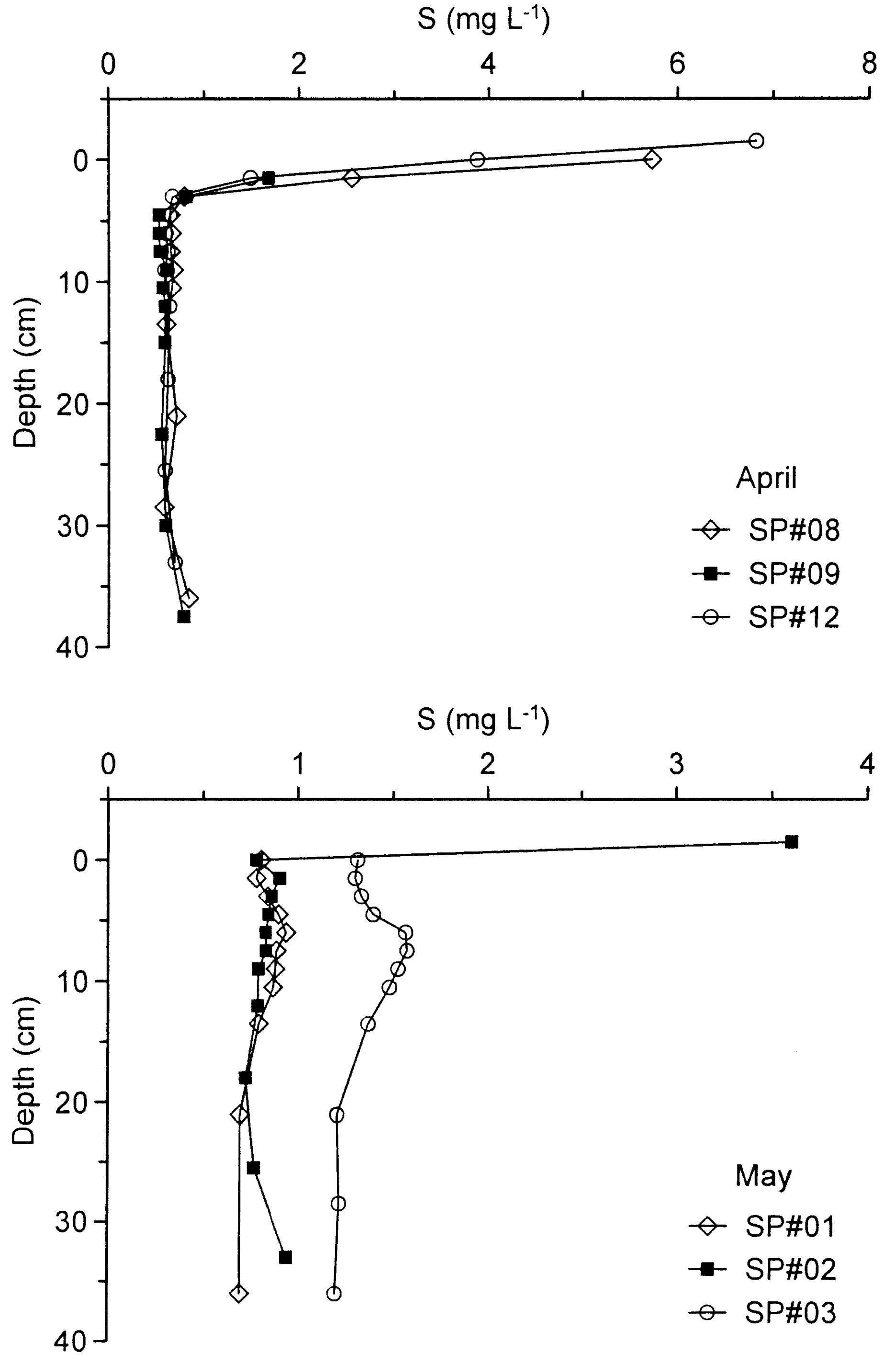


Figure 5.60. Triplicate samples of dissolved S in interstitial water from Schlepp Pond samples collected in April and May, 2004.

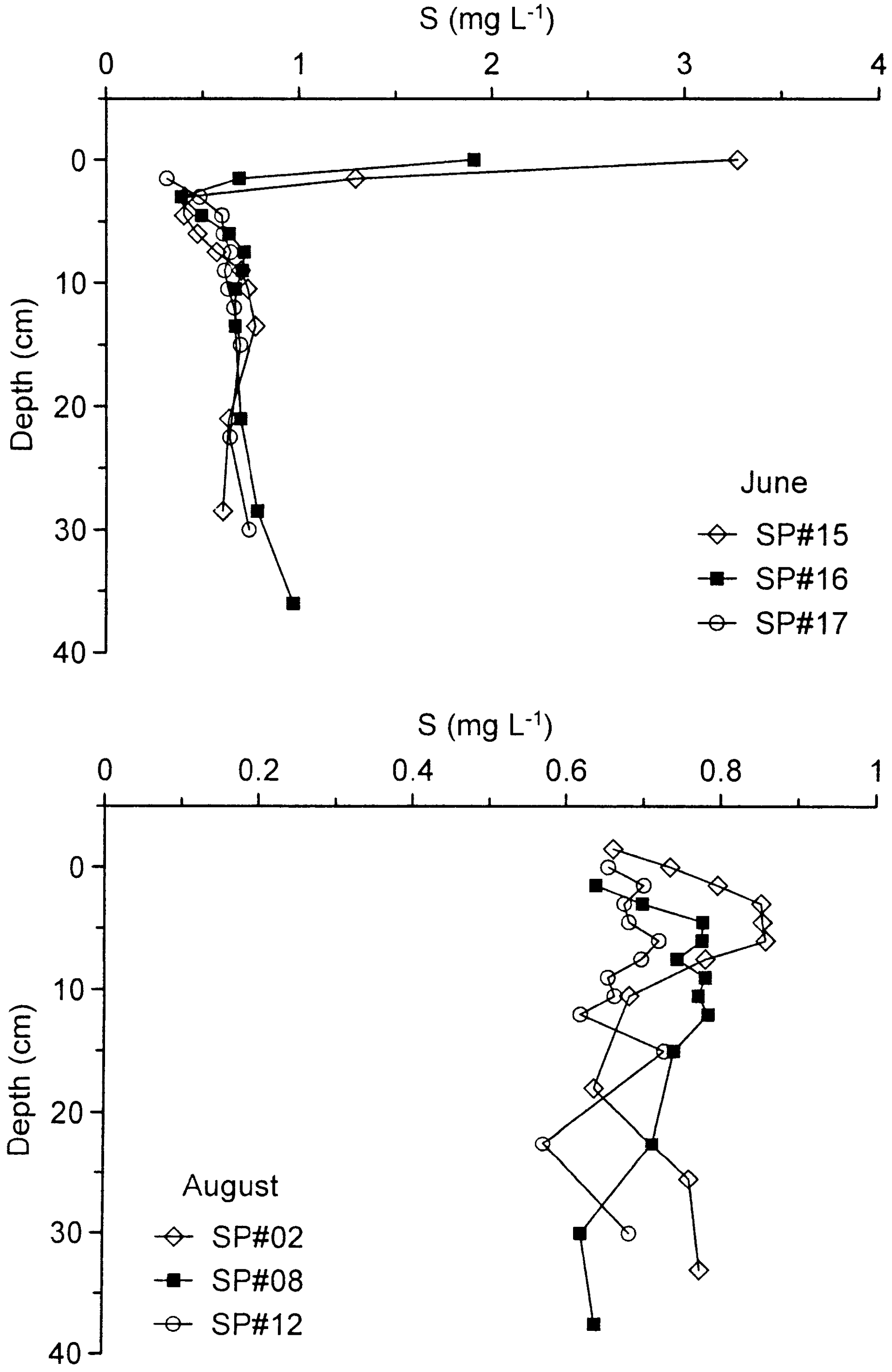


Figure 5.61. Triplicate samples of dissolved S in interstitial water from Schlepp Pond samples collected in June and August, 2004.

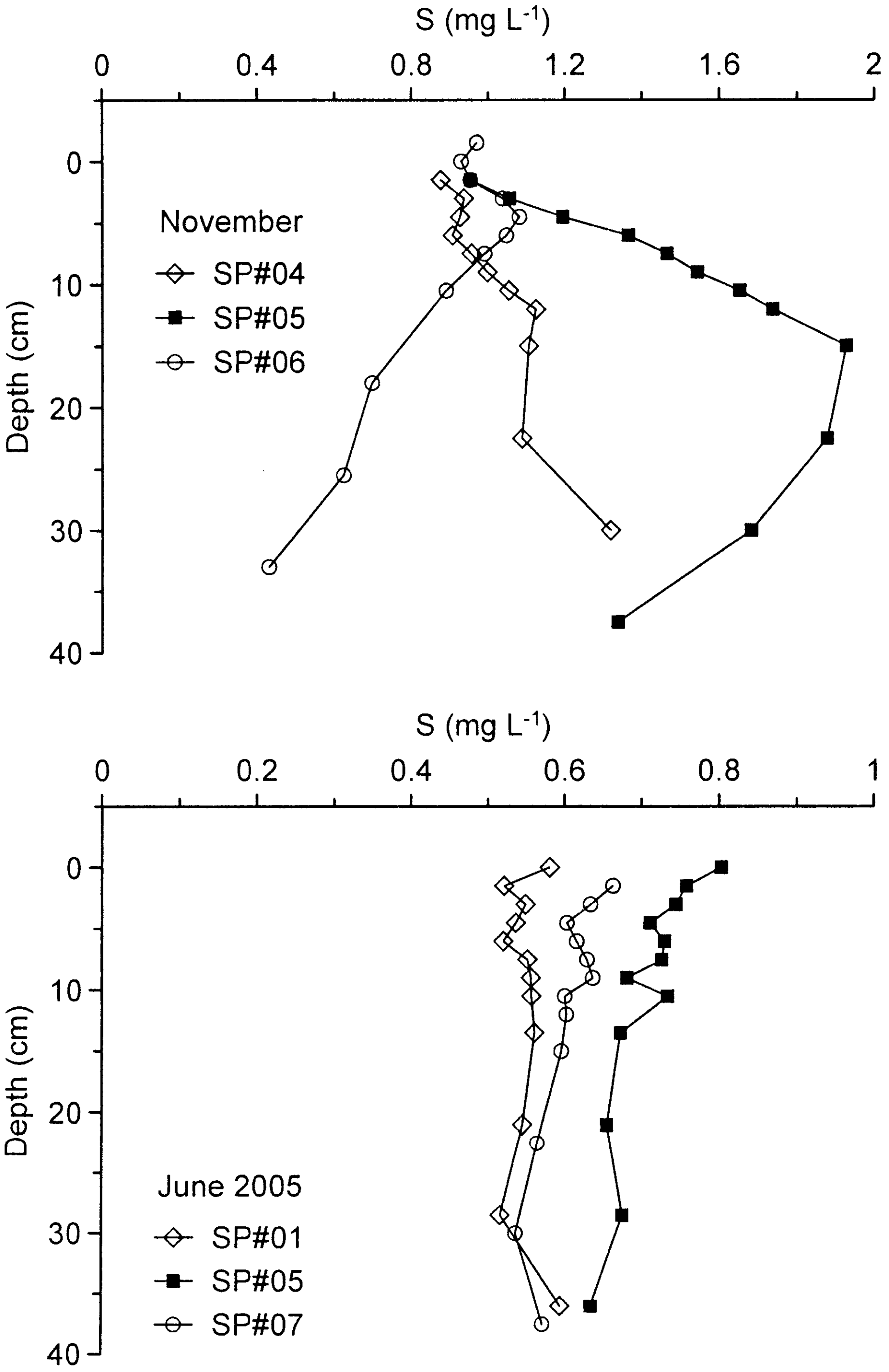


Figure 5.62. Triplicate samples of dissolved S in interstitial water from Schlepp Pond samples collected in November, 2004 and June, 2005.

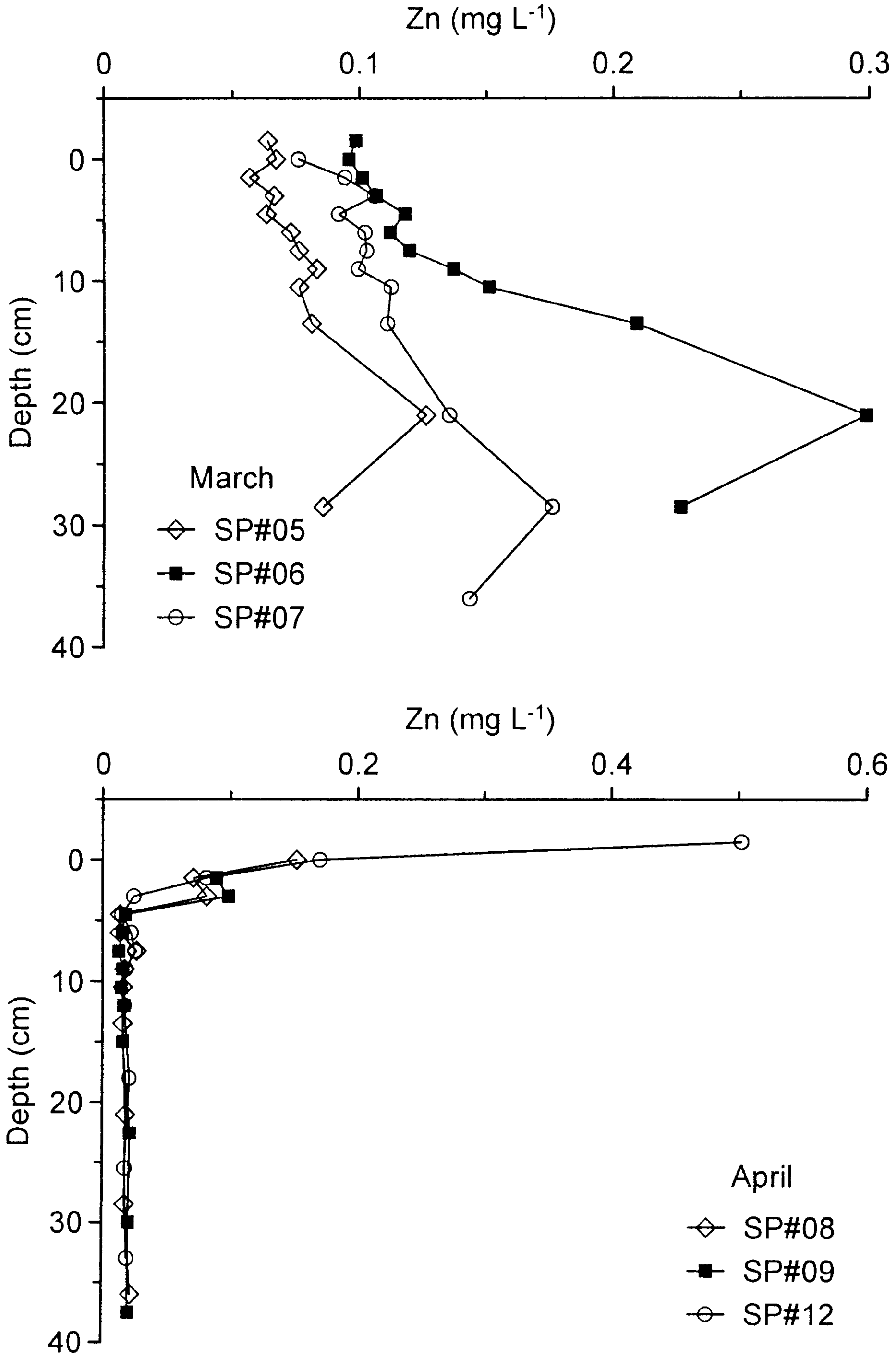


Figure 5.63. Triplicate samples of dissolved Zn in interstitial water from Schlepp Pond samples collected in March and April, 2004.

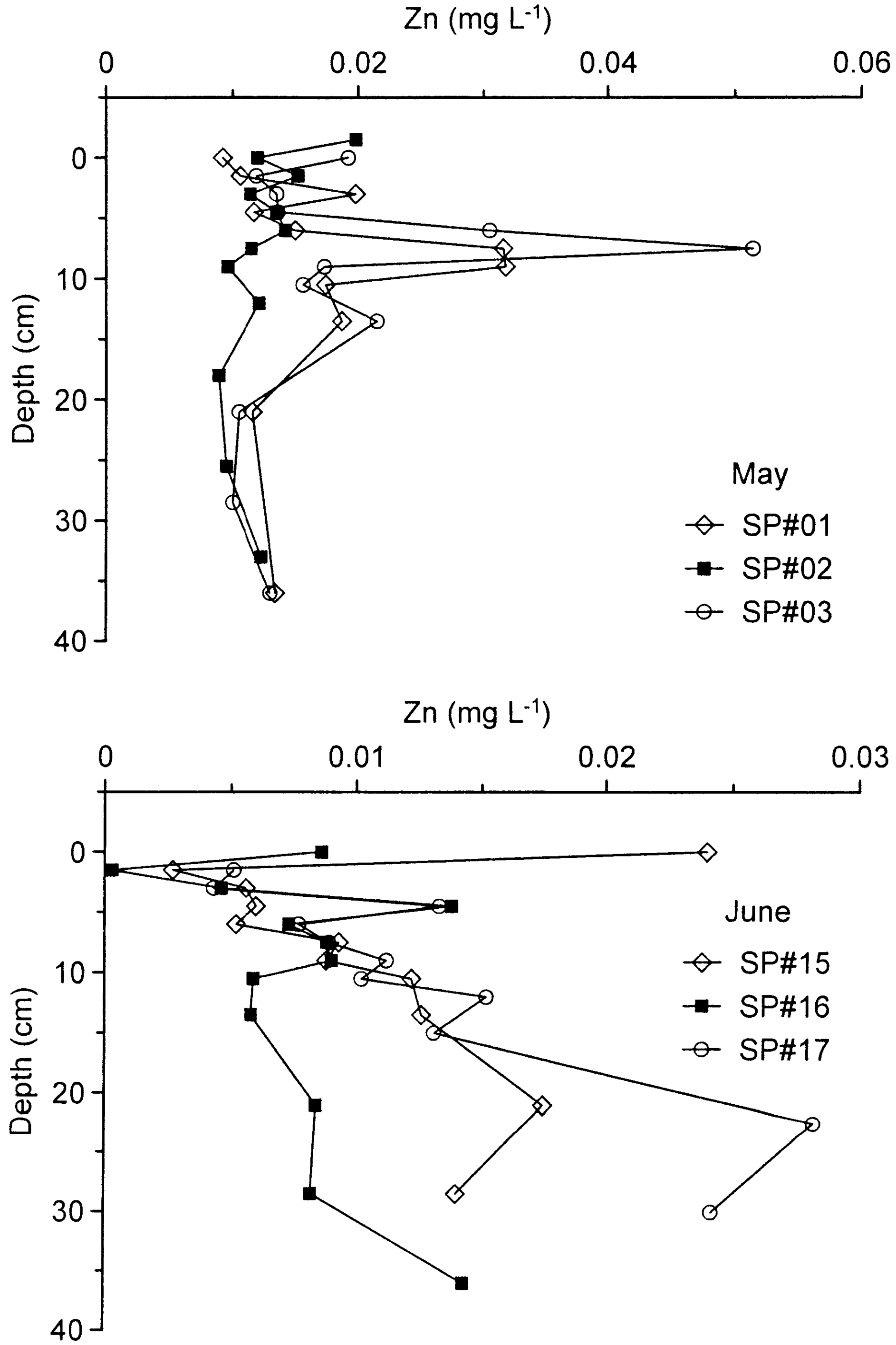


Figure 5.64. Triplicate samples of dissolved Zn in interstitial water from Schlepp Pond samples collected in May and June, 2004.

