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**Trace metal concentrations in recent lacustrine sediments from
the Devils Lake Basin, North Dakota**

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University of Nevada, Reno, 1992

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**Trace Metal Concentrations In Recent Lacustrine Sediments
from the Devils Lake Basin, North Dakota**

A thesis presented in partial
fulfillment of the
requirements for the degree of
Master of Science in
Hydrology/Hydrogeology

by

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August 1992

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Abstract

Elevated concentrations of trace metals in surface water bodies in the northern plains and prairies of the United States and Canada are of great concern to wildlife managers as this region is a very important breeding ground for migratory waterfowl. High trace metal concentrations in fish of the northern plains are also of great concern. The primary source of the metals is suspected to be natural, but detailed studies establishing sources have not been undertaken in the region.

Lake sediments provide a medium in which the historical metal loading to lake basins may be established. The concentrations of As, Cu, Fe, Pb, Se, and Zn in sediment cores from six sites in the Devils Lake Basin, a large closed basin in northeastern North Dakota, have been determined. The purpose of this work is to help establish the primary source of high Hg concentrations in fish from Devils Lake where an important tourist industry is based on fishing. Cores were dated by Pb-210 and Cs-137. Grain size determination, loss on ignition, and Q-mode factor analysis were also undertaken.

Results of this study indicate sedimentary trace metal enrichment has occurred only in Devils Lake proper over the past 60 years. The main cause of this enrichment is a combination of municipal sewage discharges and local vehicular and boat emissions. Cu and Pb concentrations in sediments reached a maximum during the early 1970's, but have most recently returned to near background concentrations. Analysis of cores from other lakes in the Devils Lake

Basin indicate that metal concentrations are not significantly greater than natural background concentrations, however, As, Se, and Pb concentrations are significantly enriched above crustal abundances. The probable source of these elevated metal concentrations is the Pierre Shale, a metal-rich Cretaceous black shale that is an important geologic unit in the region.

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Introduction

The use of lacustrine sediments to recreate historical records of metal deposition, provided sedimentation rates are known, is well established (Galloway and Likens, 1979; Hamilton-Taylor, 1979; Norton, et al, 1981; Davis and Galloway, 1981; El-Sayed, 1982; Wong, et al, 1984; Nriagu and Rao, 1987). Such studies have demonstrated the importance of various anthropogenic activities in increasing trace metal fluxes to the surficial environment. The sources of metal may be of a regional (Galloway and Likens, 1979) or local nature (El-Sayed, 1982). In cases where the sampling can be done so that different pathways for metals entering lakes can be compared, it may be possible to identify a particular source or sources of the anthropogenic trace metal influx (Hamilton-Taylor, 1979).

Lakes and wetlands in the northern plains and prairie of the United States and Canada are important breeding grounds and staging areas for migratory waterfowl. This region accounts for some 50% of the wild ducks produced annually in North America (Smith, et al, 1964). In addition, some of these water bodies are also economically important recreational fisheries. Recent studies have addressed the effect of aquatic trace metal influxes on fish and waterfowl populations (Martin and Hartman, 1984; Greene, et al, 1990; Ruelle, 1991, 1991b; Pawlaski, 1991; U.S. Fish and Wildlife Service, 1991).

Devils Lake (Fig. 1) is a large closed-basin lake in northeastern North Dakota. Recently, mercury concentrations in walleyes, *stizotiedion vitreum*, in Devils Lake

were found to be as high as 1.84 $\mu\text{g/g}$ (North Dakota State Department of Health and Consolidated Laboratories, August 28, 1991). Because of these elevated concentrations of Hg, it was suggested that other trace metals may also be enriched. The primary source of trace metal contamination in the basin is not certain, unfortunately, limited trace metal data is available for the the Devils Lake system. This was the primary motivation for this work.

A number of trace metal sources to the lakes and wetlands in this region have been suggested (May and McKinney, 1981). It is suspected that the Pierre Shale, a metal-rich Cretaceous black shale, could be a major contributor of metal into these aquatic systems (Schultz et al, 1980). Regional coal combustion, agricultural runoff, and emissions from boats and automobiles are also some of many possible anthropogenic trace metal sources (May and McKinney, 1981; Martin and Hartman, 1984).

In this study, six sediment cores from four lakes in the Devils Lake Basin (Fig. 1) were analyzed for As, Cu, Fe, Pb, Se, and Zn concentrations. This was done in order to determine if there are significant anthropogenic sources of these trace metals to Devils Lake, as well as to evaluate the possible sources of the anthropogenic trace metal fraction and the pathways by which the selected trace metals enter Devils Lake and other lakes in the Devils Lake Basin. The Devils Lake Basin should be well suited for this type of study since the lakes in this closed basin are thought to receive a like amount of regional metal influx from the atmosphere. However, local input, especially via runoff varies between the different

water bodies. Complications in interpreting historic metal loadings may arise since in some of the lakes in the Devils Lake Basin, sediments may have been disturbed by wind-induced mixing in addition to problems which arise due to drying of lake beds, farming of dry lake bottoms, variations in sedimentation rate, and variations in water chemistry. The range in sampling locations (Fig. 1) for this study is such that a comparison between the various natural and anthropogenic trace metal inputs and the historic record of development in the Devils Lake Basin and the surrounding region may be made.

Methods

Sampling Methods- Cores were obtained in January of 1992, using the ice cover as a coring platform from six sites (Fig. 1): Morrison Lake, Main Bay, Creel Bay, East Bay, East Devils Lake, and Stump Lake. Ten cm (o.d) polyvinylchloride tubing, washed with soap and rinsed thoroughly with distilled water, was used for coring. Cores were extruded within 4 hours, sectioned into 1 cm or 2 cm intervals, and sample splits sealed in either Whirl-Pak™ polyethylene bags or Falcon™ plastic sample cups. Core sections were kept in cold storage at temperatures below 5 °C for 4 d at the United States Geological Survey-Water Resources Division, Bismarck, North Dakota, until shipment for analysis. Core lengths were: Creel Bay (54 cm), Main Bay (52 cm), Stump Lake (31 cm), East Devils Lake (29 cm), Morrison Lake (25 cm), and East Bay (18 cm).