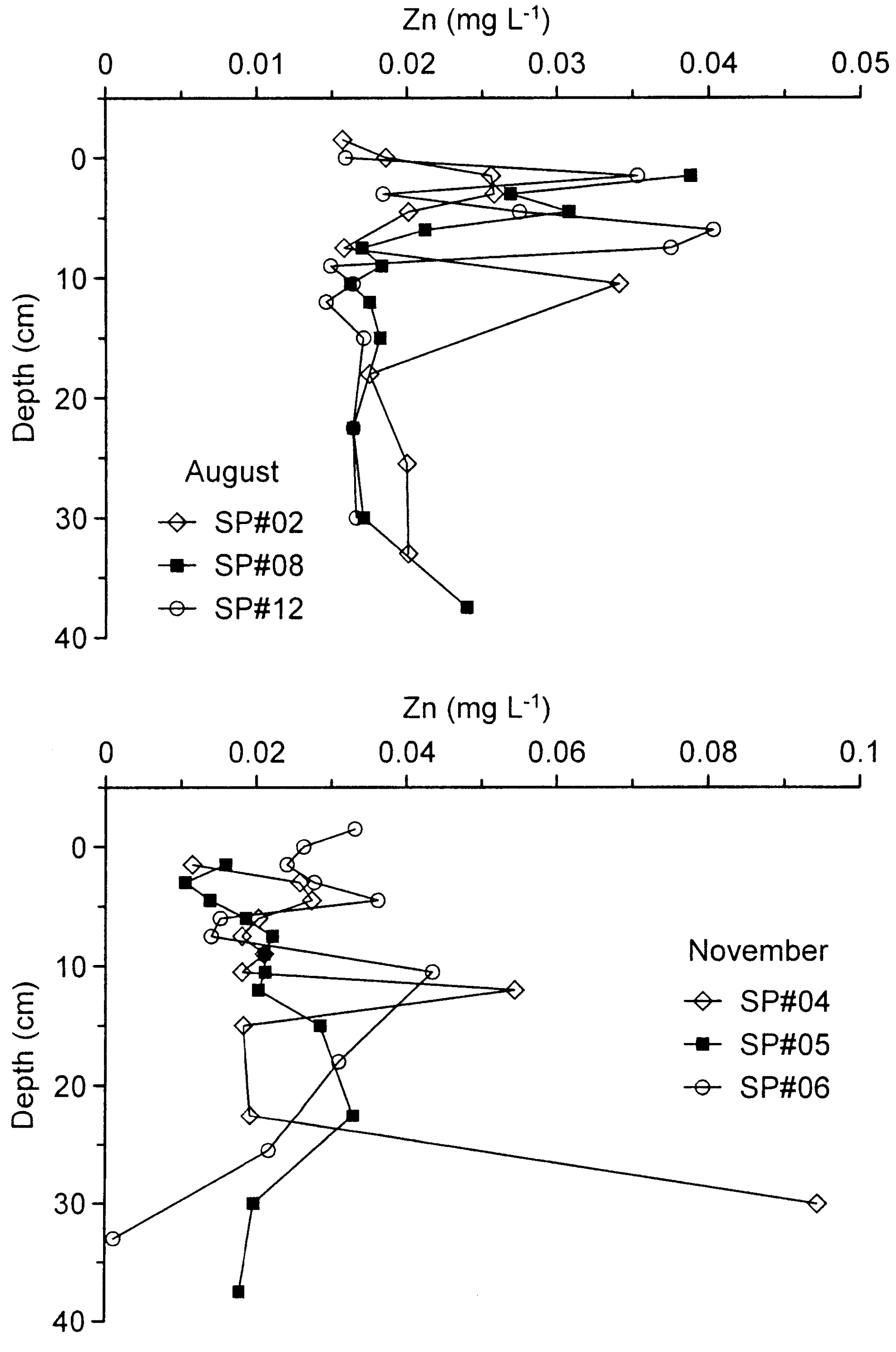


Figure 5.65. Triplicate samples of dissolved Zn in interstitial water from Schlepp Pond samples collected in August and November, 2004.

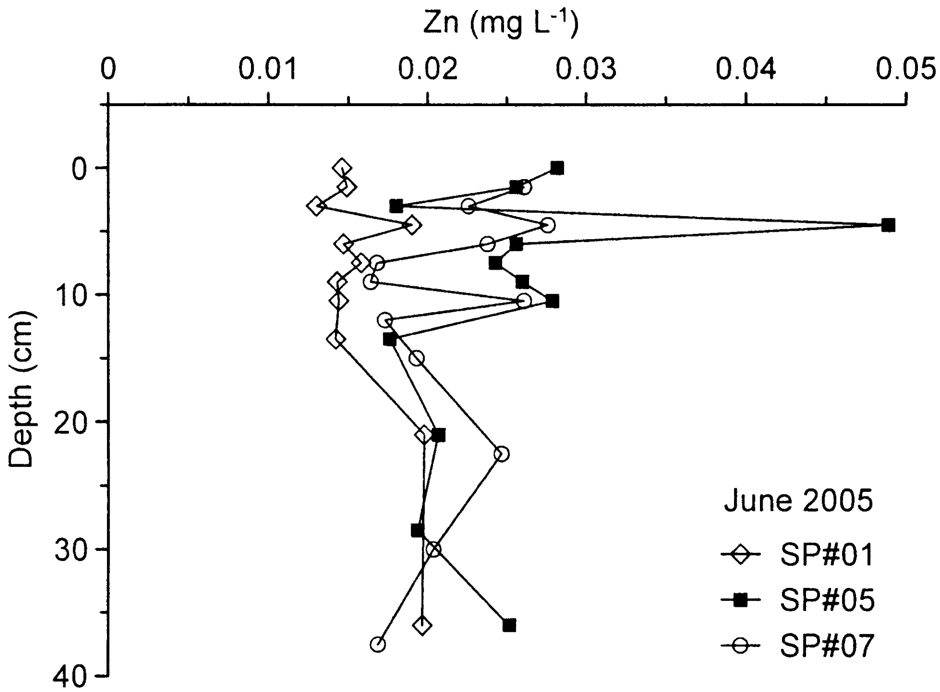


Figure 5.66. Triplicate samples of dissolved Zn in interstitial water from Schlepp Pond samples collected in June, 2005.

Dissolved Constituents, Schlepp Pond ICP-MS

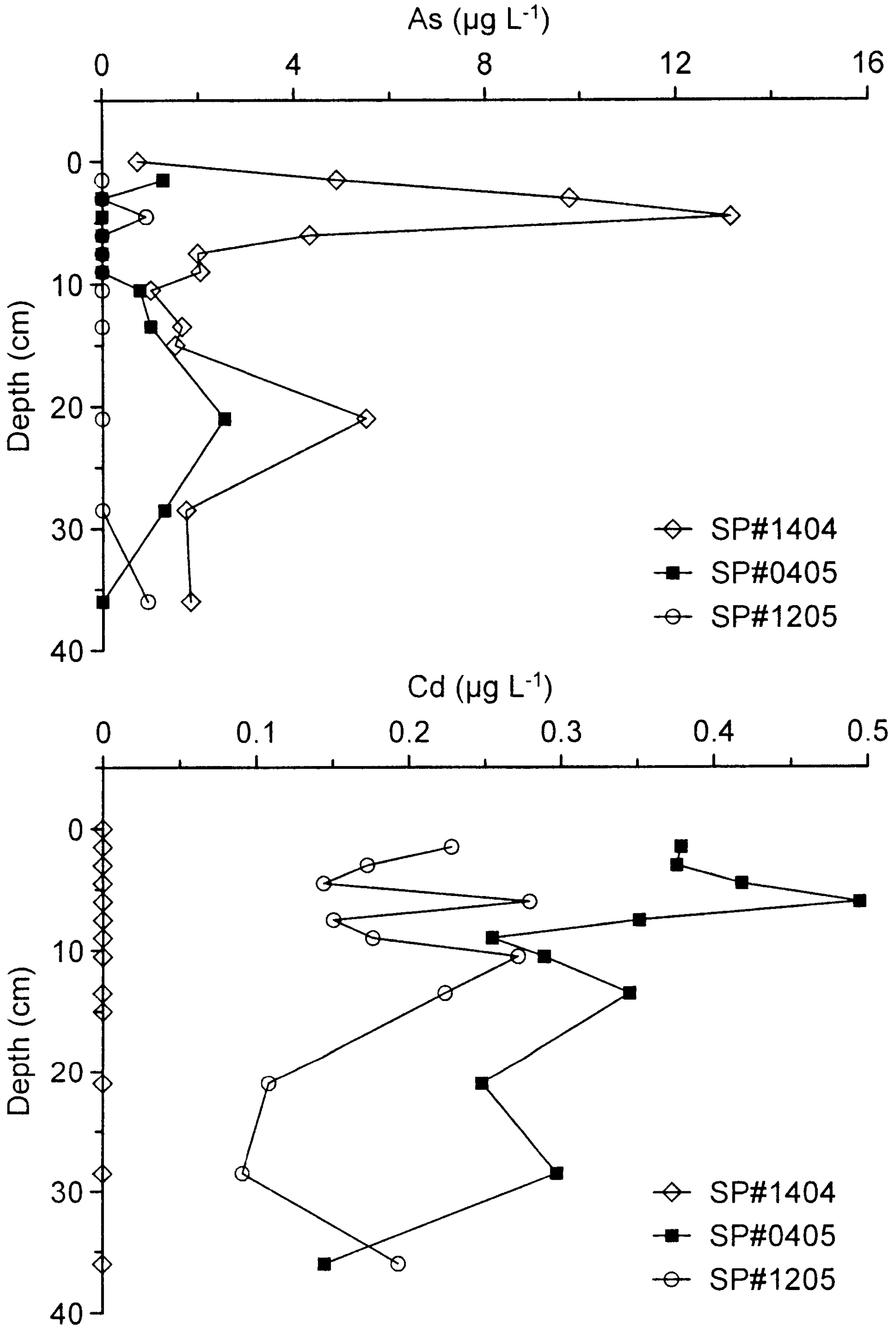


Figure 5.67. Dissolved As and Cd in interstitial water from Schlepp Pond. Sample 1404 was collected in June of 2004 and 0405 and 1205 were collected in June of 2006. Samples were analyzed by ICP-MS.

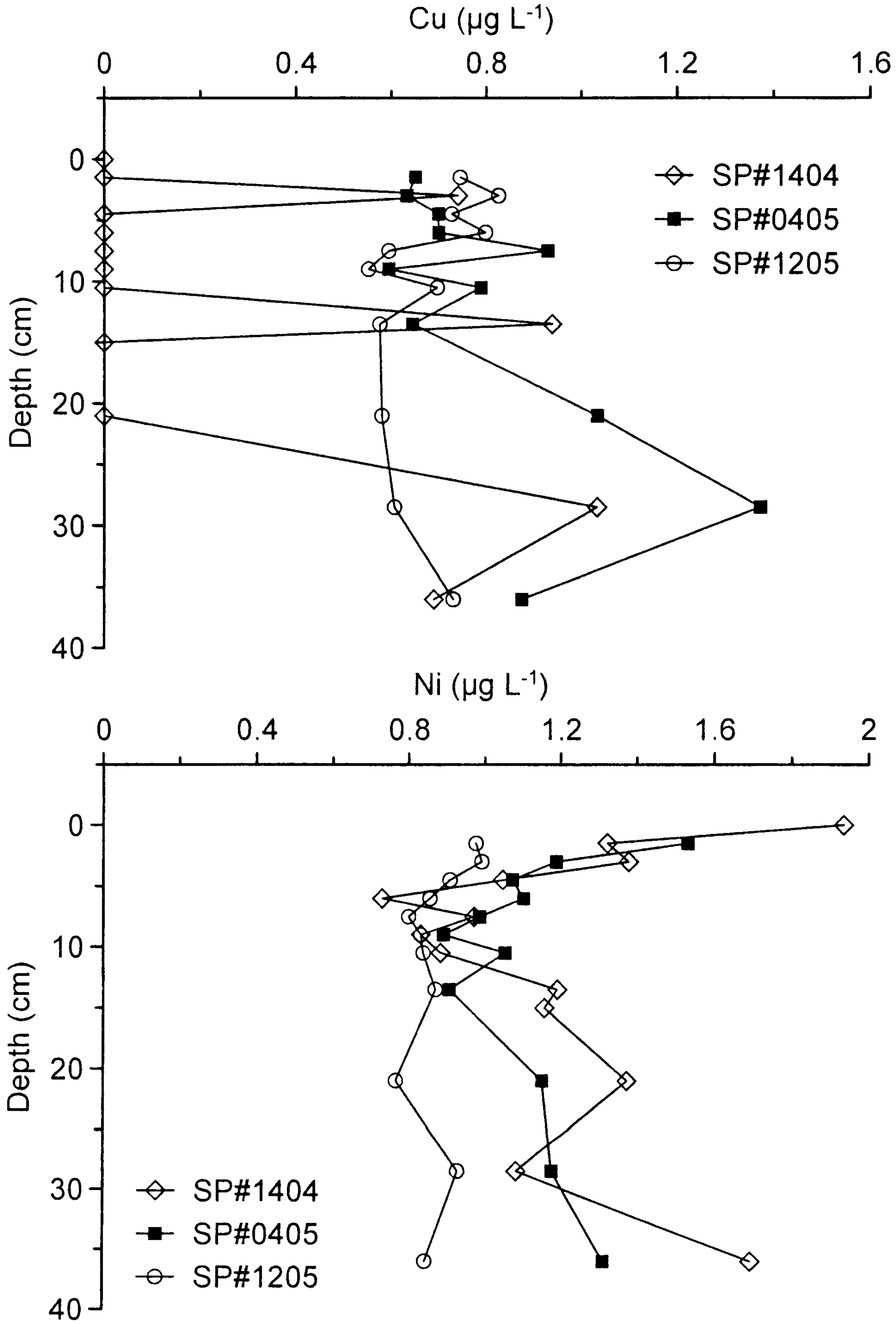


Figure 5.68. Dissolved Cu and Ni in interstitial water from Schlepp Pond. Sample 1404 was collected in June of 2004 and 0405 and 1205 were collected in June of 2006. Samples were analyzed by ICP-MS.

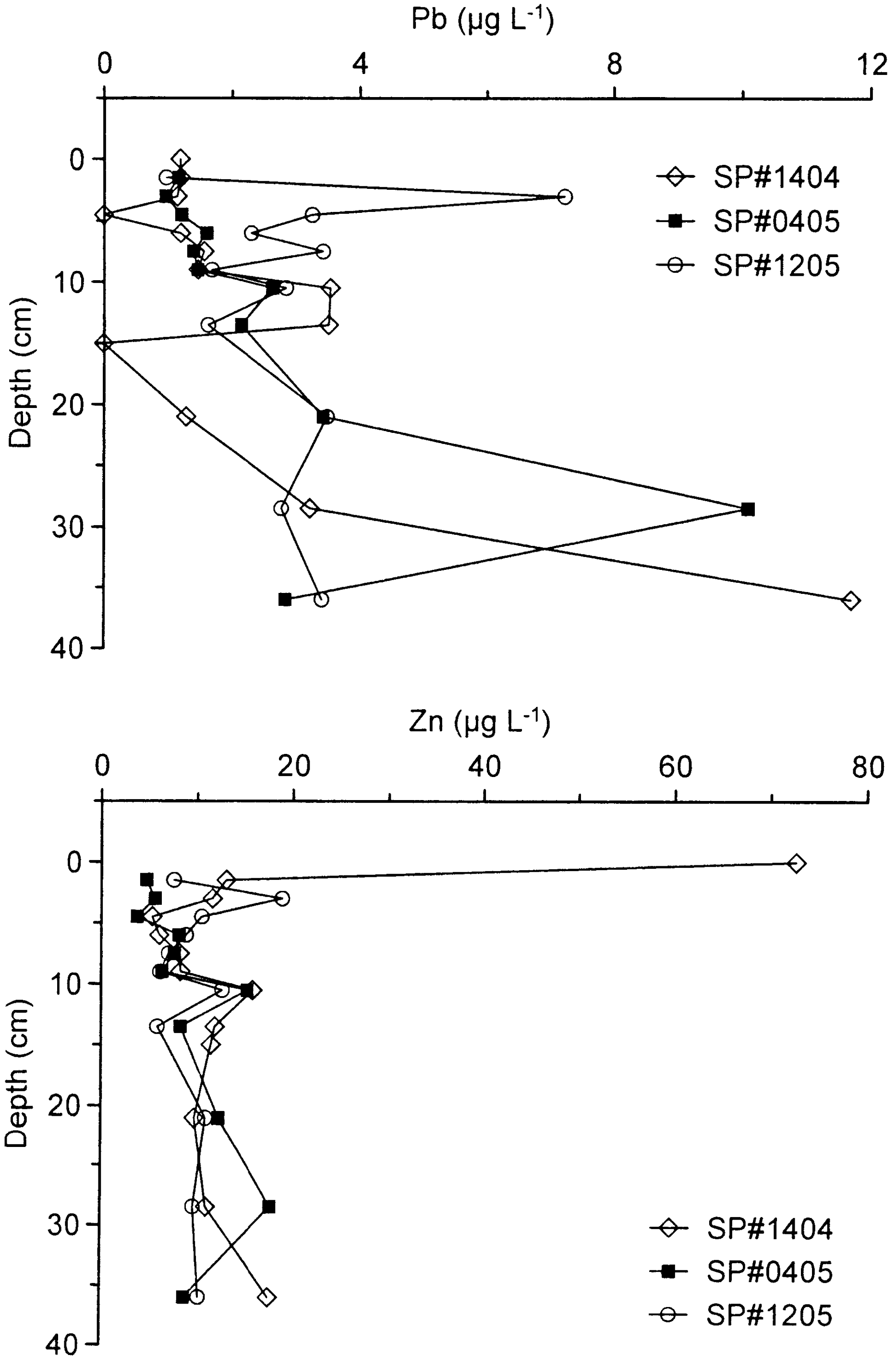


Figure 5.69. Dissolved Pb and Zn in interstitial water from Schlepp Pond. Sample 1404 was collected in June of 2004 and 0405 and 1205 were collected in June of 2006. Samples were analyzed by ICP-MS.

TABLES OF DATA

Sediment Digest, Lake Coeur d'Alene

Table 5.1. Total digest of two St. Joe site cores collected in May, 2002. Solution analyzed with ICP-AES.

Depth	Sample	Element (mg kg^{-1})						
(cm)		As	Cd	Fe	Mn	Pb	S	Zn
				St. Joe Site Core A				
3-6	SJA2-1	9.4699	0.0000	34008.338	390.411	30.31566	711.733	112.478
3-6	SJA2-2	27.2167	0.0000	35760.423	400.176	43.36465	779.213	109.777
3-6	SJA2-3	29.8378	0.0000	34965.238	380.939	27.14368	762.457	105.620
12-18	SJA4	11.9339	0.0000	33506.732	405.141	23.86781	701.346	141.218
24-30	SJA6	14.9394	0.0000	29681.818	438.485	22.36364	452.121	109.364
				St. Joe Site Core B				
0-3	SJB1	8.0701	0.0000	34610.94	524.461	33.571	520.801	118.240
3-6	SJB2	11.0101	0.0000	37480.65	568.498	41.235	639.319	151.993
6-12	SJB3	12.0176	0.0000	36530.38	774.933	273.787	644.058	183.836
12-18	SJB4	10.6374	0.0000	34267.15	423.873	43.260	609.419	131.567
18-24	SJB5	9.8289	0.0000	34520.49	430.362	46.876	639.276	143.812
24-30	SJ-6-1	8.9459	0.0000	28413.07	467.717	40.121	396.149	96.052
24-30	SJ-6-2	9.5321	0.0000	29060.32	484.919	36.756	391.725	104.002
24-30	SJ-6-3	13.6327	0.0000	27970.20	461.941	33.508	317.559	101.369

Table 5.2. Total digest of two Harlow Point site cores collected in May, 2002. Solution analyzed with ICP-AES.

Depth (cm)	Sample	Element ($mg\ kg^{-1}$)						
		As	Cd	Fe	Mn	Pb	S	Zn
				Harlow Point Site Core A				
0-3	HPA1-1	170.316	23.7302	79401.81	4523.14	4746.05	3690.74	3625.85
0-3	HPA1-2	155.503	23.7076	75347.42	4271.82	4510.84	3396.33	3424.12
0-3	HPA1-3	169.378	23.4166	82510.17	5647.88	4808.25	3704.24	3611.27
3-6	HPA2	165.832	22.2722	84983.13	6268.28	4946.57	3998.88	3560.18
6-12	HPA3	136.328	25.5962	82806.43	6128.67	5293.95	4453.69	3740.99
12-18	HPA4	162.774	30.0506	84327.52	4575.13	4817.11	4231.85	3809.79
18-24	HPA5	175.913	41.4441	68910.08	3940.05	3547.68	3626.70	3207.08
24-30	HPA6	346.064	36.1516	108367.35	9457.73	4950.44	6448.98	3967.93
				Harlow Point Site Core B				
0-3	HPB1	124.022	22.6680	74724.17	6018.05	4037.11	2503.01	3207.12
3-6	HPB2	98.282	22.6145	73473.28	5262.40	3984.73	2993.80	3218.99
6-12	HPB3	115.867	24.4987	78160.42	6473.41	4681.78	4262.86	3587.18
12-18	HPB4	119.238	25.5739	79476.58	6033.06	4497.70	3804.87	3518.82
18-24	HP-5-1	134.972	28.9326	80243.45	6362.36	4489.70	4350.66	3580.06
18-24	HP-5-2	139.341	30.9593	84932.17	6739.34	4859.50	4706.88	3913.28
18-24	HP-5-3	122.023	28.2609	77410.21	5959.36	4442.34	4246.69	3512.29
24-30	HPB6	113.583	29.6931	62319.49	4295.13	2847.47	2584.84	2553.70
30-36	HPB7	246.286	34.6531	92448.98	8261.22	4155.10	5334.69	3650.20

Table 5.3. Total digest of two Peaceful Point site cores collected in May, 2002. Solution analyzed with ICP-AES.

Depth	Sample	Element (mg kg^{-1})						
(cm)		As	Cd	Fe	Mn	Pb	S	Zn
		Peaceful Point Site Core A						
0-3	PPA1-1	451.094	22.8736	68924.67	7539.49	3435.60	1120.60	2909.17
0-3	PPA1-2	449.192	22.5751	69717.09	7459.58	3383.37	1142.61	2904.16
0-3	PPA1-3	445.615	21.9248	66714.12	7027.33	3231.78	1189.35	2887.24
3-6	PPA2	125.516	36.6667	52389.38	3604.72	2272.27	1434.51	2719.17
6-12	PPA3	259.709	29.7155	104205.32	9440.32	2368.58	2985.16	2472.79
12-18	PPA4	178.963	15.5303	80710.96	6605.48	4105.48	4117.13	3065.27
18-24	PPA5	127.527	22.3281	84950.90	8194.69	6490.47	3951.47	4081.46
24-30	PPA6	149.678	21.0819	92222.22	7789.47	4812.87	3801.17	3359.65
		Peaceful Point Site Core B						
0-3	PPB1	150.801	28.6787	72722.72	6281.28	3566.07	1831.83	3381.88
3-6	PPB2	94.893	28.0503	36420.75	3944.06	1618.57	1426.43	2292.26
6-12	PPB3	278.540	44.2224	105299.74	9374.46	2560.38	3261.51	3029.54
12-18	PP-4-1	248.250	34.7145	115147.33	10566.30	2665.75	3122.01	2762.89
12-18	PP-4-2	244.722	33.2534	113387.72	10446.26	2632.44	3000.96	2739.44
12-18	PP-4-3	249.046	35.3053	116078.24	10625.00	2674.62	3112.12	2809.64
18-24	PPB5	151.449	17.5154	81957.86	7506.58	3901.67	4241.00	3291.04
24-30	PPB6	108.445	22.7165	68336.61	7607.28	5699.80	3922.24	4064.96
30-36	PPB7	158.474	24.3806	99554.01	9043.61	5213.08	4328.05	3739.84

Sediment Carbon, Nitrogen, and Sulfur

Table 5.4. Total C, N, and S, organic C (C(org)) after treatment with HCl, and inorganic C (C(inorg)) by difference. Samples are from cores collected at the sites, May 2002 and analyzed by dry combustion.

Depth	Sample	Seq	(%)			Seq	C(org)	C(inorg)
			C(T)	N	S			
cm							%	%
			St. Joe Site, Core A					
3-6	SJ 2A	28	3.4376	0.2755	0.0670	25	3.2066	0.2310
12-18	SJ 4A	29	3.8972	0.2915	0.0650	26	3.6400	0.2572
24-30	SJ 6A1	30	2.1451	0.1627	0.0430	27	1.8667	0.2784
24-30	SJ 6A2	31	2.1683	0.1644	0.0412	28	1.9715	0.1967
			Harlow Point Site, Core A					
0-3	HP 1A	18	3.2069	0.1969	0.3197	16	2.7092	0.4977
3-6	HP 2A	19	2.9466	0.1528	0.3539	17	2.3931	0.5535
6-12	HP 3A	20	2.9515	0.1330	0.4113	18	2.3696	0.5820
12-18	HP 4A1	23	2.9085	0.1414	0.3618	23	2.3981	0.5104
12-18	HP 4A2	24	2.9137	0.1411	0.3619	24	2.4293	0.4844
18-24	HP 5A	25	2.2696	0.1061	0.3257	22	1.8045	0.4652
24-30	HP 6A1	26	3.1612	0.0757	0.6086	26	2.5243	0.6369
24-30	HP 6A2	27	3.1034	0.0746	0.6063	27	2.4941	0.6093
			Peaceful Points Site, Core A					
0-3	PP 1A	10	2.7036	0.2135	0.0792	8	2.3072	0.3964
3-6	PP 2A	11	1.7504	0.1372	0.1201	9	1.4103	0.3401
6-12	PP 3A	14	2.8033	0.0831	0.2792	12	2.0882	0.7151
12-18	PP 4A1	15	1.8614	0.0719	0.3771	13	1.3156	0.5458
12-18	PP 4A2	16	1.8608	0.0698	0.3814	14	1.3398	0.5210
18-24	PP 5A	17	2.1391	0.0719	0.3696	15	1.5313	0.6079
24-30	PP 6A1	12	2.5036	0.0813	0.3376	10	1.8731	0.6305
24-30	PP 6A2	13	2.4962	0.0810	0.3513	11	1.7984	0.6979

Particle Size Analysis, Lake Coeur d'Alene

Table 5.5. Particle Size Analysis by ultrasonic separation, centrifuge and hydrometer method on cores collected from the three sample sites, St. Joe, Harlow Point and Peaceful Point, in May, 2002.

Depth	Sample	Fraction (g)			Total	Precision	Fraction (%)		
		Sand	Silt	Clay			Sand	Silt	Clay
(cm)					(g)	(%)			
				St. Joe Site					
24-28	SJ 24-28	0.5823	5.3266	0.7548	6.6637	98.6	8.74	79.93	11.33
				Harlow Point Site					
6-12	HP 6-12	1.0093	6.2609	0.7623	8.0325	97.1	12.57	77.94	9.49
18-24	HP 18-24	1.9962	6.2459	0.7923	9.0344	97.9	22.10	69.13	8.77
30-36	HP 30-36	1.9341	7.1566	0.5948	9.6855	98.0	19.97	73.89	6.14
				Peaceful Point Site					
0-3	PP 0-3	0.0740	5.0876	1.2273	6.3889	98.4	1.16	79.63	19.21
6-12	PP 6-12	0.3292	4.9670	0.8823	6.1785	97.1	5.33	80.39	14.28
18-24	PP 18-24	0.0180	7.7253	0.8298	8.5731	96.9	0.21	90.11	9.68
30-34	PP 30-34	0.0203	10.0123	1.0873	11.1199	94.7	0.18	90.04	9.78

Sediment Porosity

Table 5.6. Porosity of cores from the St. Joe site collected May, 2002. The particle density was assumed at 2.65 g cm^{-3} to calculate the solids volume. Two cores were done to validate the method and precision.

	(g)			(g cm^{-3})		
Depth	Wet Weight	Dry Weight	Water Weight	Pore Volume	Solids Volume	Porosity
(g)						(%)
0-1.5	25.1919	5.6244	19.5675	19.5675	2.1224	90.21
1.5-3.0	28.3728	8.8308	19.5420	19.5420	3.3324	85.43
3.0-4.5	34.6878	11.8597	22.8281	22.8281	4.4754	83.61
4.5-6.0	33.9530	12.8284	21.1246	21.1246	4.8409	81.36
6.0-7.5	35.1378	14.7269	20.4109	20.4109	5.5573	78.60
7.5-9.0	35.8244	15.9270	19.8974	19.8974	6.0102	76.80
9.0-10.5	35.2818	15.4303	19.8515	19.8515	5.8228	77.32
10.5-12.0	35.6466	13.5055	22.1411	22.1411	5.0964	81.29
12.0-13.5	33.5743	12.5112	21.0631	21.0631	4.7212	81.69
13.5-15.0	32.7718	12.1889	20.5829	20.5829	4.5996	81.73
15.0-16.5	33.6018	13.0157	20.5861	20.5861	4.9116	80.74
16.5-18.0	35.7289	14.3010	21.4279	21.4279	5.3966	79.88
18.0-19.5	36.0865	15.3463	20.7402	20.7402	5.7911	78.17
19.5-21.0	33.3009	14.9351	18.3658	18.3658	5.6359	76.52
21.0-22.5	37.7903	18.2190	19.5713	19.5713	6.8751	74.00

Table 5.7. Porosity of core #11 from the St. Joe site collected May, 2002. The particle density was assumed at 2.65 g cm^{-3} to calculate the solids volume. Two cores were done to validate the method and precision.

Core 11	(g)			($g\ cm^{-3}$)		
Depth	Wet Weight	Dry Weight	Water Weight	Pore Volume	Solids Volume	Porosity
(cm)						(%)
0-1.5	35.5212	7.2616	28.2596	28.2596	2.7402	91.16
1.5-3.0	31.4423	9.6323	21.8100	21.8100	3.6348	85.71
3.0-4.5	33.1324	9.9878	23.1446	23.1446	3.7690	86.00
4.5-6.0	32.5431	11.6446	20.8985	20.8985	4.3942	82.63
6.0-7.5	32.8715	10.7381	22.1334	22.1334	4.0521	84.53
7.5-9.0	34.5231	13.0629	21.4602	21.4602	4.9294	81.32
9.0-10.5	32.9464	13.1937	19.7527	19.7527	4.9788	79.87
10.5-12.0	35.6456	14.7874	20.8582	20.8582	5.5802	78.89
12.0-13.5	33.9946	13.0443	20.9503	20.9503	4.9224	80.97
13.5-15.0	36.5952	13.1063	23.4889	23.4889	4.9458	82.61
15.0-16.5	34.1574	13.7535	20.4039	20.4039	5.1900	79.72
16.5-18.0	34.1930	14.5005	19.6925	19.6925	5.4719	78.26
18.0-19.5	37.9151	17.6093	20.3058	20.3058	6.6450	75.34
19.5-21.0	33.5387	13.2010	20.3377	20.3377	4.9815	80.33
21.0-22.5	36.5699	14.4154	22.1545	22.1545	5.4398	80.29
22.5-24.0	37.4475	19.3035	18.1440	18.1440	7.2843	71.35
24.0-25.5	42.1439	24.6932	17.4507	17.4507	9.3182	65.19
25.5-27.0	35.4605	16.4210	19.0395	19.0395	6.1966	75.45

Table 5.8. Porosity of a core from the Harlow Point site collected in May, 2002. The particle density was assumed at 2.65 g cm^{-3} to calculate the solids volume.

	(g)			(g cm^{-3})		
Depth	Wet Weight	Dry Weight	Water Weight	Pore Volume	Solids Volume	Porosity
(cm)						(%)
0-3.8	93.5666	36.0553	57.5113	57.5113	13.6058	80.87
3.8-7.6	80.3083	33.1772	47.1311	47.1311	12.5197	79.01
7.6-11.4	80.7227	39.8221	40.9006	40.9006	15.0272	73.13
11.4-15.2	99.4816	48.7681	50.7135	50.7135	18.4031	73.37
15.2-19.0	99.2505	47.6643	51.5862	51.5862	17.9865	74.15
19.0-22.9	104.5889	54.6745	49.9144	49.9144	20.6319	70.75
22.9-26.7	103.6859	57.0868	46.5991	46.5991	21.5422	68.39
26.7-28.2	49.2626	26.8732	22.3894	22.3894	10.1408	68.83
28.2-29.7	49.3532	29.1321	20.2211	20.2211	10.9932	64.78
29.7-31.2	44.6335	27.9161	16.7174	16.7174	10.5344	61.34
31.2-32.7	49.1397	30.2937	18.8460	18.8460	11.4316	62.24
32.7-34.2	44.4466	25.5065	18.9401	18.9401	9.6251	66.30

Table 5.9. Porosity of a core from the Peaceful Point site collected in May, 2002. The particle density was assumed at 2.65 g cm^{-3} to calculate the solids volume.

Depth (g)	(g) Wet Weight	Dry Weight	Water Weight	($g\ cm^{-3}$) Pore Volume	Solids Volume	Porosity (%)
0-1.5	31.3506	6.0621	25.2885	25.2885	2.2876	91.70
1.5-3.0	35.3766	8.1351	27.2415	27.2415	3.0698	89.87
3.0-4.5	30.2881	9.8734	20.4147	20.4147	3.7258	84.57
4.5-6.0	35.4649	10.3035	25.1614	25.1614	3.8881	86.62
6.0-7.5	40.1430	11.8017	28.3413	28.3413	4.4535	86.42
7.5-9.0	40.5988	13.1510	27.4478	27.4478	4.9626	84.69
9.0-10.5	41.9013	17.8477	24.0536	24.0536	6.7350	78.13
10.5-12.0	41.1309	17.8803	23.2506	23.2506	6.7473	77.51
12.0-13.5	54.8575	26.6872	28.1703	28.1703	10.0706	73.67
13.5-15.0	44.3934	22.7065	21.6869	21.6869	8.5685	71.68
15.0-16.5	43.0209	21.5442	21.4767	21.4767	8.1299	72.54
16.5-18.0	50.2791	25.6235	24.6556	24.6556	9.6692	71.83
18.0-19.5	49.7374	26.4550	23.2824	23.2824	9.9830	69.99
19.5-21.0	50.7403	26.9833	23.7570	23.7570	10.1824	70.00
21.0-22.5	54.0268	29.3558	24.6710	24.6710	11.0777	69.01
22.5-24.0	45.9017	25.3009	20.6008	20.6008	9.5475	68.33

ICP-AES Data, Lake Coeur d'Alene

Table 5.10. ICP-AES data from the St. Joe site, May 2002. Samples are from dialyzer #2.

Depth	Element (mg L^{-1})													
(cm)	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
-3.0	0.0029	5.118	0.0000	0.0000	0.000	0.6009	1.1510	0.0000	1.1520	0.0000	0.0081	0.0000	0.3097	0.0000
-1.5	0.0066	5.140	0.0000	0.0000	0.000	0.6006	1.1540	0.0000	1.1390	0.0000	0.0104	0.0034	0.3156	0.0000
0.0	0.0061	5.066	0.0000	0.0000	0.000	0.6091	1.1590	0.0000	1.1530	0.0000	0.0113	0.0000	0.3243	0.0000
1.5	0.0040	5.173	0.0000	0.0000	0.075	0.6356	1.1990	0.0041	1.2670	0.0000	0.0116	0.0057	0.3311	0.0000
3.0	0.0016	6.012	0.0000	0.0004	0.025	0.7068	1.3930	0.0123	1.2060	0.0000	0.0093	0.0023	0.3717	0.0000
4.5	0.0000	10.080	0.0000	0.0007	0.843	0.9021	2.3200	0.8353	1.4200	0.0000	0.0288	0.0000	0.3793	0.0006
6.0	0.0003	11.190	0.0008	0.0078	7.019	0.9486	2.4440	1.0020	1.5000	0.0000	0.3159	0.0000	0.4054	0.0295
7.5	0.0031	9.623	0.0012	0.0000	7.057	0.9277	2.2030	0.8317	1.5590	0.0000	0.4084	0.0000	0.3879	0.0010
9.0	0.0000	7.616	0.0005	0.0000	6.384	0.8635	1.7660	0.5457	1.5230	0.0000	0.4981	0.0000	0.3787	0.0004
10.5	0.0000	10.360	0.0014	0.0000	13.210	0.8965	2.1720	0.8819	1.7130	0.0000	0.7725	0.0033	0.3022	0.0003
12.0	0.0033	11.200	0.0018	0.0000	16.340	0.9242	2.2140	0.9502	1.8650	0.0000	0.9399	0.0000	0.2673	0.0011
13.5	0.0000	11.650	0.0019	0.0000	16.710	1.1010	2.5280	1.0280	2.2140	0.0000	0.7155	0.0033	0.2694	0.0011
15.0	0.0010	12.670	0.0024	0.0000	18.110	1.1820	2.8140	1.1610	2.2870	0.0000	0.5932	0.0044	0.2948	0.0016
16.5	0.0002	14.070	0.0025	0.0000	20.830	1.1480	2.8760	1.2000	2.1610	0.0000	0.7042	0.0044	0.3079	0.0024
18.0	0.0000	15.930	0.0029	0.0000	25.140	1.2500	3.2200	1.4300	2.2690	0.0000	0.7317	0.0022	0.3324	0.0025
21.0	0.0000	17.520	0.0034	0.0000	29.850	1.3800	3.4990	1.5470	2.5050	0.0000	0.8537	0.0087	0.3070	0.0026
24.0	0.0030	22.210	0.0047	0.0000	38.680	1.5310	4.1560	1.8820	2.7160	0.0000	1.2340	0.0044	0.3372	0.0025
27.0	0.0000	25.920	0.0061	0.0000	46.090	1.7130	4.8020	2.2070	2.9050	0.0000	1.3700	0.0098	0.3608	0.0023
30.0	0.0000	28.580	0.0068	0.0000	51.190	2.1060	5.8360	2.5550	3.5780	0.0000	1.0700	0.0033	0.3783	0.0028
33.0	0.0000	36.700	0.0073	0.0000	60.800	2.1630	6.8240	3.1670	3.6400	0.0000	1.0150	0.0033	0.4321	0.0039

Table 5.11. ICP-AES data from the St. Joe site, May 2002. Samples are from dialyzer #5.

Depth	Element (mg L^{-1})													
(cm)	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
-1.5	0.0000	4.871	0.0000	0.0019	0.048	0.6258	1.1760	0.0029	1.6120	0.0836	0.0135	0.0099	0.3289	0.0040
0.0	0.0000	4.962	0.0000	0.0004	0.028	0.5978	1.1540	0.0014	1.4150	0.0083	0.0051	0.0119	0.3281	0.0000
1.5	0.0000	5.201	0.0002	0.0003	0.039	0.7250	1.3390	0.0025	1.6130	0.0000	0.0044	0.0090	0.3590	0.0000
3.0	0.0000	7.630	0.0003	0.0007	3.707	0.8579	1.9330	0.5910	1.8200	0.0000	0.1412	0.0139	0.3878	0.0008
4.5	0.0000	7.355	0.0009	0.0000	7.662	0.8808	1.6340	0.5358	1.7830	0.0000	0.6798	0.0080	0.2735	0.0001
6.0	0.0000	6.961	0.0006	0.0000	6.726	0.7523	1.4920	0.4866	1.9740	0.0000	0.6120	0.0080	0.2994	0.0006
7.5	0.0000	7.874	0.0012	0.0000	9.285	0.8440	1.7930	0.6780	2.0600	0.0000	0.7977	0.0000	0.2494	0.0001
9.0	0.0020	10.790	0.0012	0.0000	12.170	0.7916	2.1800	0.9976	1.7100	0.0000	0.7616	0.0149	0.2438	0.0010
10.5	0.0000	12.080	0.0014	0.0000	14.420	0.9166	2.5150	1.1730	1.9470	0.0000	0.6065	0.0199	0.2540	0.0018
12.0	0.0000	12.120	0.0022	0.0000	18.130	0.9406	2.4320	1.1080	1.9180	0.0000	1.0810	0.0129	0.2295	0.0033
13.5	0.0021	12.740	0.0024	0.0000	20.720	0.9678	2.4750	1.1250	1.8580	0.0000	1.3910	0.0110	0.2091	0.0006
15.0	0.0000	13.450	0.0029	0.0000	22.590	1.0220	2.5620	1.1580	1.9610	0.0000	1.3870	0.0100	0.2184	0.0006
16.5	0.0000	13.800	0.0033	0.0000	24.040	1.2590	2.9360	1.2430	2.3030	0.0000	1.2080	0.0139	0.2304	0.0004
18.0	0.0045	16.010	0.0019	0.0000	27.560	1.2340	3.0620	1.3600	2.0570	0.0000	1.0750	0.0012	0.2689	0.0000
19.5	0.0037	17.450	0.0020	0.0000	29.760	1.3330	3.2830	1.4450	2.2300	0.0000	1.0360	0.0091	0.2748	0.0000
22.5	0.0077	19.970	0.0029	0.0000	35.010	1.4670	3.7940	1.6630	2.4510	0.0000	0.9986	0.0137	0.3216	0.0000
25.5	0.0040	23.730	0.0036	0.0000	41.260	1.6040	4.3520	1.9340	2.7110	0.0000	1.0340	0.0023	0.3293	0.0000
28.5	0.0000	26.910	0.0038	0.0000	46.520	1.7600	4.9620	2.2160	3.0410	0.0000	0.9867	0.0057	0.3716	0.0000
31.5	0.0029	30.710	0.0051	0.0000	53.280	1.9710	5.6710	2.5760	3.4830	0.0000	0.9371	0.0046	0.4183	0.0015
34.5	0.0029	36.180	0.0065	0.0000	62.200	2.2530	6.8140	3.1470	3.9450	0.0000	0.8922	0.0023	0.4524	0.0021

Table 5.12. ICP-AES data from the Harlow Point site, May 2002. Samples are from dialyzer #9.

Depth	Element (mg L^{-1})													
(cm)	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
-1.5	0.0000	4.721	0.0046	0.0016	0.047	0.6172	1.5140	0.0150	1.2860	0.0000	0.0000	0.0076	2.2190	0.4668
0.0	0.0000	5.725	0.0099	0.0022	0.017	0.7375	1.6950	0.0534	1.3320	0.0000	0.0000	0.0370	3.0550	0.9545
1.5	0.0000	5.916	0.0082	0.0013	0.003	0.7275	1.8580	0.0769	1.3830	0.0000	0.0000	0.0380	2.6760	0.8903
3.0	0.0000	6.782	0.0085	0.0016	0.008	0.6780	1.9290	0.2517	1.2430	0.0000	0.0000	0.0305	2.2090	0.8220
4.5	0.0000	7.990	0.0073	0.0014	0.119	0.6931	2.2310	0.9303	1.2360	0.0000	0.0000	0.0337	1.8550	0.7842
6.0	0.0195	10.850	0.0036	0.0004	5.018	0.7368	2.9630	4.6710	1.2760	0.0000	0.0204	0.1098	1.8290	0.4760
7.5	0.0169	11.010	0.0015	0.0000	4.442	0.8109	3.2260	5.8080	1.4190	0.0000	0.0155	0.0283	1.2920	0.5063
9.0	0.1018	8.935	0.0015	0.0000	12.530	0.8501	2.7560	3.4270	1.6860	0.0000	0.1092	0.0196	0.8798	0.2334
10.5	0.1386	8.401	0.0014	0.0000	13.850	0.7240	2.4090	2.9280	1.4950	0.0000	0.1968	0.0066	0.8151	0.1471
12.0	0.2210	8.824	0.0025	0.0000	17.780	0.7041	2.4970	3.1930	1.6450	0.0000	0.3000	0.0218	0.3184	0.1272
13.5	0.2344	8.066	0.0019	0.0000	16.250	0.7172	2.3040	2.7910	1.6310	0.0000	0.3179	0.0283	0.7342	0.1627
15.0	0.3134	9.225	0.0023	0.0000	22.180	0.7721	2.5350	3.4710	1.8770	0.0000	0.3844	0.0294	0.2458	0.1681
16.5	0.3591	9.961	0.0032	0.0000	25.230	0.8467	2.6380	3.8020	2.0170	0.0000	0.4006	0.0500	0.1995	0.1748
18.0	0.3949	10.520	0.0032	0.0000	27.980	0.9068	2.7490	4.0940	2.1320	0.0000	0.4243	0.0544	0.2301	0.1894
19.5	0.4448	11.200	0.0038	0.0000	30.630	0.9962	2.8660	4.3720	2.2680	0.0000	0.4457	0.0794	0.2367	0.2218
22.5	0.5939	12.420	0.0047	0.0000	35.560	1.2450	3.3070	4.9580	2.7930	0.0000	0.4365	0.0381	0.2625	0.2500
25.5	0.5978	14.140	0.0053	0.0000	38.830	1.2560	3.3640	5.2540	1.7990	0.0000	0.3562	0.0186	0.3153	0.2851
28.5	0.6475	15.960	0.0062	0.0000	42.890	1.4050	3.7260	5.6690	1.9410	0.0000	0.3249	0.0186	0.3126	0.3418
31.5	0.7743	17.570	0.0060	0.0000	47.740	1.4780	4.0510	6.0740	2.1550	0.0000	0.3155	0.0175	0.3508	0.3898
34.5	0.8902	20.170	0.0070	0.0000	53.460	1.6430	4.5980	6.8820	2.3460	0.0000	0.2768	0.0262	0.3752	0.4580

Table 5.13. ICP-AES data from the Harlow Point site, May 2002. Samples are from dialyzer #12.