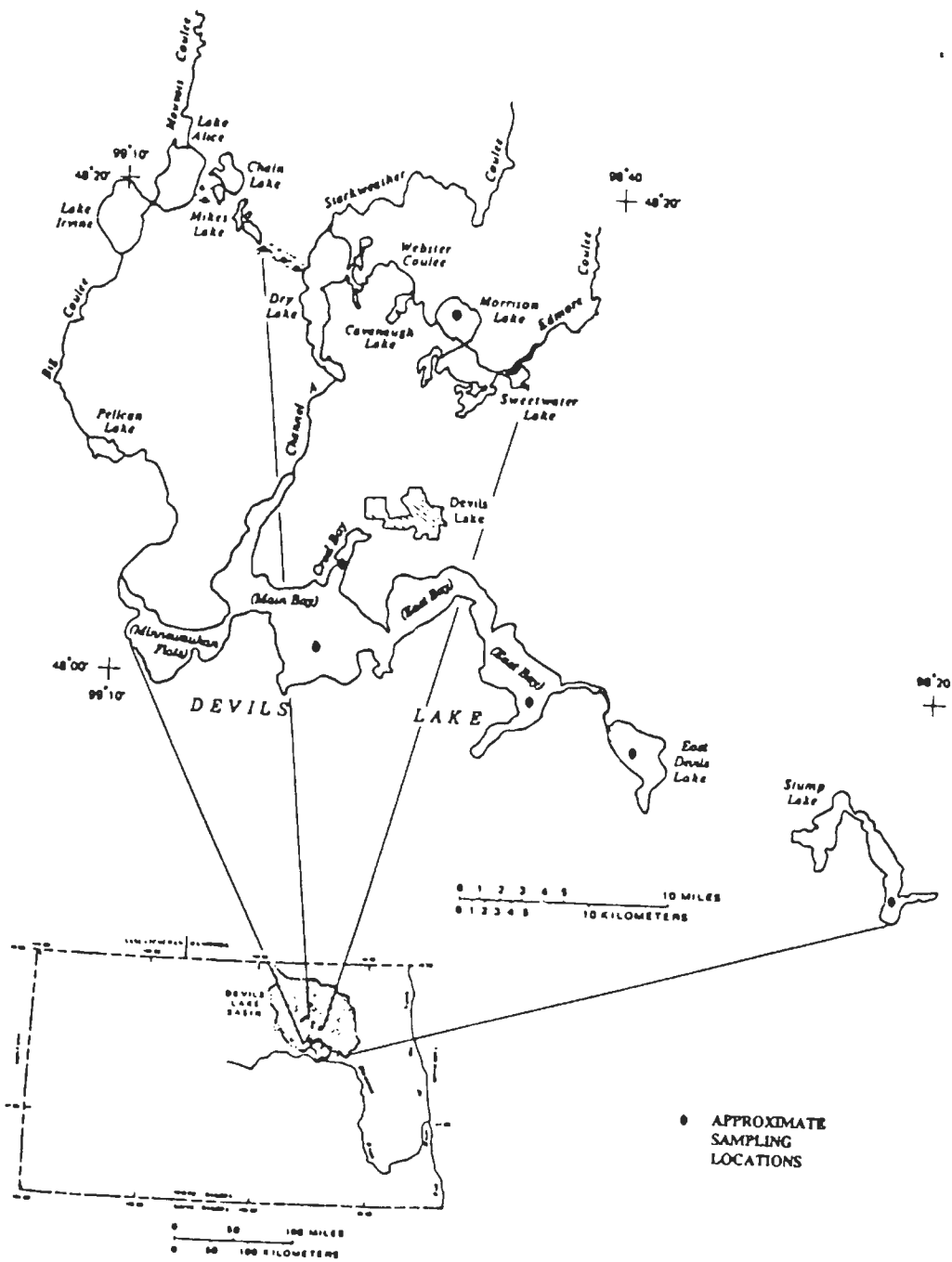


Fig. 1 (Wiche, 1986): Location of Devils Lake Basin and map of sampling sites.

Analytical Methods- All plasticware in which samples came in contact were cleaned by filling with 50% (v/v) reagent grade HCl for 24 hours and rinsing three times with distilled-deionized water. Bottles were then filled with distilled-deionized water until use. Filtering apparatus was cleaned with 50% (v/v) HCl before use and rinsed with distilled-deionized water between filterings. Distilled deionized water was prepared with a Barnstead model A56220 glass still with 8.5 l/hr capacity and Barnstead model D4741 Nanopure™ water filtration system.

Samples for determination of trace metal content and grain size were shipped by air to the University of Nevada within 5 d of core extraction. Immediately upon receipt, samples were prepared in our lab by drying at room temperature under a flowing hood for one to three days. Upon drying, sediments were crushed with a ceramic mortice and pestil that had been well rinsed with distilled-deionized water. Samples were then placed in precleaned air tight plastic vials.

For the determination of trace metal content, between 1.000 and 2.000 grams of sediment was placed in a 60 ml acid cleaned polyethylene Nalgene™ bottle. Thirty ml of 2N HNO₃ were added to the sample and the solution allowed to stand for 24 h with periodic shaking every few hours. This leaching technique extracts as much as 80-85% of the total "environmentally available" metal relative to HF/HNO₃ treatment as determined by previous investigators (Carmody, et al, 1973; Thompson, et al, 1975; Lyons and Fitzgerald, 1980). In this study, Cu, Pb, and Zn concentrations in the cores from Main Bay closely agreed with metal concentrations observed by a previous investigation (Lent, 1992). Samples were

filtered through 55 mm Whatman No. 50 filter papers held in a 250 ml Nalge 300 47 mm filter holder. Leachate samples were finally placed in acid cleaned 30 ml Nalgene™ bottles.