Depth	Element (mg L^{-1})													
(cm)	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
-1.5	0.0029	4.339	0.0014	0.0018	0.045	0.4603	1.4720	0.0221	0.8744	0.0000	0.0000	0.0197	1.5360	0.1505
0.0	0.0000	4.368	0.0015	0.0018	0.016	0.4553	1.4680	0.0193	0.8216	0.0000	0.0000	0.0142	1.5940	0.1884
1.5	0.0000	4.345	0.0025	0.0025	0.014	0.5112	1.5280	0.0236	0.9022	0.0000	0.0000	0.0153	1.7090	0.2678
3.0	0.0056	5.305	0.0034	0.0016	0.019	0.4934	1.6120	0.1281	0.7737	0.0000	0.0000	0.0186	1.8380	0.4269
4.5	0.0024	7.449	0.0058	0.0015	0.070	0.5997	2.1320	1.0030	0.8105	0.0000	0.0000	0.0109	1.4920	0.5720
6.0	0.0254	11.620	0.0023	0.0015	4.720	0.9241	3.6300	6.8720	1.0960	0.0000	0.0274	0.1563	1.4590	0.5086
7.5	0.1461	10.420	0.0024	0.0001	17.290	0.9247	3.2220	3.4370	1.1110	0.0000	0.1199	0.0339	0.3847	0.3224
9.0	0.2881	10.800	0.0031	0.0000	24.140	0.8321	3.0660	4.0970	1.1220	0.0000	0.2734	0.0339	0.2423	0.1778
10.5	0.2520	10.540	0.0027	0.0000	23.080	0.8055	2.9760	4.3740	1.2220	0.0000	0.2870	0.0503	0.2323	0.1697
12.0	0.3352	10.340	0.0032	0.0002	24.260	0.8211	2.9660	4.2180	1.3070	0.0000	0.4004	0.0710	0.2180	0.1553
13.5	0.5906	10.730	0.0051	0.0007	38.880	0.7892	2.8290	5.9060	1.2900	0.0000	0.7747	0.0940	0.3517	0.2880
15.0	0.3600	10.510	0.0034	0.0011	26.410	0.9018	2.9780	4.0490	1.4550	0.0000	0.4496	0.0459	0.2358	0.2086
16.5	0.3755	11.040	0.0036	0.0000	28.040	0.8782	2.8870	4.1690	1.3580	0.0000	0.4168	0.0940	0.2353	0.1968
18.0	0.4027	11.100	0.0042	0.0002	29.310	1.0470	3.1070	4.3660	1.6430	0.0000	0.3429	0.1202	0.2397	0.1859
19.5	0.4166	12.120	0.0037	0.0000	31.310	0.9800	3.0150	4.5220	1.4540	0.0000	0.3280	0.1071	0.2597	0.2021
22.5	0.5861	13.270	0.0047	0.0000	36.210	1.1830	3.3140	4.9480	1.7180	0.0000	0.3645	0.0568	0.2922	0.2279
25.5	0.6293	14.270	0.0051	0.0000	39.080	1.2590	3.4690	5.1490	1.7970	0.0000	0.3308	0.0229	0.3105	0.2554
28.5	0.6074	15.400	0.0056	0.0002	40.860	1.3370	3.6030	5.4040	1.8740	0.0000	0.2743	0.0197	0.3339	0.3189
31.5	0.5053	17.970	0.0057	0.0000	44.440	1.4160	4.0370	6.7650	2.0250	0.0000	0.1957	0.0219	0.3439	0.4399
34.5	0.3185	21.300	0.0062	0.0000	48.170	1.5940	4.7620	8.3620	2.2220	0.0000	0.0961	0.0317	0.3730	0.5410

Table 5.14. ICP-AES data from the Peaceful Point site, May 2002. Samples are from dialyzer #13.

Depth	Element (mg L^{-1})													
(cm)	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
0.0	0.0011	4.602	0.0007	0.0037	0.108	0.7554	1.4520	0.021	0.9979	0.0000	0.0011	0.0022	1.3480	0.0685
1.5	0.0010	4.802	0.0001	0.0030	0.011	0.7830	1.4790	0.008	0.9862	0.0000	0.0025	0.0000	1.4690	0.0631
3.0	0.0067	9.275	0.0031	0.0016	0.026	0.8834	2.6560	4.510	1.0940	0.0000	<.0000	0.0011	2.6820	0.5023
4.5	0.0139	10.290	0.0008	0.0021	0.309	0.9324	2.9030	12.040	1.2160	0.0000	0.0147	0.0077	1.4490	0.1892
6.0	0.0529	9.251	0.0004	0.0023	0.841	0.8450	2.4960	15.800	1.2250	0.0000	0.0450	0.0142	0.7235	0.0968
7.5	0.1576	8.258	0.0006	0.0019	2.928	0.9091	2.3380	17.660	1.3950	0.0000	0.1640	0.0131	0.3144	0.0807
9.0	0.1417	8.810	0.0008	0.0009	2.360	0.8355	2.2600	19.150	1.3350	0.0000	0.0913	0.0197	0.1654	0.1011
10.5	0.0817	9.108	0.0002	0.0016	1.196	0.8656	2.3170	10.640	1.4000	0.0000	0.0430	0.0098	0.1446	0.1143
12.0	0.6743	9.375	0.0012	0.0003	10.580	0.9203	2.3260	15.460	2.3670	0.0000	0.4384	0.0111	0.2119	0.0671
13.5	0.9717	9.936	0.0018	0.0000	14.540	0.9585	2.4360	14.830	2.5230	0.0000	0.6243	0.0040	0.2226	0.1077
15.0	1.0470	10.130	0.0021	0.0000	16.200	0.9885	2.4700	14.740	2.5880	0.0000	0.6505	0.0070	0.2275	0.1474
16.5	1.0270	10.290	0.0020	0.0003	17.150	0.9728	2.5010	14.890	2.6670	0.0000	0.5734	0.0111	0.2291	0.1820
18.0	1.0560	10.500	0.0022	0.0000	18.610	1.0940	2.6520	14.600	2.9780	0.0000	0.5278	0.0131	0.2221	0.1866
19.5	0.9626	10.990	0.0021	0.0000	19.900	1.0640	2.6510	14.430	2.9240	0.0000	0.4078	0.0100	0.2374	0.1787
21.0	0.9534	11.290	0.0028	0.0000	21.870	1.0720	2.6930	14.230	3.0210	0.0000	0.4142	0.0080	0.2522	0.1771
24.0	0.9323	11.420	0.0036	0.0000	25.100	1.2380	2.9630	14.060	3.6320	0.0000	0.3116	0.0231	0.2690	0.2318
27.0	0.8301	11.910	0.0032	0.0000	27.790	1.1760	2.8940	13.510	3.4630	0.0000	0.2165	0.0181	0.3052	0.2962
30.0	0.6939	12.830	0.0035	0.0000	30.670	1.2350	3.0800	13.420	3.7440	0.0000	0.1850	0.0241	0.3274	0.3717
33.0	0.6059	13.850	0.0041	0.0000	34.030	1.2630	3.2420	13.650	3.9040	0.0000	0.1544	0.0231	0.3155	0.4239
36.0	0.9926	15.690	0.0046	0.0000	36.730	1.4230	3.7360	19.130	4.5180	0.0000	0.3743	0.0181	0.3200	0.3221

Table 5.15. ICP-AES data from the Peaceful Point site, May 2002. Samples are from dialyzer #17.

Depth	Element (mg L^{-1})													
(cm)	As	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Zn
-6.0	0.0000	4.682	0.0003	0.0008	0.035	0.5016	1.3570	0.019	1.2560	0.0000	0.0000	0.0060	1.2250	0.0722
-4.5	0.0000	4.617	0.0002	0.0006	0.018	0.4858	1.3450	0.009	1.2490	0.0000	0.0000	0.0090	1.2100	0.0771
-3.0	0.0000	4.637	0.0000	0.0000	0.012	0.5094	1.3840	0.005	1.3090	0.0000	0.0000	0.0080	1.2200	0.0685
-1.5	0.0000	4.544	0.0001	0.0011	0.022	0.5149	1.3750	0.010	1.2920	0.0000	0.0022	0.0060	1.2120	0.0685
0.0	0.0000	4.657	0.0000	0.0004	0.037	0.5006	1.3680	0.009	1.2560	0.0000	0.0067	0.0010	1.2110	0.0640
1.5	0.0060	4.829	0.0000	0.0011	0.027	0.5175	1.4140	0.016	1.2810	0.0000	0.0124	0.0050	1.4360	0.0626
3.0	0.0569	7.319	0.0005	0.0007	1.336	0.7142	1.9390	12.580	1.6770	0.0000	0.1074	0.0271	1.9620	0.1289
4.5	0.3666	7.300	0.0006	0.0000	5.621	0.7069	1.8600	13.870	1.7740	0.0000	0.4556	0.0201	0.7125	0.0857
6.0	0.8198	8.351	0.0005	0.0000	9.456	0.7970	2.0820	14.340	2.0620	0.0000	0.7463	0.0121	0.2600	0.1256
7.5	0.6868	8.703	0.0010	0.0000	8.511	0.8289	2.1890	15.660	2.1630	0.0000	0.4452	0.0221	0.1678	0.1378
9.0	0.3684	9.155	0.0010	0.0000	5.682	0.8959	2.3200	18.770	2.3050	0.0000	0.1772	0.0171	0.1551	0.1360
10.5	0.2738	9.487	0.0005	0.0001	5.074	0.9322	2.4090	20.650	2.4280	0.0000	0.1215	0.0171	0.1580	0.1425
12.0	0.4231	10.080	0.0007	0.0000	8.206	0.9426	2.4810	20.270	2.4950	0.0000	0.1935	0.0091	0.1757	0.1642
13.5	0.6744	10.510	0.0018	0.0000	12.810	1.0010	2.5680	18.830	2.5900	0.0000	0.3512	0.0221	0.2250	0.1828
15.0	0.8059	10.580	0.0019	0.0002	13.530	1.1440	2.8230	19.560	3.0130	0.0000	0.3366	0.0161	0.2077	0.1662
18.0	0.5473	11.510	0.0016	0.0000	14.030	1.0960	2.8140	21.100	2.9190	0.0000	0.2801	0.0091	0.2102	0.1915
21.0	0.6878	12.090	0.0025	0.0000	19.850	1.1390	2.9230	19.340	3.2000	0.0000	0.2548	0.0091	0.2299	0.1799
24.0	1.1610	13.070	0.0031	0.0000	27.200	1.2120	3.1470	9.280	3.5150	0.0000	0.5264	0.0261	0.2678	0.1837
27.0	1.1030	13.720	0.0038	0.0001	29.360	1.2670	3.2770	18.590	3.6970	0.0000	0.4021	0.0402	0.2974	0.2297
30.0	1.1760	14.760	0.0051	0.0000	33.760	1.4810	3.7660	20.340	4.5460	0.0000	0.5290	0.0241	0.3093	0.2902

IC Data, Lake Coeur d'Alene

Table 5.16. IC data from the St. Joe site, May 2002. Samples are from dialyzer #2. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})													
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-		$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
-3.0	0.0000	0.3720	1.0044	0.0000	0.0000		0.3353	0.0000	0.0000	0.3097	-0.0256	0.0081	0.0081
-1.5		0.3878	1.0771		0.5731		0.3595	0.0000	0.1295	0.3156	-0.0439	0.0104	0.0104
0.0		0.3808	1.2519		0.0000	0.3243	**0.3200**	0.0000	0.0000	0.3243	0.0043	0.0113	0.0113
1.5		0.3819	0.8006		0.0000		0.2672	0.0000	0.0000	0.3311	0.0639	0.0116	0.0116
3.0		0.4840	0.9801		0.0000		0.3272	0.0000	0.0000	0.3717	0.0445	0.0093	0.0093
4.5		0.4037	0.9572		0.0000		0.3195	0.0000	0.0000	0.3793	0.0598	0.0288	0.0288
6.0		0.4192	1.0039		0.0000		0.3351	0.0000	0.0000	0.4054	0.0703	0.3159	0.3159
7.5		0.4999	0.6473		0.0000		0.2161	0.0000	0.0000	0.3879	0.1718	0.4084	0.4084
9.0		0.5137	0.0000		0.0000		0.0000	0.0000	0.0000	0.3787	0.3787	0.4981	0.4981
10.5		0.5098	0.0000		0.0000		0.0000	0.0000	0.0000	0.3022	0.3022	0.7725	0.7725
12.0		0.5625	0.0000		0.0000		0.0000	0.0000	0.0000	0.2673	0.2673	0.9399	0.9399
13.5		0.6304	0.0000		0.0000		0.0000	0.0000	0.0000	0.2694	0.2694	0.7155	0.7155
15.0		0.6071	0.0000		0.0000		0.0000	0.0000	0.0000	0.2948	0.2948	0.5932	0.5932
16.5		0.6819	0.0000		0.0000		0.0000	0.0000	0.0000	0.3079	0.3079	0.7042	0.7042
18.0		0.6401	0.0000		0.0000		0.0000	0.0000	0.0000	0.3324	0.3324	0.7317	0.7317
21.0		0.6448	0.0000		0.0000		0.0000	0.0000	0.0000	0.3070	0.3070	0.8537	0.8537
24.0		0.6315	0.0000		0.0000		0.0000	0.0000	0.0000	0.3372	0.3372	1.2340	1.2340
27.0		0.6522	0.0000		0.0000		0.0000	0.0000	0.0000	0.3608	0.3608	1.3700	1.3700
30.0		0.6256	0.0000		0.0000		0.0000	0.0000	0.0000	0.3783	0.3783	1.0700	1.0700
33.0		0.6565	0.0000		0.0000		0.0000	0.0000	0.0000	0.4321	0.4321	1.0150	1.0150

Table 5.17. IC data from the St. Joe site, May 2002. Samples are from dialyzer #5. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})												
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-		$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
-1.5	0.0000	0.4726	1.0192	0.0000	0.0000	0.0000	0.3402	0.0000	0.0000	0.3289	-0.0113	0.0135	0.0135
0.0		0.4961	0.9777		0.0000		0.3263	0.0000	0.0000	0.3281	0.0018	0.0051	0.0051
1.5		0.4866	0.9790		0.0000		0.3268	0.0000	0.0000	0.3590	0.0322	0.0044	0.0044
3.0		0.4725	1.1263		0.7085		0.3760	0.0000	0.1601	0.3878	0.0118	0.1412	0.1412
4.5		0.4584	1.1022		0.0000		0.3679	0.0000	0.0000	0.2735	-0.0944	0.6798	0.6798
6.0		0.4720	0.8126		0.0000		0.2712	0.0000	0.0000	0.2994	0.0282	0.6120	0.6120
7.5		0.4693	0.9820		0.0000		0.3278	0.0000	0.0000	0.2494	-0.0784	0.7977	0.7977
9.0		0.4685	1.0726		0.0000		0.3580	0.0000	0.0000	0.2438	-0.1142	0.7616	0.7616
10.5		0.5040	0.9759		0.0000		0.3258	0.0000	0.0000	0.2540	-0.0718	0.6065	0.6065
12.0		0.4878	0.8950		0.0000		0.2988	0.0000	0.0000	0.2295	-0.0693	1.0810	1.0810
13.5		0.5327	0.5167		0.0000		0.1725	0.0000	0.0000	0.2091	0.0366	1.3910	1.3910
15.0		0.5692	0.4760		0.0000		0.1589	0.0000	0.0000	0.2184	0.0595	1.3870	1.3870
16.5		0.6338	0.0000		0.0000		0.0000	0.0000	0.0000	0.2304	0.2304	1.2080	1.2080
18.0		0.6619	0.0000		0.0000		0.0000	0.0000	0.0000	0.2689	0.2689	1.0750	1.0750
19.5		0.7319	0.0000		0.0000		0.0000	0.0000	0.0000	0.2748	0.2748	1.0360	1.0360
22.5		0.7503	0.0000		0.0000		0.0000	0.0000	0.0000	0.3216	0.3216	0.9986	0.9986
25.5		0.7595	0.0000		0.0000		0.0000	0.0000	0.0000	0.3293	0.3293	1.0340	1.0340
28.5		0.7676	0.0000		0.0000		0.0000	0.0000	0.0000	0.3716	0.3716	0.9867	0.9867
31.5		0.9374	0.0000		0.0000		0.0000	0.0000	0.0000	0.4183	0.4183	0.9371	0.9371
34.5										0.4524		0.8922	

Table 5.18. IC data from the Harlow Point, May 2002. Samples are from dialyzer #8. The data were converted to elemental concentrations in the right hand columns. No corresponding ICP data was available for S and P comparison.

Depth	Element (mg L^{-1})												
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-		$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
0.0	0.0000	0.5550	10.7827	0.0000	0.6181	0.0000	3.5992	0.0000	0.1396	0.0000	0.0000	0.0000	0.0000
1.5		0.5600	8.2016		1.0053		2.7376	0.0000	0.2271				
3.0		0.5567	6.6516		0.6864		2.2202	0.0000	0.1551				
4.5		0.5646	5.7684		0.0000		1.9254	0.0000	0.0000				
6.0		0.5814	3.5609		0.0000		1.1886	0.0000	0.0000				
7.5		0.6358	2.0019		0.0000		0.6682	0.0000	0.0000				
9.0		0.6516	0.7870		0.0000		0.2627	0.0000	0.0000				
10.5		0.6704	0.0000		0.0000		0.0000	0.0000	0.0000				
12.0		0.6703	0.0000		0.0000		0.0000	0.0000	0.0000				
13.5		0.6858	0.0000		0.0000		0.0000	0.0000	0.0000				
15.0		0.7288	0.0000		0.0000		0.0000	0.0000	0.0000				
16.5		0.8627	0.0000		0.0000		0.0000	0.0000	0.0000				
18.0		0.7734	0.0000		0.0000		0.0000	0.0000	0.0000				
19.5		0.7817	0.0000		0.0000		0.0000	0.0000	0.0000				
21.0		1.0274	0.0000		0.0000		0.0000	0.0000	0.0000				
24.0		0.9580	0.0000		0.0000		0.0000	0.0000	0.0000				
27.0		0.9296	0.0000		0.0000		0.0000	0.0000	0.0000				
30.0		0.8281	0.0000		0.0000		0.0000	0.0000	0.0000				
33.0		0.9025	0.0000		0.0000		0.0000	0.0000	0.0000				
36.0		0.9325	0.0000		0.0000		0.0000	0.0000	0.0000				

Table 5.19. IC data from the Harlow Point site, May 2002. Samples are from dialyzer #12. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals. Bold numbers indicate ICP totals.

Depth	Element (mg L^{-1})												
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-		$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
-1.5	0.0000	0.6801	4.4652	0.0000	0.0008		1.4905	0.0000	0.0002	1.5360	0.0455	0.0000	0.0000
0.0		0.5778	4.5239		0.0008		1.5100	0.0000	0.0002	1.5940	0.0840	0.0000	0.0000
1.5		0.5696	5.0036		0.2348		1.6701	0.0000	0.0530	1.7090	0.0389	0.0000	0.0000
3.0		0.5648	4.9155		0.4908		1.6408	0.0000	0.1109	1.8380	0.1972	0.0000	0.0000
4.5		0.5629	4.4634		0.0008		1.4899	0.0000	0.0002	1.4920	0.0021	0.0000	0.0000
6.0		0.5956	3.7551		0.0008		1.2534	0.0000	0.0002	1.4590	0.2056	0.0274	0.0274
7.5		0.6360	3.2816		0.0008	1.0954	**0.3800**	0.0000	0.0002	0.3847	0.0047	0.1199	0.1199
9.0		0.6002	2.4942		0.0008	0.8325	**0.2400**	0.0000	0.0002	0.2423	0.0023	0.2734	0.2734
10.5		0.5884	2.3132		0.0008	0.7721	**0.2300**	0.0000	0.0002	0.2323	0.0023	0.2870	0.2870
12.0		0.6617	0.4412		0.0008		0.1473	0.0000	0.0002	0.2180	0.0707	0.4004	0.4004
13.5		2.5540	0.6435		0.4277		0.2148	0.0000	0.0966	0.3517	0.1369	0.7747	0.7747
15.0		0.7235	0.0046		0.2947		0.0016	0.0000	0.0666	0.2358	0.2342	0.4496	0.4496
16.5		0.7605	0.0046		0.0008		0.0016	0.0000	0.0002	0.2353	0.2337	0.4168	0.4168
18.0		0.7995	0.0046		0.0008		0.0016	0.0000	0.0002	0.2397	0.2381	0.3429	0.3429
19.5		0.8206	0.0046		0.0008		0.0016	0.0000	0.0002	0.2597	0.2581	0.3280	0.3280
22.5		0.8522	0.0046		0.0008		0.0016	0.0000	0.0002	0.2922	0.2906	0.3645	0.3645
25.5		0.8253	0.0046		0.0008		0.0016	0.0000	0.0002	0.3105	0.3089	0.3308	0.3308
28.5		0.8601	0.0046		0.0008		0.0016	0.0000	0.0002	0.3339	0.3323	0.2743	0.2743
31.5		0.9774	0.0046		0.0008		0.0016	0.0000	0.0002	0.3439	0.3423	0.1957	0.1957
34.5		0.8084	0.0046		0.0008		0.0016	0.0000	0.0002	0.3730	0.3714		0.0961

Table 5.20. IC data from the Peaceful Point site, May 2002. Samples are from dialyzer #13. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals. Bold numbers indicate ICP totals.