Analysis for all metals was performed at the analytical facilities of the Mackay School of Mines, UNR. Fe, Cu, Pb, and Zn were determined with a Perkin-Elmer P2 Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP). As and Se were determined by a Perkin-Elmer 3100 Atomic Absorption Spectrometer and model MHS10 Hydride Generator. Se was analyzed only on the cores from East Bay and Morrison Lake.

Instrumental variability was determined by splitting three 30 ml samples into nine 10 ml aliquots before analysis. Coefficients of variation were Fe ($\pm 2\%$), As ($\pm 10\%$), Cu ($\pm 2\%$), Pb ($\pm 13\%$), Zn ($\pm 4\%$). Sample variability was determined by leaching two subsamples of three selected sedimentary horizons prior to analysis. Coefficients of variation were Fe ($\pm 4\%$), As ($\pm 7\%$), Cu ($\pm 2\%$), Pb ($\pm 13\%$), Zn ($\pm 3\%$). The results of these experiments indicate that the best precision of our metal analysis were Fe ($\pm 4\%$), As ($\pm 10\%$), Cu ($\pm 2\%$), Pb ($\pm 13\%$), Zn ($\pm 4\%$). No coefficients of variation were determined for Se. Four sample blanks were also run. These blanks were distilled-deionized water which had been processed as a sediment leachate.

Sedimentation Rates- The accurate determination of sedimentation rates is essential to any study where metal loadings are to be calibrated with historical

events. Sedimentation rates for this study were determined at the Skidaway Institute of Oceanography by Clark Alexander. Sediment accumulation rates were determined by producing profiles of total ^{210}Pb activity with depth in the cores. Total ^{210}Pb activity was directly determined by gamma-spectroscopic measurement of its 46.5 keV gamma peak in dried homogenized sediment (Cutshall, et al, 1983). Supported levels of ^{210}Pb from the decay of ^{226}Ra were determined for each depth interval by concurrently measuring the gamma activity of ^{214}Pb and ^{214}Bi , the shortlived granddaughters or ^{226}Ra . If deep sediment mixing (i.e. below the surface mixed layer) is occurring, the calculated sedimentation rate will be a maximum estimate of the actual accumulation rate. Calculated ^{210}Pb rates were verified by measurement of ^{137}Cs activities which were directly determined by gamma-spectroscopic measurement of its 662 keV gamma peak in dry homogenized sediment (Kuehl, et al, 1986).

Grain Size and Loss on Ignition- To determine if the characteristics of metal profiles could in part be explained by sedimentological factors, the Morrison Lake and East Bay cores were analyzed for grain size and loss on ignition. In addition, the East Devils Lake core (0-14 cm) was analyzed for grain size. Samples for grain size determination were prepared by placing approximately 0.1 gram of sediment in a 50 ml beaker and adding 20 ml of 30% H_2O_2 . The samples were left until reaction ceased. The liquid portion of the sample was decanted and 30 ml of distilled water added and the solution agitated. Approximately 1 ml of this

solution was added with a micropipette to 80 ml of Isotone II™ electrolyte solution and two drops of Na-hexametaphosphate surfactant added.

Grain size determinations were done with a Coulter Electronics TAll Multichannel Particle Counter. The 100 μm orifice, which allows for classification of particles from 1.22 μm to 55.29 μm in 16 channels, and a count of 40,000 particles was used. Grain size percentages were then tabulated against sample depth.

Loss on ignition values were determined by placing carefully weighed samples of approximately 1 g in an oven at 1000 °C for 1 h and then weighing again. At this high temperature, all organic matter and most carbonate material is destroyed and water is liberated from clay minerals (e.g. Byers, et al, 1978).

Q-Mode Factor Analysis- To determine a relationship between trace metal concentrations, grain size, and loss on ignition, Q-mode factor analysis (Imbrie, 1963; Jöreskog, et al, 1976) was utilized. Unlike R-mode factor analysis in which interrelationships between variables are determined, the Imbrie Q-mode method defines inter-sample similarity with respect to factors composed of varying proportions of the different constituents (Jöreskog, et al, 1976). The aims of Q-mode analysis are to find the minimum number of end-member assemblages of which the samples may be considered combinations, to specify the compositions of the end-members in relation to the constituents, and to describe each sample in terms of the end-members (Jöreskog, et al, 1976).

In this study, the trace metal concentrations, grain size percentages for the 16

different grain size channels, and loss on ignition for each sample from Morrison Lake, East Bay, and East Devils Lake (0-14 cm) were analyzed with the computer program CABFAC (Klovan and Imbrie, 1971) which was modified by R. Karlin (unpublished).

Description of the Devils Lake Basin

The Devils Lake Basin lies in the glaciated plains, or drift prairie region, of the central lowland province and has a simple morphology with hummocky topography and very little relief (Hobbs and Bluemle, 1987).

The geology of the basin is characterized by a thick (6 to 150 meters) layer of glacial drift overlying Mesozoic and Paleozoic sedimentary rocks (Hobbs and Bluemle, 1987; Bluemle, 1973). The primary component of the drift is sediments derived from the Pierre Shale which was probably derived locally (Bluemle, 1981). As discussed later, this is an important consideration in discussing trace metal concentrations in the Devils Lake Basin. Quaternary lacustrine sediments cover the surface in low lying areas (Hobbs and Bluemle, 1987).

The Pierre Shale contains high concentrations of trace metals including As, Cu, Pb, Se, and Zn (Schultz, 1980). Table 1 presents average metal concentrations from the Pierre Shale (Schultz, 1980). Metal concentrations for bentonitic units of the Pierre Shale, from which some of the samples came, are much higher than

concentrations in the siliceous shale and shale units which make up the bedrock surface under the Devils Lake Basin (Schultz, 1980, Bluemle, 1973).

Elevations in the basin range from approximately 485 meters in the northern part, near the United States-Canada border, to approximately 435 meters at Devils Lake (Hobbs and Bluemle, 1987). Stump Lake (Fig. 1), in a separate subbasin of the Devils Lake Basin, is at an approximate elevation of 423 meters. Ice thrust hills, to the south of Devils and Stump Lakes, separate the Devils Lake Basin from the drainage of the Red River of the North, in which the basin lies (Bluemle, 1981). The surface area of the Devils Lake Basin is approximately 9900 km², including the Stump Lake subbasin which has a surface area of approximately 1000 km² (Mitten, et al, 1968).

Northeastern North Dakota has a semiarid climate with annual precipitation ranging between 26 and 65 cm/yr. Potential evaporation (100 cm/yr) is much higher than precipitation (Kohler, et al, 1959). In the Devils Lake Basin, there are few well defined drainages and most runoff occurs as overland flow and terminates in isolated depressions or sloughs (Wiche, 1986).

Description of Sampling Sites

Morrison Lake- Morrison Lake (Fig. 1) is part of the Chain of Lakes (Ryan and Wiche, 1988), which are a group of shallow, freshwater lakes in the northern part of the Devils Lake Basin. Only during times of high runoff does water flow out of these lakes into Devils Lake through Big Coulee and Channel A (Fig. 1) (Ryan and Wiche, 1988). Morrison Lake is an isolated lake surrounded by agricultural lands and over 1 km from any paved road (Fig. 1).

Devils Lake- Water enters Devils Lake from the northern chain of lakes and the surrounding subbasins primarily through Big Coulee and Channel A (Fig. 1) (Ryan and Wiche, 1988). The latter was constructed in 1979 (Ryan and Wiche, 1988). A lesser amount of water also enters Devils Lake from the area surrounding the city of Devils Lake and via overland flow from drainages adjacent to the lake (Wiche, 1986).

Devils Lake is a long (~ 25 km), shallow chain of brackish lakes containing waters of Na-SO₄ character. The water levels of Devils Lake fluctuate in response to climatic variation (Fig. 2) (Aronow, 1957; Callender, 1968; Fritz et al, 1991; Lent et al, in review). Historic lake levels have varied between 438.5 m in 1867, when lake levels were first recorded by European settlers, and 427.1 m in 1940 (Mitten, et al, 1968). Recent lake levels have ranged between 430 m in 1965 to 435.5 m in 1987 (Callender, 1968; Lent, et al, in review). Depths rarely exceed 10 m and

much of the lake bottom has been dry in the recent past (Jacobson and Engstrom, 1989; Lent, et al, in review). During very low lake levels, exposed lake bottoms have been farmed. Salinity in Devils Lake varies inversely with lake level and generally increases from west to east. In Main Bay, from 1950 to 1986, salinities varied between 2 and 12 mg/g (Engstrom, 1987).

Cores were retrieved from three sites in Devils Lake proper (Fig. 1): Creel Bay, Main Bay, and East Bay.

I. Creel Bay- Creel Bay (Fig. 1) is a narrow wind-protected arm of Devils Lake. The bay is the discharge point for waters emanating from the vicinity of the city of Devils Lake, a city of approximately 7,500 people, and the smaller community of Creel City. At some time in the past, the city has discharged sewage into Creel Bay, but discharge records and information on treatment methods are not available. A sewage treatment plant was constructed in the 1960's.

ii. Main Bay- Unlike Creel Bay, Main Bay (Fig. 1) is wide and unprotected from winds. Stoermer et al (1971) and Jacobson and Engstrom (1989) have demonstrated that wind-induced mixing has significantly disturbed the sedimentary profile in Main Bay. Jacobson and Engstrom (1989) found that the depth of sediment mixing in Main Bay may be as great as 10-12 cm.