Depth	Element (mg L^{-1})												
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-		$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
0.0	0.0000	0.7353	5.4947	0.0000	0.7986	1.8341	**1.3500**	0.0000	0.1804	1.3480	-0.0020	0.0011	0.0011
1.5		0.7781	9.0218		0.0000	3.0114	**1.4570**	0.0000	0.0000	1.4690	-0.0010	0.0025	0.0025
3.0		0.9323	5.6243		0.0000		1.8774	0.0000	0.0000	2.6820	0.8046	0.0000	0.0000
4.5		0.9338	3.5187		0.0000		1.1745	0.0000	0.0000	1.4490	0.2745	0.0147	0.0147
6.0		0.8472	0.8845		0.0000		0.2952	0.0000	0.0000	0.7235	0.4283	0.0450	0.0450
7.5		0.8621	0.0000		0.0000		0.0000	0.0000	0.0000	0.3144	0.3144	0.1640	0.1640
9.0		0.8442	0.0000		0.0000		0.0000	0.0000	0.0000	0.1654	0.1654	0.0913	0.0913
10.5		1.2094	0.0000		0.0000		0.0000	0.0000	0.0000	0.1446	0.1446	0.0430	0.0430
12.0		0.8748	0.0000		0.0000		0.0000	0.0000	0.0000	0.2119	0.2119	0.4384	0.4384
13.5		0.8263	0.0000		0.0000		0.0000	0.0000	0.0000	0.2226	0.2226	0.6243	0.6243
15.0		0.8088	0.0000		0.0000		0.0000	0.0000	0.0000	0.2275	0.2275	0.6505	0.6505
16.5		0.9175	0.0000		0.0000		0.0000	0.0000	0.0000	0.2291	0.2291	0.5734	0.5734
18.0		0.8862	0.0000		0.0000		0.0000	0.0000	0.0000	0.2221	0.2221	0.5278	0.5278
19.5		0.7709	0.0000		0.0000		0.0000	0.0000	0.0000	0.2374	0.2374	0.4078	0.4078
21.0		0.9234	0.0000		0.0000		0.0000	0.0000	0.0000	0.2522	0.2522	0.4142	0.4142
24.0		0.7944	0.0000		0.0000		0.0000	0.0000	0.0000	0.2690	0.2690	0.3116	0.3116
27.0		1.5514	0.0000		0.0000		0.0000	0.0000	0.0000	0.3052	0.3052	0.2165	0.2165
30.0		0.7382	0.0000		0.0000		0.0000	0.0000	0.0000	0.3274	0.3274	0.1850	0.1850
33.0		0.7275	0.0000		0.0000		0.0000	0.0000	0.0000	0.3155	0.3155	0.1544	0.1544
36.0		1.2433	0.0000		0.0000		0.0000	0.0000	0.0000	0.3200	0.3200	0.3743	0.3743

Table 5.21. IC data from the Peaceful Point site, May 2002. Samples are from dialyzer #17. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals. Bold numbers indicate ICP totals.

Depth	Element (mg L^{-1})												
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-		$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
-6.0	0.0000	0.6736	3.5478	0.0000	0.1646		1.1842	0.0000	0.0372	1.2250	0.0408	0.0000	0.0000
-4.5		0.7848	3.5058		0.3086		1.1702	0.0000	0.0697	1.2100	0.0398	0.0000	0.0000
-3.0		0.6605	3.5840		0.1646		1.1963	0.0000	0.0372	1.2200	0.0237	0.0000	0.0000
-1.5		0.6538	3.5445		0.3126		1.1831	0.0000	0.0706	1.2120	0.0289	0.0022	0.0022
0.0		0.6663	3.6192		0.3176		1.2081	0.0000	0.0718	1.2110	0.0029	0.0067	0.0067
1.5		0.6560	3.6145		0.3187		1.2065	0.0000	0.0720	1.4360	0.2295	0.0124	0.0124
3.0		1.1021	5.0101		0.6247		1.6723	0.0000	0.1411	1.9620	0.2897	0.1074	0.1074
4.5		0.7472	4.8762		0.0000	1.6276	**0.7100**	0.0000	0.0000	0.7125	0.0025	0.4556	0.4556
6.0		0.7649	1.3285		0.0000	0.4434	**0.2600**	0.0000	0.0000	0.2600	0.0000	0.7463	0.7463
7.5		0.7810	0.0000		0.0000		0.0000	0.0000	0.0000	0.1678	0.1678	0.4452	0.4452
9.0		0.8300	0.0000		0.0000		0.0000	0.0000	0.0000	0.1551	0.1551	0.1772	0.1772
10.5		0.7995	0.0000		0.0000		0.0000	0.0000	0.0000	0.1580	0.1580	0.1215	0.1215
12.0		0.8035	0.0000		0.0000		0.0000	0.0000	0.0000	0.1757	0.1757	0.1935	0.1935
13.5		0.8062	0.0000		0.0000		0.0000	0.0000	0.0000	0.2250	0.2250	0.3512	0.3512
15.0		0.8015	0.0000		0.0000		0.0000	0.0000	0.0000	0.2077	0.2077	0.3366	0.3366
18.0		0.8519	0.0000		0.0000		0.0000	0.0000	0.0000	0.2102	0.2102	0.2801	0.2801
21.0		0.7928	0.0000		0.0000		0.0000	0.0000	0.0000	0.2299	0.2299	0.2548	0.2548
24.0		0.7856	0.0000		0.0000		0.0000	0.0000	0.0000	0.2678	0.2678	0.5264	0.5264
27.0		0.7425	0.0000		0.0000		0.0000	0.0000	0.0000	0.2974	0.2974	0.4021	0.4021
30.0		0.7373	0.0000		0.0000		0.0000	0.0000	0.0000	0.3093	0.3093	0.5290	0.5290

IC Data, Schlepp Pond

Table 5.22. IC data from the Schlepp Pond, March 2004. Samples are from dialyzer #5. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						March 2004, #5						
-1.5	0.0600	3.5800	1.6371	1.3400	0.0600	0.5464	0.4324	0.0136	0.9226	0.3762	0.9517	0.5193
0.0	0.0600	3.8900	1.7970	1.1300	0.0800	0.5998	0.3647	0.0181	0.9209	0.3211	1.0190	0.6543
1.5	0.0600	3.9800	1.7817	1.7000	0.0500	0.5947	0.5486	0.0113	0.9606	0.3659	1.1260	0.5774
3.0	0.0600	3.8600	1.9721	1.3300	0.0700	0.6583	0.4292	0.0158	1.0280	0.3697	1.0810	0.6518
4.5	0.0600	3.5200	2.0025	1.3500	0.0400	0.6684	0.4357	0.0090	1.0300	0.3616	1.0230	0.5873
6.0	0.0700	3.1700	2.3376	1.2300	0.0400	0.7803	0.3969	0.0090	1.0980	0.3177	0.9764	0.5795
7.5	0.0700	2.8300	2.2234	0.9700	0.0200	0.7421	0.3130	0.0045	1.1050	0.3629	0.9607	0.6477
9.0	0.0700	2.7000	2.2843	0.6100	0.0400	0.7625	0.1969	0.0090	1.1080	0.3455	0.9911	0.7942
12.0	0.0800	2.5000	2.1701	1.5000	0.0200	0.7243	0.4841	0.0045	1.0450	0.3207	1.0820	0.5979
19.5	0.0700	2.6000	2.3223	1.4400	0.0300	0.7752	0.4647	0.0068	1.0840	0.3088	1.0390	0.5743
27.0	0.0800	2.8400	2.5964	0.6800	0.1100	0.8667	0.2194	0.0248	1.2140	0.3473	0.8921	0.6727
34.5	0.0700	3.0600	2.2538	0.8000	0.0600	0.7523	0.2582	0.0136	1.0860	0.3337	1.0350	0.7768

Table 5.23. IC data from the Schlepp Pond, March 2004. Samples are from dialyzer #6 and #7. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						March 2004, #6						
-1.5	0.0300	4.4100	3.2665	0.1100	0.0300	1.0903	0.0355	0.0068	1.4530	0.3627	0.9098	0.8743
0.0	0.0600	4.2700	3.5102	0.2600	0.1500	1.1717	0.0839	0.0339	1.5230	0.3513	0.8124	0.7285
1.5	0.0500	3.9000	3.2665	0.1800	0.0400	1.0903	0.0581	0.0090	1.5090	0.4187	0.8091	0.7510
3.0	0.0500	3.6100	3.5863	0.3200	0.0400	1.1971	0.1033	0.0090	1.4830	0.2859	0.8329	0.7296
4.5	0.0400	3.0800	3.3503	0.4700	0.0300	1.1183	0.1517	0.0068	1.4360	0.3177	0.7373	0.5856
6.0	0.0600	3.0300	3.2360	0.4900	0.0300	1.0802	0.1581	0.0068	1.3680	0.2878	0.8531	0.6950
7.5	0.0700	2.9500	3.5711	1.3000	0.0400	1.1920	0.4195	0.0090	1.4340	0.2420	0.9276	0.5081
9.0	0.0700	2.9600	4.0736	2.8400	0.0400	1.3597	0.9165	0.0090	1.5290	0.1693	1.0230	0.1065
12.0	0.0800	2.8300	4.2716	3.2200	0.0500	1.4258	1.0392	0.0113	1.6270	0.2012	1.0630	0.0238
19.5	0.0900	2.6500	5.5279	1.4900	0.0300	1.8452	0.4809	0.0068	2.1890	0.3438	0.8437	0.3628
27.0	0.0900	2.9100	6.4188	1.9200	0.1400	2.1425	0.6196	0.0316	2.3180	0.1755	0.8786	0.2590
34.5	0.0700	3.0200	4.5533	2.8400	0.1000	1.5199	0.9165	0.0226	1.8870	0.3671	1.0960	0.1795
						March 2004, #7						
0.0	0.0700	3.0200	3.7995	0.2100	0.0300	1.2682	0.0678	0.0068	1.6130	0.3448	0.5287	0.4609
1.5	0.0700	3.0400	3.3731	0.2700	0.0400	1.1259	0.0871	0.0090	1.3850	0.2591	0.4579	0.3708
3.0	0.0700	3.2300	3.5787	0.1700	0.0500	1.1945	0.0549	0.0113	1.4070	0.2125	0.3969	0.3420
4.5	0.0700	3.0400	2.9239	0.1200	0.0200	0.9760	0.0387	0.0045	1.2380	0.2620	0.2898	0.2511
6.0	0.0700	2.9900	3.2665	0.1300	0.0300	1.0903	0.0420	0.0068	1.3190	0.2287	0.3023	0.2603
7.5	0.0600	2.8400	3.2589	0.2200	0.0400	1.0878	0.0710	0.0090	1.3030	0.2152	0.3199	0.2489
9.0	0.0700	2.7300	3.0609	0.1900	0.0300	1.0217	0.0613	0.0068	1.2760	0.2543	0.2749	0.2136
10.5	0.0700	2.8700	3.3503	0.2300	0.0300	1.1183	0.0742	0.0068	1.3140	0.1957	0.3152	0.2410
13.5	0.0600	2.6600	3.2893	0.4700	0.0300	1.0980	0.1517	0.0068	1.3030	0.2050	0.4000	0.2483
21.0	0.0800	2.4700	4.4848	1.0900	0.0500	1.4970	0.3518	0.0113	1.7450	0.2480	0.5726	0.2208
28.5	0.0800	2.6000	7.4239	1.7100	0.0200	2.4780	0.5519	0.0045	2.7860	0.3080	0.7444	0.1925
36.0	0.0700	2.8600	3.5482	1.8800	0.0500	1.1844	0.6067	0.0113	1.4800	0.2956	0.7845	0.1778

Table 5.24. IC data from the Schlepp Pond, April 2004. Samples are from dialyzer #8 and #9. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						April 2004, #8						
0.0	0.0200	0.3400	3.3900		0.0200	1.1316	0.0000	0.0045	5.7320	4.6004	0.2228	0.2228
1.5	0.0500	1.1700	3.2400	0.0300	0.0400	1.0815	0.0097	0.0090	2.5550	1.4735	0.3228	0.3131
3.0	0.0500	1.4200	0.6600	0.0600	0.0500	0.2203	0.0194	0.0113	0.7963	0.5760	0.3614	0.3420
4.5	0.0400	1.3300	0.3100	0.1000	0.0200	0.1035	0.0323	0.0045	0.6508	0.5473	0.7462	0.7139
6.0	0.0300	1.6000	0.3600	0.5900	0.0400	0.1202	0.1904	0.0090	0.6621	0.5419	1.0110	0.8206
7.5	0.0300	1.5700	0.3600	0.5600	0.0300	0.1202	0.1807	0.0068	0.6522	0.5320	0.9889	0.8082
9.0	0.0400	1.8000	0.3800	0.5900	0.0300	0.1268	0.1904	0.0068	0.6829	0.5561	1.0230	0.8326
10.5	0.0300	1.8400	0.3900	0.5900	0.0300	0.1302	0.1904	0.0068	0.6639	0.5337	1.0890	0.8986
13.5	0.0300	1.9000	0.4000	0.6300	0.0300	0.1335	0.2033	0.0068	0.6060	0.4725	1.1370	0.9337
21.0	0.0300	2.1800	0.4100	0.8300	0.0100	0.1369	0.2679	0.0023	0.7122	0.5753	1.3110	1.0431
28.5	0.0300	1.4100	0.3900	0.9700	0.0100	0.1302	0.3130	0.0023	0.5843	0.4541	1.5000	1.1870
36.0	0.0300	2.5100	0.3200	0.8400	0.0100	0.1068	0.2711	0.0023	0.8437	0.7369	1.3990	1.1279
						April 2004, #9						
1.5	0.0600	1.1300	1.9700	0.0600	0.0900	0.6576	0.0194	0.0203	1.6780	1.0204	0.2642	0.2448
3.0	0.0700	1.8200	0.6900	0.2100	0.0700	0.2303	0.0678	0.0158	0.8117	0.5814	0.4522	0.3844
4.5	0.0300	1.3400	0.3400	1.2900	0.0600	0.1135	0.4163	0.0136	0.5301	0.4166	1.3620	0.9457
6.0	0.0300	1.4800	0.3400	1.4300	0.0200	0.1135	0.4615	0.0045	0.5293	0.4158	1.4850	1.0235
7.5	0.0400	1.5400	0.3500	1.4700	0.0200	0.1168	0.4744	0.0045	0.5404	0.4236	1.5970	1.1226
9.0	0.0300	1.2900	0.3800	0.7400	0.1500	0.1268	0.2388	0.0339	0.6079	0.4811	1.2640	1.0252
10.5	0.0300	1.5200	0.3800	0.8800	0.0500	0.1268	0.2840	0.0113	0.5702	0.4434	1.2280	0.9440
12.0	0.0300	1.5000	0.4000	0.7700	0.0400	0.1335	0.2485	0.0090	0.5913	0.4578	1.1660	0.9175
15.0	0.0300	1.1300	0.3300	0.3600	0.0200	0.1102	0.1162	0.0045	0.5909	0.4807	1.2680	1.1518
22.5	0.0400	1.1900	0.4600	0.7800	0.0400	0.1535	0.2517	0.0090	0.5558	0.4023	1.0740	0.8223
30.0	0.0400	1.1200	0.4300	0.7300	0.0300	0.1435	0.2356	0.0068	0.5997	0.4562	1.1730	0.9374
37.5	0.0300	1.5500	0.5000	1.0800	0.1000	0.1669	0.3485	0.0226	0.7875	0.6206	1.1420	0.7935

Table 5.25. IC data from the Schlepp Pond, April and May 2004. Samples are from dialyzer #12 (April) and #1 (May). The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						April 2004, #12						
-1.5	0.0300	0.6400	8.7600	0.1200	14.8300	2.9240	0.0387	3.3502	6.8210	3.8970	0.0184	-0.0203
0.0	0.0300	0.6200	4.6700	0.1200	12.6000	1.5588	0.0387	2.8464	3.8810	2.3222	0.1346	0.0959
1.5	0.0500	1.2000	1.6400	0.1000	0.1300	0.5474	0.0323	0.0294	1.4860	0.9386	0.4076	0.3753
3.0	0.0400	1.2100	0.4600	1.0400	0.0200	0.1535	0.3356	0.0045	0.6689	0.5154	1.2130	0.8774
4.5	0.0300	1.2900	0.3800	1.0400	0.0700	0.1268	0.3356	0.0158	0.6423	0.5155	1.1940	0.8584
6.0	0.0300	1.4900	0.3800	0.5000	0.0400	0.1268	0.1614	0.0090	0.6029	0.4761	1.0860	0.9246
7.5	0.0300	1.6600	0.5000	0.4200	0.1100	0.1669	0.1355	0.0248	0.6204	0.4535	0.9435	0.8080
9.0	0.0400	1.6400	0.4000	0.2400	0.0300	0.1335	0.0775	0.0068	0.5879	0.4544	0.8901	0.8126
12.0	0.0300	1.5500	0.5900	0.3500	0.0200	0.1969	0.1130	0.0045	0.6376	0.4407	0.9040	0.7910
18.0	0.0300	1.4400	0.5300	0.6600	0.1800	0.1769	0.2130	0.0407	0.6202	0.4433	0.9306	0.7176
25.5	0.0300	1.5500	0.4300	0.9200	0.0100	0.1435	0.2969	0.0023	0.5930	0.4495	1.0510	0.7541
33.0	0.0400	1.9900	0.4000	1.8000	0.0700	0.1335	0.5809	0.0158	0.6982	0.5647	1.7540	1.1731
						May 2004, #1						
0.0	0.0400	2.1400	1.7200	0.2800	0.0500	0.5740	0.0904	0.0113	0.8053	0.2313	0.2290	0.2177
1.5	0.0500	2.9400	1.0000	0.1100	0.0200	0.3337	0.0355	0.0045	0.7800	0.4463	0.3138	0.3093
3.0	0.0500	3.3200	0.7100	0.1000	0.0200	0.2370	0.0323	0.0045	0.8401	0.6031	0.3674	0.3629
4.5	0.0500	3.5900	1.5200	0.2700	0.0400	0.5073	0.0871	0.0090	0.8991	0.3918	0.4012	0.3922
6.0	0.0500	3.7800	0.9500	0.2200	0.0300	0.3171	0.0710	0.0068	0.9395	0.6224	0.4282	0.4214
7.5	0.0600	4.0300	0.9200	0.2800	0.0300	0.3070	0.0904	0.0068	0.8898	0.5828	0.4788	0.4720
9.0	0.0500	3.9000	1.0400	0.3000	0.0500	0.3471	0.0968	0.0113	0.8828	0.5357	0.4169	0.4056
10.5	0.0500	3.9700	0.9100	0.2500	1.3600	0.3037	0.0807	0.3071	0.8706	0.5669	0.5856	0.2785
13.5	0.0700	0.2900	1.4800	0.9200	0.9600	0.4939	0.2969	0.2168	0.7936	0.2997	0.9030	0.6862
21.0	0.0600	3.5400	0.8900	0.5000	0.0700	0.2970	0.1614	0.0158	0.6955	0.3985	0.9179	0.9021
28.5	0.0700	2.0800	0.6700	3.2100		0.2236	1.0359	0.0000				0.0000
36.0	0.0800	2.6500	0.4000	4.6800		0.1335	1.5103	0.0000	0.6957	0.5622	1.1390	1.1390