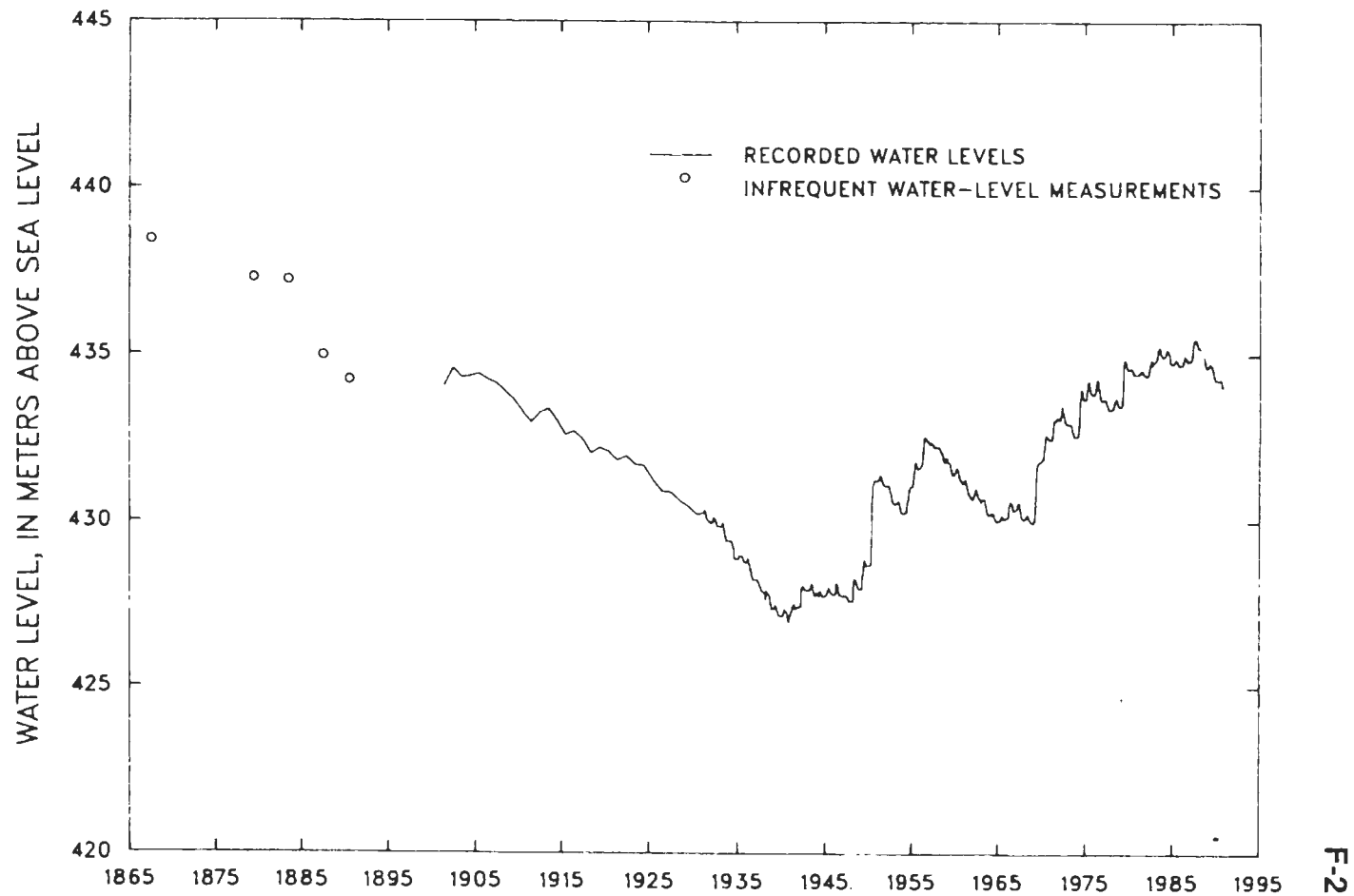


Fig. 2 (Lent, 1992): Water levels of Devils Lake measured between 1867 and 1992.

III. East Bay- East Bay (Fig. 1) is also wide and unprotected from winds. Mitten (et al, 1968) found that East Bay was dry much of the time between 1952 and 1960 and that there was rarely flow from other parts of Devils Lake to East Bay. These authors believed that much of the input of water in East Bay is due solely to direct precipitation as the waters in East Bay had a lower salinity than in the rest of Devils Lake. Since approximately 1970, however, Devils Lake has been above the elevation (>431.8 m) given by Mitten et al (1968) in which water may flow from Main Bay to East Bay, and the salinity today is greater than elsewhere in Devils Lake.

East Devils Lake- Until the 1980's, East Devils Lake (Fig. 1) had probably not received water from East Bay since the lowering of lake levels in the 1930's, and only received water from within the surrounding subbasin. The flow of water between East Bay and East Devils Lake ceased in the summer of 1990. East Devils Lake is deeper than Main Bay and sediments here are probably protected from wind-induced mixing.

Lent (1992) determined that at times, waters in East Devils Lake and Stump Lake (Fig. 1) are isotopically lighter than waters in East Bay indicating that the water in these lakes have undergone less evaporation than those in East Bay. Some water may enter East Devils Lake and Stump Lake via baseflow, but the contributing influence of the nearby shallow aquifers is unknown and may be important. Wiche (1991) determined that there is very little groundwater influx to

Devils Lake, but it is not known if this is true for the other lakes in the Devils Lake Basin including East Devils Lake.

In 1987, salinity in East Devils Lake was approximately 10 mg/g (Lent, et al, in review)

Stump Lake- As mentioned above, Stump Lake is in an isolated subbasin within the Devils Lake Basin. When Devils Lake reaches an elevation of 440.5 m, water flows from Devils Lake to Stump Lake, but this is generally not thought to have occurred since late Wisconsinan time (see Bluemle, 1988). Like Devils Lake, Stump Lake was at its highest recorded elevation when the first european settlers arrived in the Devils Lake Basin (Aronow, 1957). Shortly after 1927, the lake was divided into two seperate bays, due to a decline in lake levels, of which the east bay is more saline (Aronow, 1957).

Stump Lake is by far the most saline of all lakes in the Devils Lake Basin. In 1987, the salinity was approximately 75 mg/g in West Stump Lake and approximately 150 mg/g in East Stump Lake (Lent, et al, in review), from which our core was obtained (Fig. 1).

Results and Discussion

Grain Size and Loss on Ignition- Grain size analyses show that for the cores from Morrison Lake, East Bay, and East Devils Lake, on average, 50% of particles were below 1.6 μm in diameter and 90% were less than 5.6 μm . The coarsest layers were 5-6 cm and 20-21 cm for Morrison Lake and 4-5 cm and 13-14 cm for East Bay. In the core from East Devils Lake, grain size varies considerably more than in the cores from Morrison Lake and East Bay and the intervals (3-4 cm, 7-8 cm, 8-9 cm) were the most coarse.

Loss on ignition ranged from 19 to 33%, which is somewhat less than the combined organic and carbonate content (~ 30-35%) in cores from Main and Creel Bays by Jacobson and Engstrom (1989). These authors found that organic content ranged from ~12 to ~20% while carbonate content ranged from ~10 to ~30%. Recent work shows that for the six sites studied here, the organic carbon content in surface sediments ranged from 4.9 to 9% (Lent, unpublished data, 1992). Carbon content was highest in Devils Lake and lowest in East Bay.

Q-mode Factor Analysis- The factor scores obtained with the program CABFAC are plotted in Figure 3. Scaled Factor plots depict the loading (scaled factor scores in Fig. 3) of each variable within a factor. These plots show that three factors account for 98.7%, 98.0%, and 95.8% of the total variance in the cores from Morrison Lake, East Bay, and East Devils Lake respectively. In all of

the cores, factor 1 contains most of the trace metals, the finest grain fractions (grain size channels are indicated by the numbers 1-16 in Fig 3 with 1 being the finest grain size fraction), and loss on ignition and demonstrates a clear relationship between these variables. Factor 2 is dominated by the coarsest grain fraction which composes less than 5% of the total sediment. The high amount of the total variance accounted for by factor 2 may be misleading since there was a considerable amount of subsample variability in the coarse grain size fraction. In the cores from East Devils Lake and Morrison Lake, factor 3 is controlled by the intermediate grain sizes, but accounts for much less of the combined variance than factor 1. In the core from East Bay, a sporadically high Se concentration at 2-3 cm created a need for a separate Se factor. If this high Se value is discounted, then the plot of factor 3 for the core from East Bay is nearly identical to plots of factor 3 for the cores from Morrison Lake and East Devils Lake. This high Se concentration is discussed later.