Table 5.26. IC data from the Schlepp Pond, May 2004. Samples are from dialyzer #2 and #3. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						May 2004, #2						
-1.5	0.0300	2.7900	9.3000	0.0300	0.0400	3.1039	0.0097	0.0090	3.6020	0.4981	0.1103	0.1013
0.0	0.0400	4.9700	0.2900	0.0800	0.1000	0.0968	0.0258	0.0226	0.7786	0.6818	0.3317	0.3091
1.5	0.0500	7.4500	0.3100	0.1400	0.0200	0.1035	0.0452	0.0045	0.9043	0.8008	0.7104	0.7059
3.0	0.0600	7.4300	0.3200	0.2600	0.0700	0.1068	0.0839	0.0158	0.8600	0.7532	0.8164	0.8006
4.5	0.0600	7.3900	0.2900	0.3100	0.0800	0.0968	0.1000	0.0181	0.8437	0.7469	1.0540	1.0359
6.0	0.0600	7.4300	1.2900	0.7300	0.0400	0.4305	0.2356	0.0090	0.8306	0.4001	1.1960	1.1870
7.5	0.0500	6.8100	1.1800	0.4400	0.0300	0.3938	0.1420	0.0068	0.8325	0.4387	1.2760	1.2692
9.0	0.0700	7.5100	1.2900	0.4400	0.0600	0.4305	0.1420	0.0135	0.7908	0.3603	1.2490	1.2355
12.0	0.0700	6.8300	0.3200	0.6800	0.1000	0.1068	0.2194	0.0226	0.7865	0.6797	1.4100	1.3874
19.5	0.0700	4.4500	0.3100	0.3800	0.0900	0.1035	0.1226	0.0203	0.7237	0.6202	1.2830	1.2627
27.0	0.0800	4.0000	0.3400	0.5100	0.1500	0.1135	0.1646	0.0339	0.7693	0.6558	1.3600	1.3261
34.5	0.0800	8.3100	0.3900	0.6700	0.2600	0.1302	0.2162	0.0587	0.9426	0.8124	1.1880	1.1293
						May 2004, #3						
0.0	0.0600	4.2700	0.2600	0.1300	0.0500	0.0868	0.0420	0.0113	1.3130	1.2262	0.2877	0.2764
1.5	0.0600	4.2900	0.3200	0.1500	0.0300	0.1068	0.0484	0.0068	1.3010	1.1942	0.4519	0.4451
3.0		0.4400	0.2000			0.0667	0.0000	0.0000	1.3330	1.2663	0.6092	0.6092
4.5	0.0600	5.3300	2.4900	0.1200	0.0700	0.8310	0.0387	0.0158	1.3960	0.5650	0.6852	0.6694
6.0	0.0600	5.9000	2.5000	0.2100	0.0200	0.8344	0.0678	0.0045	1.5680	0.7336	0.5534	0.5489
7.5	0.0300	3.0900	0.3000	0.0800	0.0200	0.1001	0.0258	0.0045	1.5750	1.4749	0.4402	0.4357
9.0	0.0700	5.1000	0.2900	0.0900	0.0100	0.0968	0.0290	0.0023	1.5270	1.4302	0.4333	0.4310
10.5	0.0600	4.4000	2.0600	0.1200	0.0200	0.6875	0.0387	0.0045	1.4820	0.7945	0.4685	0.4640
13.5	0.0800	4.8900	2.5200	0.1800	0.0400	0.8410	0.0581	0.0090	1.3710	0.5300	0.7521	0.7431
21.0	0.0800	3.3900	2.4300	0.4100	0.0300	0.8110	0.1323	0.0068	1.2090	0.3980	1.2050	1.1982
28.5	0.0800	2.9400	2.5300	1.3200	0.0800	0.8444	0.4260	0.0181	1.2200	0.3756	1.1320	1.1139
36.0	0.0900	3.8300	2.1900	0.3300	0.0200	0.7309	0.1065	0.0045	1.2000	0.4691	0.8174	0.8129

Table 5.27. IC data from the Schlepp Pond, June 2004. Samples are from dialyzer #15 and #16. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						June 2004, #15						
-1.5	0.0400	1.0000	10.1500	0.0000	0.0200	3.3876	0.0000	0.0045	3.2750	-0.1126	0.0736	0.0736
0.0	0.0400	1.3100	3.6600	0.2400	0.1200	1.2215	0.0774	0.0271	1.2930	0.0715	0.1592	0.0818
1.5	0.0400	2.5200	0.6400	0.2800	0.1000	0.2136	0.0904	0.0226	0.4087	0.1951	0.4888	0.3984
3.0	0.0400	4.2200	0.7500	0.2800	0.0400	0.2503	0.0904	0.0090	0.4040	0.1537	0.7783	0.6879
4.5	0.0300	7.1800	0.6000	0.5200	0.1600	0.2002	0.1678	0.0361	0.4728	0.2726	0.9055	0.7377
6.0	0.0400	10.1900	0.5300	1.0300	0.0100	0.1769	0.3324	0.0023	0.5726	0.3957	1.0910	0.7586
7.5	0.0500	11.3700	0.5800	1.7800	0.0500	0.1936	0.5744	0.0113	0.6993	0.5057	1.4420	0.8676
9.0	0.0600	11.8700	0.6300	1.8700	0.3900	0.2103	0.6035	0.0881	0.7348	0.5245	1.4250	0.8215
12.0	0.0600	12.5000	0.5700	1.5200	0.0200	0.1902	0.4905	0.0045	0.7759	0.5857	1.6940	1.2035
19.5	0.0600	7.5700	0.6300	1.6800	0.0400	0.2103	0.5421	0.0090	0.6375	0.4272	1.7760	1.2339
27.0		4.6900	0.7500	2.4600	0.0400	0.2503	0.7939	0.0090	0.6067	0.3564	1.8010	1.0071
34.5	0.0900	4.5300	0.8300	2.1400	0.0000	0.2770	0.6906	0.0000	0.6514	0.3744	1.6440	0.9534
						June 2004, #16						
0.0	0.0200	1.0300	5.1500	0.0000	0.0500	1.7188	0.0000	0.0113	1.9080	0.1892	0.0000	0.0000
1.5	0.0200	1.2100	1.5400		0.0800	0.5140	0.0000	0.0181	0.6882	0.1742	0.0018	0.0018
3.0	0.0200	1.5500	0.6000	0.0300	0.0500	0.2002	0.0097	0.0113	0.3903	0.1901	0.0525	0.0428
4.5	0.0300	2.8700	0.6500	0.3700	0.0800	0.2169	0.1194	0.0181	0.4947	0.2778	0.0367	-0.0827
6.0	0.0300	3.2600	0.6600	0.1900	0.0600	0.2203	0.0613	0.0135	0.6363	0.4160	0.3243	0.2630
7.5	0.0400	3.7300	0.7100	0.3400	0.0700	0.2370	0.1097	0.0158	0.7177	0.4807	0.5072	0.3975
9.0	0.0300	3.9900	0.6900	0.4100	0.0700	0.2303	0.1323	0.0158	0.7043	0.4740	0.5987	0.4664
10.5	0.0200	4.0200	0.7300	0.4000	0.0400	0.2436	0.1291	0.0090	0.6703	0.4267	0.6356	0.5065
13.5						0.0000	0.0000	0.0000	0.6682	0.6682	0.7328	0.7328
21.0						0.0000	0.0000	0.0000	0.6990	0.6990	1.6390	1.6390
28.5						0.0000	0.0000	0.0000	0.7883	0.7883	1.0180	1.0180
36.0						0.0000	0.0000	0.0000	0.9743	0.9743	0.5693	0.5693

Table 5.28. IC data from the Schlepp Pond, June and August 2004. Samples are from dialyzer #17 (June) and #2 (August). The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						June 2004, #17						
1.5	0.0300	1.9700	0.2800	0.0200	0.1400	0.0934	0.0065	0.0316	0.3148	0.2214	0.1652	0.1587
3.0	0.0300	2.5800	0.4600	0.0400	0.1100	0.1535	0.0129	0.0248	0.4849	0.3314	0.4799	0.4670
4.5	0.0400	3.4500	0.4900	0.0500	0.0900	0.1635	0.0161	0.0203	0.6001	0.4366	0.6456	0.6295
6.0	0.0100	0.3200		0.4900	0.1200	0.0000	0.1581	0.0271	0.6074	0.6074	0.8735	0.7154
7.5	0.0500	4.9800	0.5400	0.1300	0.7200	0.1802	0.0420	0.1626	0.6455	0.4653	0.9808	0.9388
9.0	0.0500	4.9600	0.5400	0.0700	0.0600	0.1802	0.0226	0.0135	0.6138	0.4336	1.0350	1.0124
10.5		0.3400		0.1600		0.0000	0.0516	0.0000	0.6318	0.6318	0.9547	0.9031
12.0	0.0500	5.5900	0.6200	0.0800	0.1100	0.2069	0.0258	0.0248	0.6630	0.4561	0.9895	0.9637
13.5	0.0500	0.3200		0.1000		0.0000	0.0323	0.0000	0.6960	0.6960	0.9973	0.9650
16.5	0.0500	5.3700	0.6700	0.0900	0.2000	0.2236	0.0290	0.0452	0.6427	0.4191	1.2000	1.1710
24.0	0.0500	7.8900	0.6300	0.1200	0.1200	0.2103	0.0387	0.0271	1.6427	1.4324	2.2000	2.1613
31.5	0.0500	9.4400	0.6700	0.1400	0.0600	0.2236	0.0467	0.0200				
						August 2002, #2						
-3.0	0.0600	2.5300	0.2900	0.0900	0.1800	0.0968	0.0290	0.0407	0.5371	0.4403	0.2159	0.1869
-1.5	0.0500	3.0800	0.8200	0.1100	0.2200	0.2737	0.0355	0.0497	0.6612	0.3875	0.2508	0.2153
0.0	0.0500	3.4400	0.3500	0.1500	0.1100	0.1168	0.0484	0.0248	0.7354	0.6186	0.0000	-0.0484
1.5	0.0500	3.6600	0.4000	0.3500	0.0700	0.1335	0.1130	0.0158	0.7967	0.6632	0.5708	0.4578
3.0	0.0500	3.9900	0.3700	0.8300	0.2400	0.1235	0.2679	0.0542	0.8532	0.7297	0.7882	0.5203
4.5	0.0500	4.0500	0.4400	0.8700	0.3100	0.1469	0.2808	0.0700	0.8545	0.7076	0.8300	0.5492
6.0	0.0600	4.1600	0.4200	1.0000	0.0800	0.1402	0.3227	0.0181	0.8589	0.7187	0.7674	0.4447
7.5	0.0600	4.1800	0.4500	0.9600	0.0800	0.1502	0.3098	0.0181	0.7816	0.6314	0.9244	0.6146
10.5	0.0700	4.0300	1.8500	0.6400	0.9100	0.6175	0.2065	0.2056	0.6833	0.0658	1.1600	0.9535
18.0	0.0700	5.4600	1.2200	0.6300	0.0600	0.4072	0.2033	0.0136	0.6383	0.2311	1.2760	1.0727
25.5	0.0700	8.2600	0.4200	0.6600	0.1000	0.1402	0.2130	0.0226	0.7619	0.6217	1.1650	0.9520
33.0	0.0700	8.9700	0.2300	0.4600	0.1000	0.0768	0.1485	0.0226	0.7764	0.6996	1.0090	0.8605

Table 5.29. IC data from the Schlepp Pond, August 2004. Samples are from dialyzer #8 and #12. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						August 2004, #8						
1.5	0.0600	3.6500	0.3400	0.3500	0.7500	0.1135	0.1130	0.1694	0.6391	0.5256	0.4142	0.3012
3.0	0.0600	4.0600	0.3500	0.6400	0.1300	0.1168	0.2065	0.0294	0.6996	0.5828	0.6801	0.4736
4.5	0.0600	4.5900	0.3200	0.6700	0.0600	0.1068	0.2162	0.0136	0.7778	0.6710	0.8282	0.6120
6.0	0.0600	5.1100	0.3500	1.3700	0.0700	0.1168	0.4421	0.0158	0.7766	0.6598	0.9428	0.5007
7.5	0.0600	5.9300	0.4700	1.8300	1.3100	0.1569	0.5906	0.2959	0.7450	0.5881	1.1670	0.5764
9.0	0.0700	5.8700	0.4200	2.2400	0.1400	0.1402	0.7229	0.0316	0.7814	0.6412	1.3490	0.6261
10.5	0.0700	5.3400	0.7900	2.2200	0.0400	0.2637	0.7164	0.0090	0.7724	0.5087	1.4030	0.6866
12.0	0.0700	4.9600	0.4100	2.1400	0.0700	0.1369	0.6906	0.0158	0.7854	0.6485	1.4670	0.7764
15.0	0.0700	4.2100	0.7600	2.1500	0.0800	0.2537	0.6938	0.0181	0.7414	0.4877	1.4060	0.7122
22.5	0.0800	3.6200	0.3600	1.3100	0.2500	0.1202	0.4228	0.0565	0.7141	0.5939	1.4490	1.0262
30.0	0.0800	3.5800	0.4200	1.6700	0.0600	0.1402	0.5389	0.0136	0.6222	0.4820	1.7570	1.2181
37.5	0.0900	2.7200	0.4000	2.1200	0.0300	0.1335	0.6842	0.0068	0.6408	0.5073	1.6700	0.9858
						August 2004, #12						
0.0	0.0500	2.6400	0.2300		0.0800	0.0768	0.0000	0.0181	0.6549	0.5781	0.2584	0.2584
1.5	0.0500	2.8100	0.3200	0.3200	0.5000	0.1068	0.1033	0.1130	0.7013	0.5945	0.6186	0.5153
3.0	0.0600	2.7300	0.2400	0.4300	0.0700	0.0801	0.1388	0.0158	0.6759	0.5958	0.8363	0.6975
4.5	0.0500	2.4100	0.1500	0.9000	0.1400	0.0501	0.2904	0.0316	0.6821	0.6320	1.1280	0.8376
6.0	0.0600	2.6500	0.3200	0.6600	0.1000	0.1068	0.2130	0.0226	0.7211	0.6143	1.1570	0.9440
7.5	0.0600	2.5900	0.3500	0.7400	0.3200	0.1168	0.2388	0.0723	0.6985	0.5817	1.2150	0.9762
9.0	0.0600	2.5500	0.4100	0.5800	0.6000	0.1369	0.1872	0.1355	0.6554	0.5185	1.2790	1.0918
10.5	0.0700	2.4900	0.2500	0.9900	0.1400	0.0834	0.3195	0.0316	0.6641	0.5807	1.4140	1.0945
13.5	0.0700	2.3600	0.3100	1.5000	0.2200	0.1035	0.4841	0.0497	0.6202	0.5167	1.4770	0.9929
21.0	0.0900	2.4400	0.2900	1.3800	0.1000	0.0968	0.4454	0.0226	0.7289	0.6321	1.4040	0.9586
28.5	0.0900	2.7400	0.8300	1.2700	0.1000	0.2770	0.4099	0.0226	0.5727	0.2957	1.7390	1.3291
36.0	0.0800	3.4600	0.2800	1.2500	0.3900	0.0935	0.4034	0.0881	0.6850	0.5915	1.4780	1.0746

Table 5.30. IC data from the Schlepp Pond, November 2004. Samples are from dialyzer #4 and #5. The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
					November 2004, #4							
1.5	0.0500	0.3400	0.7400	1.7300	0.0300	0.2470	0.5583	0.0068	0.8766	0.6296	0.7933	0.2350
3.0	0.0400	0.2700	0.6200	1.8700	0.0600	0.2070	0.6035	0.0136	0.9371	0.7301	0.9286	0.3251
4.5	0.0400	0.3900	1.0500	2.8100	0.0700	0.3505	0.9068	0.0158	0.9272	0.5767	1.3390	0.4322
6.0	0.0300	0.3800	0.5700	2.5300	0.0200	0.1903	0.8165	0.0045	0.9077	0.7174	1.5940	0.7775
7.5	0.0300	0.4800	0.7000	2.9600	0.0200	0.2337	0.9553	0.0045	0.9572	0.7235	1.7230	0.7677
9.0	0.0300	0.7600	0.7000	3.5900	0.3700	0.2337	1.1586	0.0836	0.9990	0.7653	1.7890	0.6304
10.5	0.0200	0.2000	0.6400	3.5100	0.1500	0.2136	1.1327	0.0339	1.0550	0.8414	1.8030	0.6703
12.0	0.0300	0.5800	0.7400	5.0100	0.0600	0.2470	1.6168	0.0136	1.1250	0.8780	2.0330	0.4162
15.0	0.0200	0.2400	0.5600	0.1400	0.0100	0.1869	0.0452	0.0023	1.1060	0.9191	2.0250	1.9798
22.5	0.0300	0.9700	0.7200	0.2100	0.0500	0.2403	0.0678	0.0113	1.0890	0.8487	1.7010	1.6332
30.0	0.0400	0.8800	0.5500	0.1200	0.5100	0.1836	0.0387	0.1152	1.3190	1.1354	2.3020	2.2633
37.5	0.0400	0.8800	0.8000	5.7600	0.2200	0.2670	1.8589	0.0497	0.5111	0.2441	0.1019	-1.7570
					November 2004, #5							
1.5	0.0300	12.7600	0.6400	1.2700	0.5600	0.2136	0.4099	0.1265	0.9534	0.7398	1.0140	0.6041
3.0	0.0300	15.3500	0.4400	1.5300	0.2600	0.1469	0.4938	0.0587	1.0570	0.9101	1.2000	0.7062
4.5	0.0200	17.6400	0.4800	1.8100	0.2300	0.1602	0.5841	0.0520	1.1950	1.0348	1.2580	0.6739
6.0	0.0300	22.0200	0.6900	1.9500	0.2700	0.2303	0.6293	0.0610	1.3650	1.1347	1.4780	0.8487
7.5	0.0200	23.7200	0.5700	1.9100	0.5000	0.1903	0.6164	0.1130	1.4650	1.2747	1.4300	0.8136
9.0	0.0300	25.6500	0.5800	1.9300	0.2600	0.1936	0.6228	0.0587	1.5440	1.3504	1.3860	0.7632
10.5	0.0000	26.3700	0.6500	2.3900	0.3000	0.2170	0.7713	0.0678	1.6520	1.4350	1.5260	0.7547
12.0	0.0000		0.6500	2.0100		0.2170	0.6487	0.0000	1.7370	1.5200	1.4370	0.7883
15.0	0.0000	31.4600	0.8000	2.3800	0.5400	0.2670	0.7681	0.1220	1.9280	1.6610	1.3420	0.5739
22.5	0.0000	35.4300	0.7500	4.6600	0.4300	0.2503	1.5039	0.0971	1.8780	1.6277	2.1220	0.6181
30.0	0.0000	31.9000	0.6400	8.7500	0.3700	0.2136	2.8238	0.0836	1.6820	1.4684	2.9260	0.1022
37.5	0.0000	29.9400	0.5700	6.4900	0.1000	0.1903	2.0945	0.0226	1.3380	1.1477	1.9350	-0.1595

Table 5.31. IC data from the Schlepp Pond, November 2004 and June 2005. Samples are from dialyzer #6 (November) and #1 (June). The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						November 2004, #6						
1.5	0.0400	12.0900	0.7300	1.4000	0.2900	0.2437	0.4518	0.0655	0.9778	0.7341	1.1640	0.7122
3.0	0.0500	13.3500	0.6800	1.6600	0.0400	0.2270	0.5357	0.0090	0.9709	0.7439	1.2000	0.6643
4.5	0.0500	13.7600	0.5800	0.9400	0.0200	0.1936	0.3034	0.0045	0.9301	0.7365	1.3350	1.0316
6.0	0.0500	13.8600	0.6500	2.4100	0.0000	0.2170	0.7778	0.0000	0.9535	0.7365	1.4000	0.6222
7.5	0.0500	14.9500	0.6500	3.1800	0.0500	0.2170	1.0262	0.0113	1.0380	0.8210	1.5790	0.5528
9.0	0.0500	15.3300	0.6200	3.6100	0.0200	0.2070	1.1650	0.0045	1.0820	0.8750	1.7050	0.5400
10.5	0.0600	15.4800	0.6100	3.7200	0.0600	0.2036	1.2005	0.0136	1.0480	0.8444	1.7120	0.5115
12.0	0.0600	15.3500	0.8500	3.9400	0.0100	0.2837	1.2715	0.0023	0.9909	0.7072	1.6840	0.4125
15.0	0.0700	14.3000	0.7100	4.9100	0.0400	0.2370	1.5846	0.0090	0.8911	0.6541	1.7060	0.1214
22.5	0.0800	12.1300	0.6900	6.2400	0.0000	0.2303	2.0138	0.0000	0.6975	0.4672	1.9210	-0.0928
30.0	0.0700	10.7100	0.3800	7.0200	0.0000	0.1268	2.2655	0.0000	0.6237	0.4969	2.0970	-0.1685
37.5	0.0700	4.9400	0.3100	4.6600	0.0400	0.1035	1.5039	0.0090	0.4311	0.3276	2.3725	0.8686
						June 2005, #1						
0.0	0.0500	3.3000	0.5800	0.6633	0.2000	0.1936	0.2141	0.0452	0.5812	0.39	0.9493	0.74
1.5	0.0600	4.1100	0.7500	0.6341	0.2100	0.2503	0.2046	0.0474	0.5220	0.27	0.7952	0.59
3.0	0.0400	3.2900	0.6000	0.6035	0.2000	0.2003	0.1948	0.0452	0.5497	0.35	0.9664	0.77
4.5	0.0400	3.5500	0.7400	0.6162	0.8200	0.2470	0.1989	0.1852	0.5372	0.29	1.1110	0.91
6.0	0.0400	2.9300	0.8400	0.6299	1.1300	0.2804	0.2033	0.2553	0.5209	0.24	1.1400	0.94
7.5	0.0400	2.9900	0.8100	0.6372	0.3800	0.2704	0.2056	0.0858	0.5523	0.28	1.1110	0.91
9.0	0.0500	2.5900	0.6700	0.6009	0.2200	0.2236	0.1939	0.0497	0.5571	0.33	0.8493	0.66
10.5	0.0500	2.6500	0.8600	0.6031	0.4000	0.2871	0.1946	0.0904	0.5576	0.27	0.7379	0.54
13.5	0.0400	2.0900	0.6700	0.5968	0.3200	0.2236	0.1926	0.0723	0.5618	0.34	1.2760	1.08
21.0	0.0600	1.9900	0.7400	0.5657	0.3300	0.2470	0.1826	0.0745	0.5466	0.30	1.2340	1.05
28.5	0.0600	1.7900	0.3700	0.5377	0.0800	0.1235	0.1735	0.0181	0.5175	0.39	0.0144	-0.16
36.0	0.0700	2.1700	0.3800	0.5732	0.1100	0.1268	0.1850	0.0248	0.5961	0.47	1.6510	1.47

Table 5.32. IC data from the Schlepp Pond. Samples are from dialyzer #5 (November) and #7 (June). The data were converted to elemental concentrations in the right hand columns and S and P are compared to ICP totals.