Plots of factor loading (factor score in Fig. 3) versus depth for each factor and core are also presented in Figure 3. These profiles may be compared with metal profiles in Figures 5 and 6.

Morrison Lake- The sedimentation rate determined for Morrison Lake is greater than 1 cm/yr. Radionuclide profiles, which were unavailable for this study, suggest that sediments in Morrison Lake have been considerably reworked. It is also probable that this high rate may be due in part, to sediment focusing within the

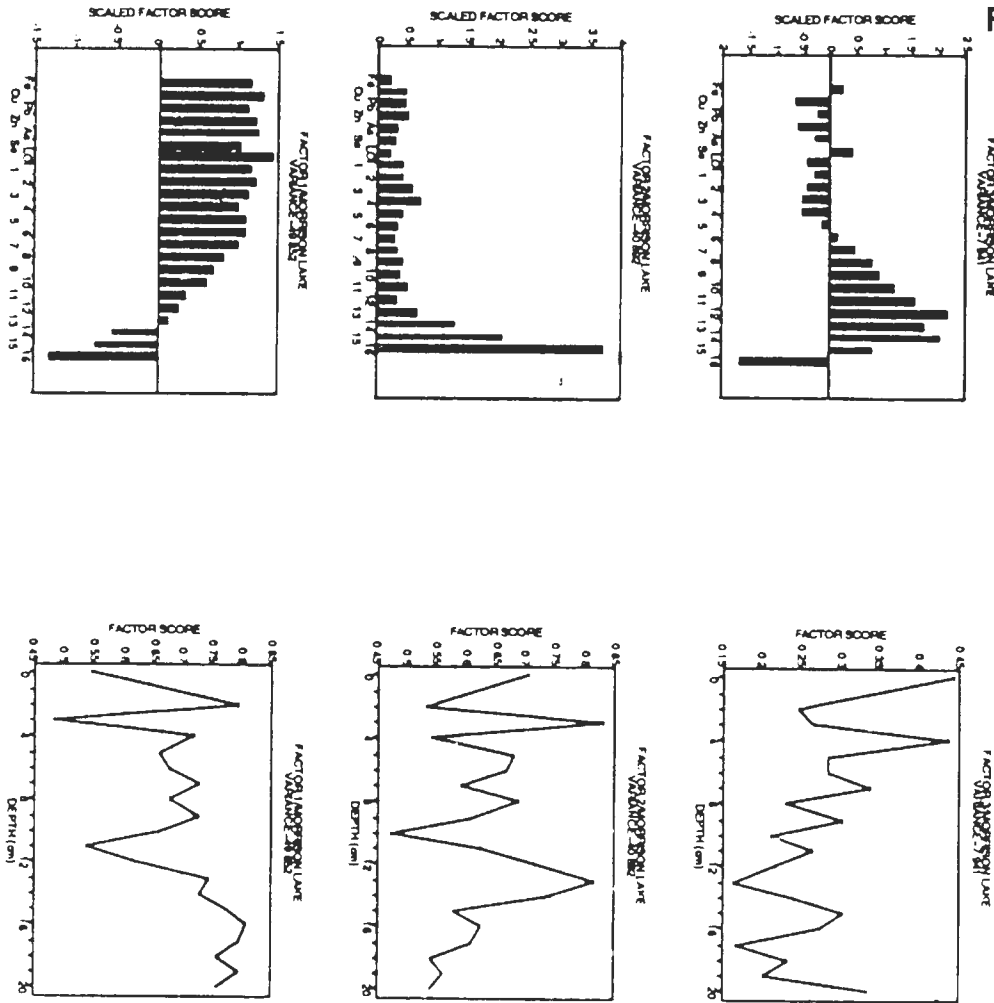


Fig. 3a: Scaled factor plots (top) and factor loadings versus depth for Morrison Lake core.