Depth	Element (mg L^{-1})											
(cm)	F	Cl	SO_4^{2-}	HPO_4^{2-}	NO_3^-	$(SO_4^{2-})S$	$(HPO_4^{2-})P$	$(NO_3^-)N$	S(ICP)	dif S	P(ICP)	dif P
						June 2005, #5						
0.0	0.0300	12.6200	0.8500	2.8400	0.5300	0.2837	0.9165	0.1197	0.8030	0.5193	1.8410	0.9245
1.5	0.0300	14.1300	0.9300	3.8100	0.5000	0.3104	1.2296	0.1130	0.7584	0.4480	1.9330	0.7034
3.0	0.0300	10.7000	0.8300	2.0900	0.5300	0.2770	0.6745	0.1197	0.7447	0.4677	1.6980	1.0235
4.5	0.0300	8.6900	0.8400	4.5200	0.5300	0.2804	1.4587	0.1197	0.7114	0.4310	2.0960	0.6373
6.0	0.0300	9.1300	0.8200	4.6900	0.4300	0.2737	1.5136	0.0971	0.7305	0.4568	2.1000	0.5864
7.5	0.0400	6.9600	0.9600	4.9100	0.5000	0.3204	1.5846	0.1130	0.7269	0.4065	2.6260	1.0414
9.0	0.0400	5.6500	0.7600	3.6800	0.4100	0.2537	1.1876	0.0926	0.6816	0.4279	2.2110	1.0234
10.5	0.0400	5.0900	1.4700	8.0300	0.5300	0.4907	2.5914	0.1197	0.7346	0.2439	3.8040	1.2126
13.5	0.0500	3.6900	1.0300	13.2100	0.4700	0.3438	4.2631	0.1062	0.6737	0.3299	1.8280	-2.4351
21.0	0.0600	2.2800	0.9300	2.5000	0.1600	0.3104	0.8068	0.0361	0.6562	0.3458	1.5820	0.7752
28.5	0.0600	1.8500	1.0200	3.0200	0.3700	0.3405	0.9746	0.0836	0.6764	0.3359	1.9390	0.9644
36.0	0.0700	2.1900	0.7200	6.1900	0.5100	0.2403	1.9976	0.1152	0.6358	0.3955	2.1160	0.1184
						June 2005, #7						
1.5	0.0400	3.3100	0.7400	2.2800	0.2900	0.2470	0.7358	0.0655	0.6633	0.4163	1.4680	0.7322
3.0	0.0500	3.2400	0.7100	1.5300	0.2500	0.2370	0.4938	0.0565	0.6341	0.3971	1.3320	0.8382
4.5	0.0500	2.6000	0.7500	1.9600	0.0900	0.2503	0.6325	0.0203	0.6035	0.3532	1.1870	0.5545
6.0	0.0400	2.3700	0.8300	2.1000	0.1400	0.2770	0.6777	0.0316	0.6162	0.3392	1.1730	0.4953
7.5	0.0600	2.4900	0.3900	1.1900	0.1700	0.1302	0.3840	0.0384	0.6299	0.4997	1.3540	0.9700
9.0	0.0600	2.3400	0.3600	1.5300	0.1500	0.1202	0.4938	0.0339	0.6372	0.5170	1.3670	0.8732
10.5	0.0500	1.9900	0.3600	0.6500	0.0700	0.1202	0.2098	0.0158	0.6009	0.4807	1.1380	0.9282
12.0	0.0600	2.0100	0.9000	1.2400	0.4200	0.3004	0.4002	0.0949	0.6031	0.3027	1.1760	0.7758
15.0	0.0600	1.9000	0.3200	0.5000	0.1200	0.1068	0.1614	0.0271	0.5968	0.4900	1.3630	1.2016
22.5	0.0700	2.2000	0.3600	0.4300	0.2000	0.1202	0.1388	0.0452	0.5657	0.4455	1.2930	1.1542
30.0	0.0500	2.3700	0.3600	1.4400	0.2200	0.1202	0.4647	0.0497	0.5377	0.4175	1.3210	0.8563
37.5	0.0700	2.7000	0.2500	3.4000	0.1400	0.0834	1.0972	0.0316	0.5732	0.4898	1.3160	0.2188

Table 5.33. ICP-AES data from the Schlepp Pond, March 2004. Samples are from dialyzer #5 and #6.

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
					March 2004, #5							
-1.5	0.0000	22.960	0.0013	84.250	3.978	10.750	21.870	2.382	0.952	0.012	0.923	0.064
0.0	0.0000	32.340	0.0018	84.390	5.625	15.340	24.130	3.667	1.019	0.021	0.921	0.067
1.5	0.0000	31.940	0.0019	88.400	5.465	15.190	23.030	3.815	1.126	0.012	0.961	0.057
3.0	0.0000	30.730	0.0024	92.000	5.431	14.750	22.640	3.751	1.081	0.010	1.028	0.067
4.5	0.0000	30.040	0.0022	98.270	5.389	14.550	22.970	3.502	1.023	0.010	1.030	0.064
6.0	0.0000	28.390	0.0013	90.700	5.172	13.610	22.430	3.255	0.976	0.013	1.098	0.073
7.5	0.0000	27.420	0.0017	87.770	5.140	13.060	22.480	3.118	0.961	0.017	1.105	0.076
9.0	0.0000	26.480	0.0017	84.640	5.106	12.540	22.380	3.162	0.991	0.016	1.108	0.083
12.0	0.0000	25.380	0.0016	83.020	5.077	11.740	23.020	2.941	1.082	0.014	1.045	0.076
19.5	0.0000	25.070	0.0017	86.070	5.216	11.270	23.040	3.101	1.039	0.010	1.084	0.081
24.0	0.0000	24.410	0.0020	92.200	5.092	10.870	19.220	3.062	0.892	0.009	1.214	0.126
31.5	0.0000	26.580	0.0019	99.980	5.366	11.570	19.040	3.259	1.035	0.019	1.086	0.086
					March 2004, #6							
-1.5	0.0000	33.410	0.0021	95.440	7.099	14.770	30.220	3.381	0.910	0.015	1.453	0.099
0.0	0.0000	33.500	0.0015	97.350	7.216	14.850	29.940	3.431	0.812	0.014	1.523	0.096
1.5	0.0000	33.480	0.0028	95.780	7.241	14.840	29.520	3.484	0.809	0.006	1.509	0.101
3.0	0.0000	30.780	0.0022	89.850	6.762	13.600	26.100	3.311	0.833	0.010	1.483	0.107
4.5	0.0000	29.070	0.0023	84.290	6.543	12.870	24.460	3.197	0.737	0.015	1.436	0.118
6.0	0.0000	27.500	0.0022	83.400	6.230	12.190	23.040	3.099	0.853	0.013	1.368	0.112
7.5	0.0000	26.610	0.0018	84.070	6.106	11.810	23.050	3.092	0.928	0.017	1.434	0.120
9.0	0.0000	25.880	0.0014	84.810	5.968	11.450	22.860	3.072	1.023	0.016	1.529	0.137
12.0	0.0000	24.990	0.0019	84.030	5.754	11.020	22.540	3.007	1.063	0.005	1.627	0.151
19.5	0.0000	24.230	0.0017	83.310	5.687	10.820	20.780	2.966	0.844	0.015	2.189	0.209
24.0	0.0000	24.350	0.0021	87.960	5.837	10.850	17.720	3.034	0.879	0.022	2.318	0.299
31.5	0.0000	25.500	0.0015	95.150	6.053	10.990	15.430	3.185	1.096	0.044	1.887	0.227

Table 5.34. ICP-AES data from the Schlepp Pond, March and April 2004. Samples are from dialyzer #7 (March) and #8 (April).

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
						March 2004, #7						
0.0	0.0000	29.88	0.0017	59.72	6.978	14.34	21.61	3.930	0.5287	0.0104	1.613	0.0760
1.5	0.0000	28.92	0.0019	63.21	6.840	13.96	20.05	3.885	0.4579	0.0125	1.385	0.0942
3.0	0.0000	28.45	0.0017	66.80	6.837	13.92	19.84	3.857	0.3969	0.0038	1.407	0.1059
4.5	0.0000	27.08	0.0019	69.99	6.421	13.22	19.25	3.633	0.2898	0.0091	1.238	0.0918
6.0	0.0000	26.81	0.0017	74.75	6.221	13.11	20.00	3.483	0.3023	0.0089	1.319	0.1021
7.5	0.0000	26.86	0.0021	79.27	6.246	13.01	20.84	3.505	0.3199	0.0047	1.303	0.1028
9.0	0.0000	26.91	0.0027	80.84	6.276	12.83	21.80	3.361	0.2749	0.0010	1.276	0.0995
10.5	0.0000	26.29	0.0021	83.68	6.207	10.41	21.66	3.240	0.3152	0.0046	1.314	0.1124
13.5	0.0000	24.79	0.0023	80.84	6.206	10.41	21.56	3.127	0.4000	0.0065	1.303	0.1110
21.0	0.0000	22.35	0.0022	76.98	6.122	9.170	22.84	3.061	0.5726	0.0119	1.745	0.1355
25.5	0.0000	21.67	0.0019	80.24	5.983	8.765	19.92	2.941	0.7444	0.0114	2.786	0.1761
33.0	0.0000	24.70	0.0024	90.08	6.688	9.870	18.59	3.317	0.7845	0.0126	1.480	0.1437
						April 2004, #8						
-1.5	0.0005	10.75	0.0019	20.87	2.26	5.662	6.949	3.206	0.2228	0	5.732	0.1519
0.0	0	19.34	0.0056	74.82	4.416	10.07	12.30	3.932	0.3228	0.0034	2.555	0.0709
1.5	0.0024	25.45	0.0060	90.27	6.331	13.94	15.27	5.034	0.3614	0.0099	0.7963	0.0813
3.0	0.0086	27.28	0.0073	104.5	7.549	14.24	17.60	4.509	0.7462	0.0088	0.6508	0.0135
4.5	0.0038	29.61	0.0070	109.7	8.111	14.53	19.51	4.648	1.011	0.0040	0.6621	0.0133
6.0	0.0012	30.57	0.0074	109.6	8.432	14.75	19.53	4.836	0.9889	0.0102	0.6522	0.0267
7.5	0.0081	30.24	0.0079	114.5	8.835	15.10	19.96	4.909	1.023	0.0041	0.6829	0.0171
9.0	0	31.62	0.0081	111.8	9.098	15.29	20.16	4.995	1.089	0.0093	0.6639	0.0160
12.0	0.0015	30.65	0.0072	108.9	8.916	14.62	21.26	4.840	1.137	0.0057	0.6060	0.0158
19.5	0.0055	28.51	0.0094	134.6	8.503	12.96	21.27	4.659	1.311	0.0107	0.7122	0.0180
27.0	0.0011	25.53	0.0072	113.0	7.335	11.41	17.40	4.434	1.500	0.0082	0.5843	0.0176
34.5	0.0119	30.86	0.0133	179.3	8.409	13.72	20.68	4.611	1.399	0.0231	0.8437	0.0223

Table 5.35. ICP-AES data from the Schlepp Pond, April 2004. Samples are from dialyzer #9 and #12.

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
						April 2004, #9						
0.0	0	19.35	0.0036	40.8	4.867	10.79	15.54	3.948	0.2642	0	1.678	0.0890
1.5	0.0059	24.41	0.0047	59.66	6.405	13.05	16.71	4.969	0.4522	0	0.8117	0.0981
3.0	0.0017	28.58	0.0063	82.77	7.736	14.74	17.71	4.318	1.362	0	0.5301	0.0176
4.5	0	31.49	0.0066	93.99	8.352	15.87	18.06	4.416	1.485	0.0054	0.5293	0.0153
6.0	0.0005	33.23	0.0076	101.9	8.924	16.71	17.66	4.746	1.597	0.0043	0.5404	0.0126
7.5	0	32.73	0.0080	108.2	9.478	17.26	17.37	4.944	1.264	0	0.6079	0.0160
9.0	0	33.69	0.0075	109.5	9.262	17.06	16.99	4.774	1.228	0.0148	0.5702	0.0146
10.5	0	32.06	0.0068	111.5	8.794	16.38	17.47	4.646	1.166	0.0126	0.5913	0.0166
13.5	0	30.58	0.0065	110.1	8.362	15.38	17.34	4.568	1.268	0.0172	0.5909	0.0158
21.0	0	25.57	0.0057	99.73	7.027	12.24	16.54	4.093	1.074	0.0071	0.5558	0.0215
28.5	0.0018	26.73	0.0069	111.6	6.79	12.26	16.96	3.972	1.173	0.0082	0.5997	0.0205
36.0	0	29.66	0.0109	158.3	7.192	13.73	15.68	4.221	1.142	0.0195	0.7875	0.0205
						April 2004, #12						
-1.5	0	7.224	***0***	0.0419	1.511	3.633	1.593	2.804	0.0184	0.0084	6.821	0.5021
0.0	0	12.56	0.0006	15.09	2.433	6.345	10.63	3.140	0.1346	0.0039	3.881	0.1700
1.5	0.0014	22.78	0.0044	70.38	5.254	12.88	16.65	4.318	0.4076	0.0041	1.486	0.081
3.0	0.0039	28.71	0.005	81.54	7.438	16.00	19.29	4.222	1.213	0.0115	0.6689	0.0242
4.5	0	32.34	0.0054	83.47	8.878	17.71	19.91	4.754	1.194	0.0052	0.6423	0.0152
6.0	0.0013	32.53	0.0054	84.18	9.014	17.33	18.19	4.735	1.086	0.0127	0.6029	0.0222
7.5	0.0017	34.06	0.0064	92.19	9.858	18.17	17.32	5.118	0.9435	0.0084	0.6204	0.0252
9.0	0	34.24	0.0068	99.48	9.799	18.03	16.65	5.098	0.8901	0.0148	0.5879	0.0182
12.0	0.0011	33.43	0.0073	115.7	9.318	17.13	17.61	4.829	0.904	0.0078	0.6376	0.0170
19.5	0.0006	29.44	0.0075	115.6	8.430	14.53	17.34	4.425	0.9306	0.0082	0.6202	0.0210
27.0	0	29.23	0.0071	106.4	8.266	13.98	17.42	4.412	1.051	0.0111	0.5930	0.0175
34.5	0	33.59	0.0101	134.0	9.467	15.91	18.62	5.095	1.754	0.0069	0.6982	0.0195

Table 5.36. ICP-AES data from the Schlepp Pond, May 2004. Samples are from dialyzer #1 and #2.

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
						May 2004, #1						
0.0	0	19.88	0.007	77.05	6.266	10.15	18.630	3.410	0.2290	0	0.8053	0.0092
1.5	0	22.76	0.010	103.1	7.691	10.94	24.220	3.670	0.3138	0.0104	0.7800	0.0106
3.0	0	24.20	0.011	116.3	8.520	11.40	24.430	3.856	0.3674	0.0193	0.8401	0.0198
4.5	0.003	24.86	0.011	130.3	9.200	11.49	22.680	3.984	0.4012	0.0199	0.8991	0.0117
6.0	0.019	25.16	0.013	139.0	9.808	11.47	21.250	4.104	0.4282	0.0132	0.9395	0.0150
7.5	0.017	25.06	0.013	141.3	9.756	11.28	20.930	4.216	0.4788	0.0109	0.8898	0.0316
9.0	0.030	24.96	0.013	146.1	10.03	11.13	20.850	4.476	0.4169	0.0285	0.8828	0.0318
10.5	0.019	24.87	0.013	146.0	10.43	10.94	21.600	4.476	0.5856	0.0272	0.8706	0.0174
13.5	0	24.22	0.011	134.4	10.45	10.45	22.830	4.090	0.9030	0.0203	0.7936	0.0187
21.0	0	23.54	0.010	108.3	8.328	10.16	20.190	3.363	0.9179	0.0150	0.6955	0.0116
28.5												
36.0	0	29.27	0.0131	152.7	9.292	12.70	22.250	4.375	1.1390	0.0221	0.6957	0.0134
						May 2004, #2						
-1.5	0.0029	19.71	0.0043	41.24	6.770	11.210	11.140	3.967	0.1103	0.0214	3.602	0.0198
0.0	0	23.44	0.0081	97.93	9.256	12.620	15.690	4.652	0.3317	0.0120	0.7786	0.0120
1.5	0.0020	28.33	0.0118	132.6	11.75	14.810	21.700	5.702	0.7104	0.0192	0.9043	0.0152
3.0	0	29.55	0.0117	132.6	11.70	14.840	24.590	5.479	0.8164	0.0240	0.8600	0.0114
4.5	0	30.20	0.0104	126.1	11.91	14.750	27.940	5.478	1.054	0.0263	0.8437	0.0135
6.0	0	29.93	0.0099	119.6	12.06	14.350	28.580	5.487	1.196	0.0097	0.8306	0.0142
7.5	0	29.08	0.0096	114.5	11.99	13.860	28.050	5.496	1.276	0.0202	0.8325	0.0115
9.0	0	28.21	0.0092	107.2	12.40	13.470	26.640	5.685	1.249	0.0178	0.7908	0.0096
12.0	0	26.71	0.0083	100.7	11.99	12.600	24.480	5.569	1.410	0.0205	0.7865	0.0121
19.5	0	24.84	0.0091	100.6	10.15	11.380	20.330	4.833	1.283	0.0184	0.7237	0.0089
27.0	0	26.98	0.0110	120.4	10.86	11.890	19.860	4.428	1.360	0.0208	0.7693	0.0095
34.5	0	34.26	0.0144	166.1	14.61	15.110	23.580	5.757	1.188	0.0106	0.9426	0.0123

Table 5.37. ICP-AES data from the Schlepp Pond, May and June 2004. Samples are from dialyzer #3 (May) and #15 (June).

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
						May 2004, #3						
0.0	0.0000	25.62	0.0094	113.0	9.513	13.21	20.99	4.080	0.2877	0.0185	1.313	0.0192
1.5	0.0003	27.89	0.0102	116.5	10.16	13.98	23.39	4.180	0.4519	0.0138	1.301	0.0119
3.0	0.0053	29.12	0.0107	121.7	10.91	14.56	22.95	4.366	0.6092	0.0157	1.333	0.0135
4.5	0.0000	30.00	0.0104	126.1	11.21	14.74	25.77	4.466	0.6852	0.0113	1.396	0.0136
6.0	0.0205	29.66	0.0121	145.8	11.56	14.66	22.47	4.647	0.5534	0.0247	1.568	0.0305
7.5	0.0324	29.73	0.0134	157.0	11.94	14.55	20.78	4.718	0.4402	0.0130	1.575	0.0514
9.0	0.0063	29.77	0.0140	153.1	11.95	14.25	20.81	4.672	0.4333	0.0309	1.527	0.0173
10.5	0.0025	29.58	0.0133	150.8	11.42	13.75	22.18	4.562	0.4685	0.0225	1.482	0.0156
13.5	0.0026	27.86	0.0123	138.8	11.25	12.73	23.77	4.496	0.7521	0.0207	1.371	0.0215
21.0	0.0000	24.85	0.0096	115.2	9.953	11.10	23.48	3.982	1.2050	0.0191	1.209	0.0105
28.5	0.0000	26.11	0.0104	118.3	9.029	11.46	23.25	3.918	1.1320	0.0184	1.220	0.0100
36.0	0.0000	29.60	0.0121	135.5	9.781	13.19	21.73	4.639	0.8174	0.0182	1.200	0.0130
						June 2004, #15						
-1.5	0.0047	9.583	0.0008	4.050	2.339	4.434	12.00	1.698	0.0736	0.0088	3.275	0.0240
0.0	0.0002	11.00	0.0014	12.43	2.884	4.891	15.83	1.760	0.1592	0.0021	1.293	0.0027
1.5	0	13.61	0.0049	36.40	4.651	6.202	11.90	3.189	0.4888	0.0121	0.4087	0.0056
3.0	0	15.45	0.0043	43.33	6.681	7.319	11.31	2.717	0.7783	0.0181	0.4040	0.0060
4.5	0	17.21	0.0047	54.74	9.774	8.739	13.28	4.979	0.9055	0.0214	0.4728	0.0052
6.0	0	21.34	0.0080	90.06	13.19	11.08	18.95	3.975	1.091	0.0288	0.5726	0.0093
7.5	0.0004	26.19	0.0110	115.6	15.35	13.44	25.06	5.111	1.442	0.0307	0.6993	0.0088
9.0	0	30.28	0.0120	126.1	16.37	15.09	29.08	5.522	1.425	0.0309	0.7348	0.0122
12.0	0	32.23	0.0126	135.6	17.32	15.53	30.72	5.916	1.694	0.0305	0.7759	0.0126
19.5	0	28.20	0.0112	122.7	13.39	12.79	33.39	4.303	1.776	0.0266	0.6375	0.0175
27.0	0	26.54	0.0095	108.2	8.314	11.44	26.84	4.019	1.801	0.0333	0.6067	0.0140
34.5												

Table 5.38. ICP-AES data from the Schlepp Pond, June 2004. Samples are from dialyzer #16 and #17.

Dpeth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
						June 2004, #16						
0.0	0.0016	10.28	0.0013	7.505	2.714	4.693	10.95	1.941	0	0	1.908	0.0086
1.5	0.0059	10.02	0.0021	17.83	3.144	4.691	9.919	1.968	0.0018	0.0026	0.6882	0.0003
3.0	0.0066	10.83	0.0033	**32.16**	3.915	5.122	11.56	2.166	0.0525	0	0.3903	0.0046
4.5	0.0083	13.96	0.005	52.59	5.5	6.719	15.33	2.622	0.0367	0	0.4947	0.0138
6.0	0	18.17	0.0063	71.43	6.854	9.141	20.19	3.21	0.3243	0.0113	0.6363	0.0073
7.5	0	21.6	0.0076	89.13	8.102	11.05	23.45	3.794	0.5072	0.0021	0.7177	0.0088
9.0	0	22.58	0.0075	91.19	8.505	11.4	23.83	4.045	0.5987	0.0102	0.7043	0.009
10.5	0	22.92	0.0075	89.28	8.49	11.31	22.95	4.141	0.6356	0.0011	0.6703	0.0059
13.5	0	22.89	0.0078	91.83	8.678	11.01	20.83	4.292	0.7328	0.0061	0.6682	0.0058
21.0	0	23.91	0.0082	101.5	10.08	10.99	22.24	4.507	1.639	0.0173	0.699	0.0084
28.5	0	28.07	0.01	120.4	13.93	13.82	28.8	5.258	1.018	0.0164	0.7883	0.0082
36.0	0.0021	31.82	0.0116	138.4	15.19	16.43	28.37	6.434	0.5693	0.0168	0.9743	0.0143
						June 2004, #17						
1.5	0.0037	11.78	0.0034	**36.01**	3.995	5.41	17.9	2.768	0.1652	0.011	0.3148	0.0051
3.0	0.0030	15.79	0.0054	61.61	5.147	7.612	19.94	2.451	0.4799	0.0014	0.4849	0.0043
4.5	0.0000	19.99	0.0077	84.75	6.62	9.769	21.54	2.897	0.6456	0.0171	0.6001	0.0133
6.0	0.0000	22.7	0.0085	96.12	8.379	11.28	22.84	4.987	0.8735	0.0199	0.6074	0.0077
7.5	0.0000	24.09	0.0091	107	9.503	11.94	23.49	3.921	0.9808	0.0206	0.6455	0.0089
9.0	0.0000	24.29	0.0095	107.9	9.543	11.81	23.44	4.034	1.035	0.0253	0.6138	0.0112
10.5	0.0000	25.48	0.0097	112.9	10.07	12.42	23.64	4.461	0.9547	0.0207	0.6318	0.0102
12.0	0.0000	25.78	0.0112	123.8	10.39	12.67	24.18	4.569	0.9895	0.0228	0.663	0.0152
15.0	0.0000	25.62	0.0102	118.9	9.364	12.14	25.67	4.228	0.9973	0.0143	0.696	0.0131
22.5	0.0000	26	0.0097	110.2	9.202	11.67	29.74	5.333	1.2	0.0327	0.6427	0.0282
30.0	0.0000	28.92	0.012	133.9	12.02	13.54	27.02	5	1.014	0.0315	0.7439	0.0242
37.5												

Table 5.39. ICP-AES data from the Schlepp Pond, August 2004. Samples are from dialyzer #2 and #8.

Depth	Element (mg L^{-1})										
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
					August 2004, #2							
-3.0	0.0553	16.77	0.0037	140.0	4.905	7.192	21.60	1.807	0.2159	0.0113	0.5371	0.0134
-1.5	0.0623	18.39	0.0040	157.2	5.999	8.149	21.86	2.102	0.2508	0.0033	0.6612	0.0157
0.0	0.0728	19.60	0.0047	172.7	6.786	8.674	21.84	2.312	0	0	0.7354	0.0186
1.5	0.0728	20.72	0.0049	177.7	7.604	9.614	21.08	2.759	0.5708	0.0066	0.7967	0.0256
3.0	0.0392	23.64	0.0047	172.5	7.760	11.20	21.13	3.047	0.7882	0.0180	0.8532	0.0258
4.5	0.0177	25.90	0.0048	164.8	8.063	12.31	22.50	3.408	0.8300	0.0197	0.8545	0.0201
6.0	0.0198	27.17	0.0045	158.2	8.312	12.78	24.03	3.639	0.7674	0.0170	0.8589	0.0634
7.5	0.0070	27.46	0.0039	146.7	8.943	12.92	25.77	3.848	0.9244	0.0135	0.7816	0.0158
10.5	0	26.79	0.0030	121.5	9.993	11.97	27.06	4.120	1.160	0.0067	0.6833	0.0341
18.0	0	26.45	0.0035	117.0	11.92	11.84	28.36	4.543	1.276	0.0097	0.6383	0.0175
25.5	0	27.77	0.0041	153.4	16.74	13.64	28.86	5.377	1.165	0.0181	0.7619	0.0200
33.0	0.0042	28.91	0.0039	155.6	16.83	14.58	26.38	5.916	1.009	0.0160	0.7764	0.0201
					August 2004, #8							
1.5	0.0853	20.62	0.0043	160.6	4.913	8.965	22.69	2.207	0.4142	0.0175	0.6391	0.0388
3.0	0.0640	23.58	0.0045	168.0	5.005	10.60	22.94	2.655	0.6801	0.0177	0.6996	0.0269
4.5	0.0470	28.49	0.0046	166.6	5.618	13.24	24.55	3.066	0.8282	0.0144	0.7778	0.0308
6.0	0.0351	31.03	0.0039	156.9	7.068	14.42	25.42	3.446	0.9428	0.0100	0.7766	0.0212
7.5	0.0190	32.98	0.0039	151.7	9.380	15.84	25.36	3.928	1.167	0.0067	0.7450	0.0170
9.0	0.0072	33.62	0.0037	149.7	10.90	16.62	24.88	4.172	1.349	0.0138	0.7814	0.0183
10.5	0.0010	34.13	0.0040	149.7	10.79	16.62	25.04	4.314	1.403	0.0164	0.7724	0.0162
12.0	0.0007	33.45	0.0035	152.4	10.89	16.14	24.99	4.362	1.467	0.0116	0.7854	0.0175
15.0	0	32.99	0.0041	149.9	11.15	15.60	23.37	4.725	1.406	0.0101	0.7414	0.0182
22.5	0.0037	27.99	0.0040	144.5	11.32	12.92	24.12	4.517	1.449	0.0174	0.7141	0.0164
30.0	0.0015	25.90	0.0033	128.6	10.71	11.68	24.59	4.601	1.757	0.0087	0.6222	0.0171
37.5	0.0032	26.72	0.0031	123.4	8.915	11.23	18.84	4.523	1.670	0.0158	0.6408	0.0240

Table 5.40. ICP-AES data from the Schlepp Pond, August and November 2004. Samples are from dialyzer #12 (August) and #4 (November).

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
						August 2004, #12						
0.0	0.0432	19.64	0.0043	158.00	6.642	8.628	22.810	2.142	0.2584	0.0127	0.6549	0.0159
1.5	0.0328	22.07	0.0045	156.90	7.840	9.721	21.530	2.515	0.6186	0.0131	0.7013	0.0353
3.0	0.0395	25.01	0.0043	144.30	8.798	10.930	20.710	2.928	0.8363	0.0105	0.6759	0.0184
4.5	0.0296	25.89	0.0039	145.30	9.004	11.400	20.700	3.241	1.1280	0.0098	0.6821	0.0275
6.0	0.0151	26.74	0.0039	141.90	9.373	11.790	20.920	3.406	1.1570	0.0150	0.7211	0.0403
7.5	0.0051	26.95	0.0037	141.00	9.290	11.910	21.400	4.112	1.2150	0.0195	0.6985	0.0375
9.0	**0**	27.11	0.004	139.00	9.444	12.110	21.540	3.771	1.2790	0.0140	0.6554	0.0149
10.5	0.0026	26.86	0.0036	140.00	9.138	11.910	20.940	3.837	1.4140	0.0147	0.6641	0.0164
13.5	**0**	26.7	0.0036	127.50	9.127	11.930	20.620	4.461	1.4770	0.0153	0.6202	0.0146
21.0	0.0386	28.99	0.0045	171.70	10.930	13.210	22.120	5.164	1.4040	0.0109	0.7289	0.0171
28.5	**0**	26.5	0.0032	130.40	9.575	11.530	23.080	4.559	1.7390	0.0074	0.5727	0.0164
36.0	0.0066	28.38	0.0036	146.50	10.820	12.780	21.420	5.100	1.4780	0.0135	0.6850	0.0166
						November 2004, #4						
1.5	0.014	23.180	0.006	145.300	11.800	9.576	30.240	4.008	0.793	0.008	0.877	0.012
3.0	0.011	28.820	0.007	168.700	13.240	11.570	37.270	4.424	0.929	0.017	0.937	0.026
4.5	0.016	34.360	0.009	187.800	17.640	13.640	44.310	5.505	1.339	0.017	0.927	0.027
6.0	0.012	38.140	0.009	**199.700**	19.850	15.220	49.290	6.679	1.594	0.000	0.908	0.020
7.5	0.012	41.090	0.011	216.600	22.770	16.610	50.430	7.984	1.723	0.000	0.957	0.018
9.0	0.009	41.950	0.011	229.800	25.760	17.550	52.480	9.143	1.789	0.000	0.999	0.021
10.5	0.016	43.660	0.012	241.600	28.310	18.380	54.480	9.992	1.803	0.000	1.055	0.018
12.0	0.014	44.720	0.014	247.600	28.290	18.940	53.450	10.370	2.033	0.000	1.125	0.055
15.0	0.011	44.530	0.014	246.800	24.690	18.390	48.360	10.110	2.025	0.000	1.106	0.018
22.5	*0.011*	*47.710*	*0.005*	*247.600*	*18.720*	*19.140*	*49.280*	*9.874*	*1.701*	*0.002*	*1.089*	*0.019*
30.0	0.014	45.010	0.006	232.000	17.730	18.730	43.520	9.181	2.302	0.021	1.319	0.095

Table 5.41. ICP-AES data from the Schlepp Pond, November 2004. Samples are from dialyzer #5 and #6.

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
					November 2004, #5							
1.5	0.020	27.73	0.010	177.1	14.91	11.55	31.30	5.788	1.014	0.018	0.9534	0.0159
3.0	0.017	32.74	0.012	200.4	17.64	13.61	34.18	6.882	1.200	0.000	1.057	0.0105
4.5	0.018	37.17	0.014	223.6	19.56	15.54	35.91	7.852	1.258	0.000	1.195	0.0138
6.0	0.024	41.38	0.015	248.7	23.02	17.79	36.64	9.155	1.478	0.000	1.365	0.0186
7.5	0.020	43.68	0.016	264.3	24.40	18.60	36.60	10.05	1.430	0.000	1.465	0.0222
9.0	0.023	45.83	0.017	281.0	25.98	19.32	36.41	10.83	1.386	0.000	1.544	0.0211
10.5	0.020	46.36	0.020	294.1	26.17	19.74	36.04	11.18	1.526	0.000	1.652	0.0212
12.0	0.029	48.05	0.019	308.3	27.39	20.49	36.04	11.94	1.437	0.000	1.737	0.0203
15.0	0.041	51.77	0.023	331.7	29.36	21.78	36.82	13.60	1.342	0.000	1.928	0.0285
22.5	0.035	58.77	0.021	332.6	32.71	24.14	43.94	15.11	2.122	0.000	1.878	0.0329
30.0	0.027	56.11	0.018	317.0	31.36	22.18	57.34	14.40	2.926	0.000	1.682	0.0197
37.5	0.018	44.99	0.014	264.8	28.69	17.31	68.32	9.243	1.935	0.000	1.338	0.0178
					November 2004, #6							
-3.0	0.015	30.04	0.009	190.8	19.43	12.39	35.50	5.661	1.164	0.018	0.9778	0.0209
-1.5	0.015	34.07	0.009	194.1	19.65	14.29	37.06	6.335	1.200	0.024	0.9709	0.0331
0.0	0.008	35.93	0.009	197.1	21.71	15.40	38.70	6.652	1.335	0.020	0.9301	0.0263
1.5	0.009	37.45	0.009	197.6	21.30	16.14	39.20	6.649	1.400	0.025	0.9535	0.0241
3.0	0.012	37.50	0.011	210.5	22.63	16.41	38.27	7.041	1.579	0.000	1.0380	0.0277
4.5	0.009	37.94	0.011	213.7	22.84	16.60	37.94	7.378	1.705	0.000	1.0820	0.0362
6.0	0.006	38.20	0.011	207.8	21.20	16.87	39.07	7.403	1.712	0.000	1.0480	0.0152
7.5	0.012	38.14	0.010	200.6	19.11	16.98	39.98	7.424	1.684	0.000	0.9909	0.0140
10.5	0.003	36.86	0.009	184.6	16.52	16.43	39.29	7.474	1.706	0.034	0.8911	0.0435
18.0	0.006	33.23	0.007	157.2	12.94	14.42	31.62	6.824	1.921	0.027	0.6975	0.0310
25.5	0.007	31.57	0.006	150.8	12.37	13.52	26.46	6.754	2.097	0.022	0.6237	0.0217
33.0	0.004	43.24	0.011	227.0	20.20	18.67	43.42	8.114	2.373	0.007	0.4311	0.0012

Table 5.42. ICP-AES data from the Schlepp Pond, June 2005. Samples are from dialyzer #1 and #5.

Depth	Element (mg L^{-1})										
(cm)	As	Ca	Cd	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
					June 2005, #1						
-1.5	0.0074	28.99	0.0027	78.48	5.768	20.75	15.83	2.883	0.9493	0.0167	0.5812	0.0146
0.0	0.0129	27.96	0.0019	68.78	6.628	21.15	15.87	3.119	0.7952	0.0205	0.5220	0.0149
1.5	0.0083	24.88	0.0029	70.17	7.111	19.11	15.25	3.529	0.9664	0.0090	0.5497	0.0130
3.0	0.0047	21.92	0.0026	77.18	7.251	16.21	14.88	3.701	1.111	0.0139	0.5372	0.0190
4.5	0.0103	19.44	0.0023	79.05	7.133	13.04	14.54	3.817	1.140	0.0129	0.5209	0.0147
6.0	0.0092	18.36	0.0025	82.71	6.887	10.94	14.93	3.846	1.111	0.0168	0.5523	0.0158
7.5	0.0094	18.17	0.0027	84.69	6.844	9.808	15.69	3.769	0.8493	0.0097	0.5571	0.0143
9.0	0.0129	18.54	0.0025	84.93	6.591	9.398	15.57	3.714	0.7379	0.0195	0.5576	0.0144
12.0	0.0159	19.91	0.0027	85.40	6.385	9.728	16.41	3.803	1.276	0.0185	0.5618	0.0142
19.5	0.0094	22.75	0.0033	91.08	6.871	10.75	17.56	3.862	1.234	0.0140	0.5466	0.0198
27.0	0.0057	21.29	0.0002		7.090	11.17	12.29	7.828	0.0144	0.0144	0.5175	0.1019
34.5	0.0106	26.82	0.0035	107.3	8.005	12.48	14.24	4.343	1.651	0.0149	0.5961	0.0197
					June 2005, #5						
-1.5	0.0120	35.61	0.0036	117.0	9.576	24.30	22.10	4.520	1.841	0.0200	0.8030	0.0282
0.0	0.0046	32.22	0.0043	112.5	10.30	22.19	21.27	5.105	1.933	0.0242	0.7584	0.0256
1.5	0.0019	30.18	0.0034	123.9	11.10	20.16	21.74	5.577	1.698	0.0204	0.7447	0.0180
3.0	0.0100	29.50	0.0036	120.5	12.03	19.69	21.37	7.290	2.096	0.0268	0.7114	0.0489
4.5	0.0070	26.58	0.0039	132.5	9.951	14.74	20.82	5.929	2.100	0.0280	0.7305	0.0256
6.0	0.0082	25.95	0.0043	129.9	12.92	14.95	21.51	9.935	2.626	0.0276	0.7269	0.0243
7.5	0.0092	24.08	0.0048	130.4	9.920	12.21	20.82	7.478	2.211	0.0239	0.6816	0.0260
9.0	0.0086	25.18	0.0041	133.8	13.48	13.08	21.63	12.76	3.804	0.0221	0.7346	0.0279
12.0	0.0064	24.60	0.0040	120.0	7.773	11.62	19.80	5.630	1.828	0.0163	0.6737	0.0176
19.5	0.0083	25.52	0.0037	118.0	6.741	11.74	19.61	4.554	1.582	0.0201	0.6562	0.0207
27.0	0.0168	27.43	0.0040	120.8	6.898	12.62	19.16	4.668	1.939	0.0165	0.6764	0.0194
34.5	0.0140	30.23	0.0047	130.0	7.275	14.24	18.51	5.087	2.116	0.0241	0.6358	0.0252

Table 5.43. ICP-AES data from the Schlepp Pond, June 2005. Samples are from dialyzer #7.

Depth	Element (mg L^{-1})											
(cm)	As	Ca	Cd 7	Fe	K	Mg	Mn	Na	P	Pb	S	Zn
					June 2005, #7							
0.0	0.0103	24.24	0.0037	113.5	7.453	12.43	19.59	4.315	1.468	0.0107	0.6633	0.0261
1.5	0.0102	24.12	0.0036	110.0	7.282	12.08	19.26	4.172	1.332	0.0147	0.6341	0.0226
3.0	0.0112	23.32	0.0037	104.9	6.962	11.44	18.76	3.935	1.187	0.0232	0.6035	0.0276
4.5	0.0103	23.71	0.0033	104.0	7.318	11.61	18.90	4.036	1.173	0.0116	0.6162	0.0238
6.0	0.0213	23.81	0.0035	106.0	7.172	11.62	18.66	3.992	1.354	0.0105	0.6299	0.0168
7.5	0.0048	24.24	0.0028	103.9	7.347	11.74	18.52	4.030	1.367	0.0195	0.6372	0.0164
9.0	0.0140	24.30	0.0032	101.5	7.303	11.67	18.40	3.980	1.138	0.0215	0.6009	0.0261
10.5	0.0092	24.77	0.0034	104.2	7.374	11.94	18.49	4.021	1.176	0.0203	0.6031	0.0173
13.5	0.0101	25.48	0.0034	102.3	7.649	12.01	17.51	4.089	1.363	0.0223	0.5968	0.0193
21.0	0.0066	26.24	0.0032	100.3	8.213	12.25	14.29	4.288	1.293	0.0190	0.5657	0.0247
28.5	0.0130	27.54	0.0027	98.70	8.389	12.17	11.93	4.163	1.321	0.0273	0.5377	0.0204
36.0	0.0123	29.13	0.0032	112.8	9.099	13.48	11.70	4.978	1.316	0.0141	0.5732	0.0169

Table 5.44. ICP-MS data from the Schlepp Pond, June 2004. Samples are from dialyzer #14.

Depth	Element (µg L^{-1})					
Depth	As	Cd	Cu	Ni	Pb	Zn
			June 2004, #14			
0.0	0.73890	0	0	1.93600	1.1910	72.620
1.5	4.8910	0	0	1.32300	1.1940	13.010
3.0	9.7840	0	0.74010	1.37900	1.1450	11.590
4.5	13.150	0	0	1.04800	0	5.3450
6.0	4.3300	0	0	0.72990	1.1970	6.0780
7.5	1.9870	0	0	0.97290	1.5650	8.2000
9.0	2.0410	0	0	0.83210	1.4680	8.2900
10.5	1.0110	0	0	0.88470	3.5410	15.810
13.5	1.6580	0	0.93900	1.1930	3.5140	11.890
15.0	1.5170	0	0	1.1590	0	11.490
21.0	5.5060	0	0	1.3760	1.2860	9.7740
28.5	1.7390	0	1.03400	1.0860	3.2210	11.010
36.0	1.8260	0	0.69040	1.6980	11.710	17.600

Table 5.45. ICP-MS data from the Schlepp Pond, June 2005. Samples are from dialyzer #4 and #12.

Depth (cm)	Element (µg L^{-1})					
	As	Cd	Cu	Ni	Pb	Zn
			June 2005, #4			
0.0	2.8960	0.42930	0.50260	1.6890	1.1560	4.2870
1.5	1.2650	0.37860	0.65100	1.5320	1.1660	4.7220
3.0	0	0.37580	0.63240	1.1890	0.9623	5.6200
4.5	0	0.41830	0.69930	1.0740	1.2070	3.7510
6.0	0	0.49510	0.69970	1.1030	1.6030	8.1280
7.5	0	0.35150	0.93020	0.98730	1.3960	7.6590
9.0	0	0.25470	0.59450	0.89220	1.4620	6.3640
10.5	0.78520	0.28910	0.78910	1.0550	2.6330	15.240
13.5	1.0090	0.34530	0.64470	0.90730	2.1460	8.3000
21.0	2.5370	0.24810	1.03400	1.1530	3.4280	12.300
28.5	1.2850	0.29770	1.37300	1.1790	10.100	17.720
36.0	0	0.14470	0.87600	1.3150	2.8410	8.7780
			June 2005, #12			
0.0	0	0.08211	0.79310	0.96760	1.9540	6.7860
1.5	0	0.22790	0.74470	0.97710	0.96860	7.5760
3.0	0	0.17260	0.82590	0.99240	7.2290	18.880
4.5	0.91540	0.14400	0.72680	0.90880	3.2560	10.480
6.0	0	0.27950	0.79840	0.85620	2.3030	8.8580
7.5	0	0.15040	0.59450	0.79990	3.4260	7.0500
9.0	0	0.17620	0.55150	0.83220	1.6850	6.1450
10.5	0	0.27200	0.69660	0.83860	2.8470	12.620
13.5	0	0.22390	0.57510	0.87080	1.6280	5.9060
21.0	0	0.10820	0.57970	0.76740	3.4890	10.940
28.5	0	0.09091	0.60680	0.93020	2.7750	9.6780
36.0	0.94020	0.19320	0.73110	0.84560	3.4130	10.290