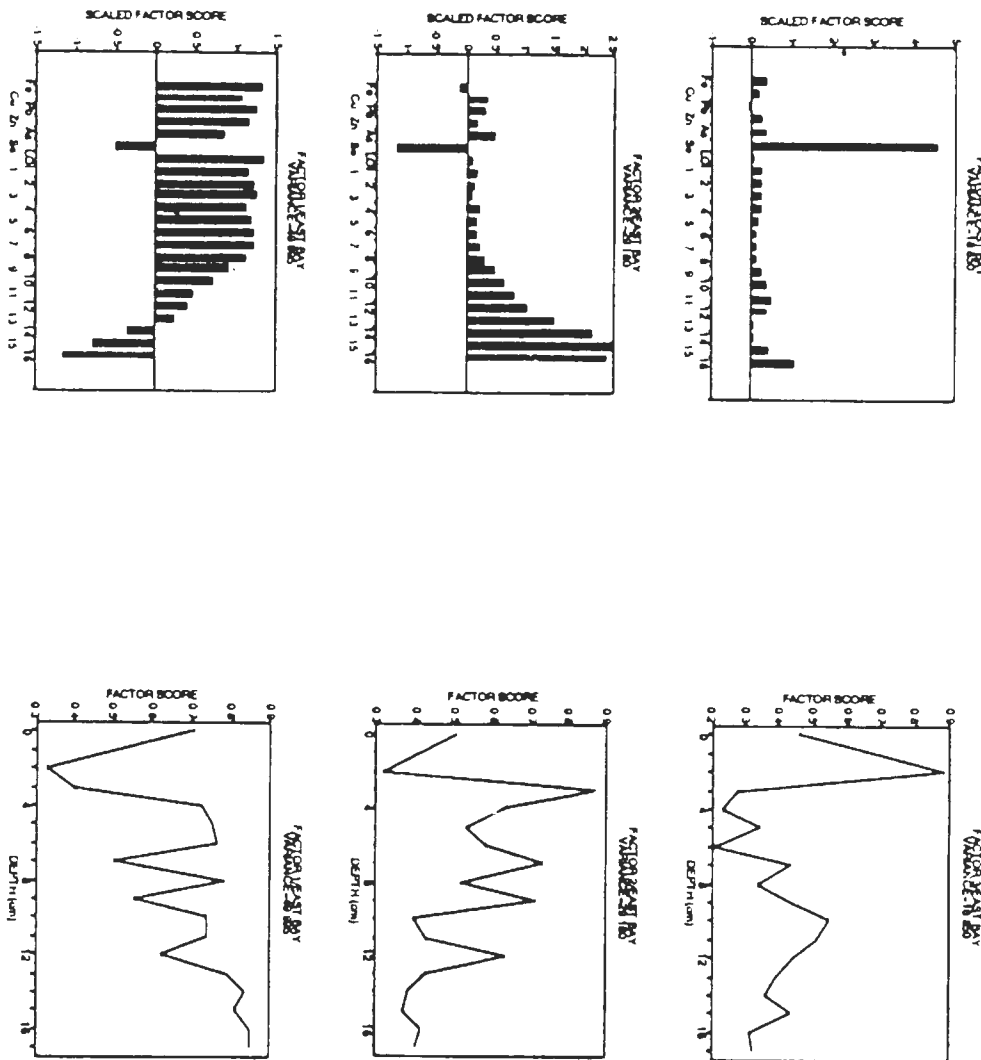


Fig. 3b: Scaled factor plots (top) and plots of factor loading versus depth for East Bay core.

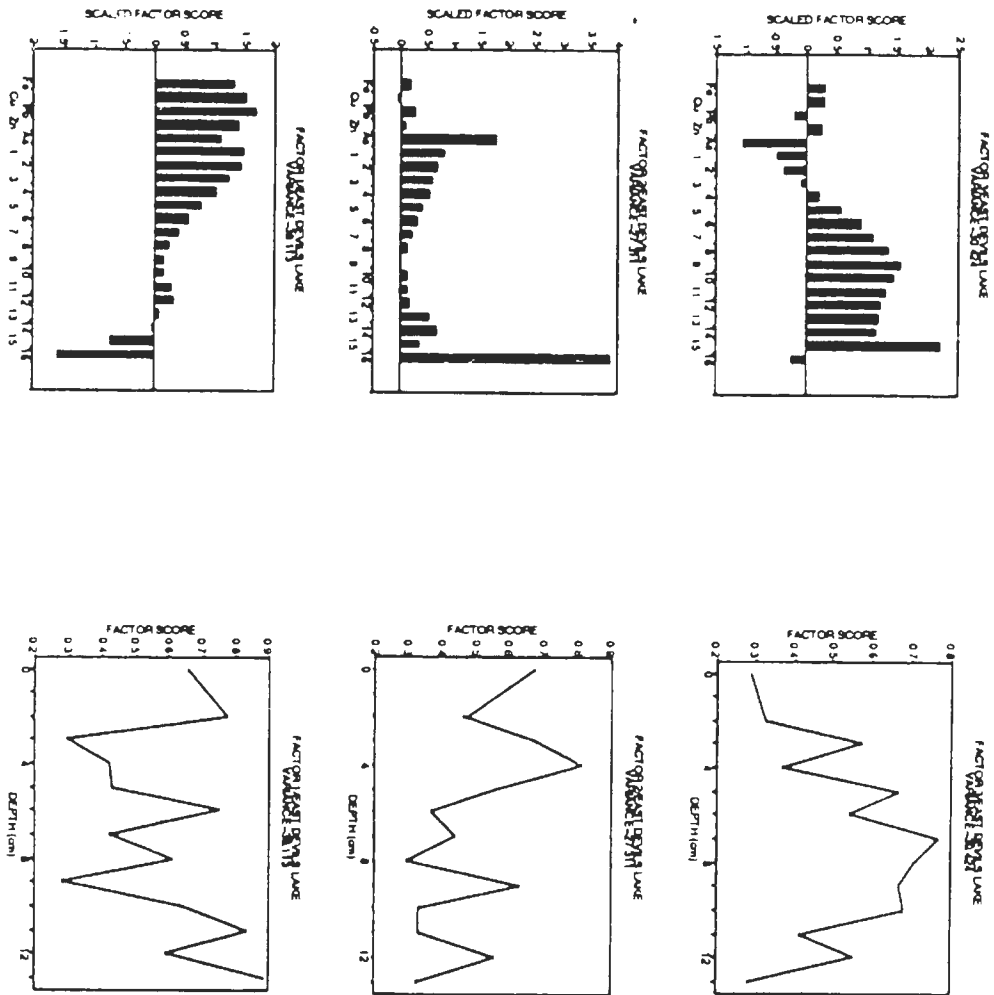


Fig. 3c: Scaled factor plots (top) and plots of factor loading versus depth for East Devils Lake core.

lake and that storms contribute most of the sediments to the lake. In addition, Ryan and Wiche (1988) mention that the channel between Sweetwater Lake (Fig. 1) and Morrison Lake has been dredged at least once, however, the coring site was quite far from the channel inlet.

The effect of benthic organisms and wind on sediment mixing in Morrison Lake is unknown, but it may be substantial, even at such a high sedimentation rate. A large number of genus *Chironomus* larvae were seen at the surface in some cores and burrows seen at depth in most of the cores.

Metal profiles obtained from Morrison Lake show little surface enrichment, yet with such a high sedimentation rate, the core only represent 25 years of deposition as shown in Fig. 5a. Ranges of concentrations and average concentrations for all metals and cores are shown in table 1.

In interpreting the metal profiles, an added complication is the changing levels of the lakes in the Devils Lake Basin. Low lake levels could possibly be reflected in the metal profiles with low concentrations at low lake levels due to minimal detrital input and high lake levels may yield high metal concentrations due to an increased sediment influx. In the terminal lakes in the basin, high metal concentrations could also result, in part, to evapo-concentration and hence the precipitation of soluble metals from solution. In addition, iron fluxes should be proportional to natural fluxes of other metals, but during low lake stages, iron may be more readily mobilized in the sediments than other metals. Iron mobilization occurs as the redox chemistry of the sediments change with depth as soluble Fe^{2+}

diffuses upward or downward in the porewater (Berner, 1980; McKee et al, 1989; Carignan and Lean, 1991).

Although the potential for Fe remobilization exists in lacustrine sediments, we believe that it has been insignificant throughout the Devils Lake system. This is based on two important observations: 1) the relationship between lake level and Fe concentration discussed below and 2) the large amounts of sulfate in the porewaters and hence high rates of sulfate reduction observed in the sediments (Lent, 1992). The production of sulfide via sulfate reduction immobilizes Fe^{2+} in the sediment column limiting its diffusional movement. Lent (1992) has observed dissolved Fe^{2+} in near surface (0-15 cm) pore waters from Devils Lake at concentrations that do not exceed $8.3 \mu\text{M/L}$ at four locations. At one site, he found higher Fe^{2+} concentrations at depth (20-30 cm), but, in general, the Fe^{2+} pore water values are low, with two sites having values less than $2 \mu\text{M/L}$ in the top 15 cm. Therefore, due to removal of dissolved iron as FeS_2 , little remobilization probably occurs.

In Morrison Lake, high lake levels at Devils Lake should be reflective of high flow through the former. In the iron profile (Fig. 4), high iron concentrations correspond to years of high lake level and low iron concentrations correspond to periods of low lake level at Devils Lake (Fig. 2). Loss on ignition percentages (Fig. 4) show a slight inverse relationship with iron concentrations and high loss on ignition may indicate periods of stagnation and/or periods of high primary production at Morrison Lake when precipitation in the Devils Lake Basin is low. At the high sedimentation

rate observed in Morrison Lake, it is doubtful that significant iron remobilization could have occurred as Fe deposition would be much faster than Fe diffusion (Berner, 1980). Comparison of the Fe profile for Morrison Lake and factor plots in Figure 3a reveals no direct relationship, although the scaled factor plots indicate that Fe and the fine grain size fractions correlate.

In order to remove the effect of increased natural flux, and to minimize the effects of changing grain size, metal profiles were normalized to iron concentrations (Fig. 5a). Scaled factor plots shown in Fig. 3a show that iron normalization should work well to minimize the effects of grain size changes as metal concentrations correlate with the fine grain sediment fraction to which many metals are preferentially bound, even if in a particular sample, iron may not correlate to grain size as well as in another sample.

Except for Se, iron normalized trace metal profiles from Morrison Lake (fig. 5a) correlate with one another quite well. Coefficients of variation for the normalized values obtained by taking the geometric mean of the variations for the two attributes are As ($\pm 9\%$), Cu ($\pm 3.0\%$), Pb ($\pm 13\%$), Zn ($\pm 5\%$). Normalized metal profiles do not appear to show enrichment within the time frame demonstrated by the profiles. The highest normalized concentrations of As, Cu, Pb, and Zn generally occur between 19 and 11 cm which corresponds to the years between 1973 and 1981 (shown in Fig. 5a), but the profiles and peaks are not distinct enough to ascertain if the increase is due to anthropogenic sources. Higher than background Pb concentrations, as determined from Creel Bay (Tab. 1), indicate

Table 1: Ranges of trace metal concentrations and average metal concentrations for cores and average metal concentrations in Pierre Shale and soils in northeastern North Dakota

Sampling Site	Metals				
	As	Cu	Pb	Se	Zn
Morrison Lake Ave.	3.19-5.20 4.0	9.0-15.0 11.9	6.4-11.6 9.4	0.094-0.21 0.16	20.2-30.0 24.7
Creol Bay Ave.	0.64-9.85 3.1	10.5-17.9 14.2	3.3-20.5 9.8		21.1-38.5 29.0
Main Bay Ave.	1.74-4.86 3.0	8.9-16.9 12.5	4.7-14.8 8.4		19.7-34.7 26.2
East Bay Ave.	2.47-5.01 3.3	6.1-9.9 8.4	3.3-8.4 6.4	0.00-0.45 0.08	16.2-19.7 18.4
East Devils Lake Ave.	3.32-12.5 6.3	1.5-9.5 11.4	1.7-9.7 5.9		4.5-35.7 23.5
Stump Lake Ave.	2.69-8.12 3.6	4.1-9.4 6.8	3.4-9.2 5.9		8.2-22.4 14.7
Soils	6.5	20	15	1.0	45
Pierre Shale	9.2	28	20	0.74	96

All concentrations in ug/g

Sources: Soils, Shacklette and Boemgen (1984); Shale, Schultz et al (1984)

a possible anthropogenic source of this metal.

Inorganic and organo-arsenicals have been utilized as pesticides and herbicides and many fertilizers contain appreciable As concentrations (Woolser, 1975; Senesi et al, 1979). The normalized As profile (Fig. 5a) does not seem to show the effect of nearby agricultural activities on Morrison Lake. Arsenic concentrations are not particularly high, as well.

Creel Bay- Sedimentation rates determined for Creel Bay were between 0.28 and 0.30 cm/yr. This agrees with sedimentation rates determined for Creel Bay (0.3 cm/yr) by Jacobson and Engstrom (1989) who found that Creel Bay sediments have undergone little to no mixing.

Metal concentrations in Creel Bay were the highest observed in this study (Tab. 1). It is interesting to note that the metal profiles from Creel Bay do not show a correlation with the large population increase that occurred in the Devils Lake area prior to the 1930's, but instead reach a maximum slope after 1940 when regional automobile use increased and hence combustion of leaded gasoline increased (Eisenreich et al, 1986). The iron profile in Creel Bay sediments (Fig. 4) also seems to reflect the lake level profile (Fig. 2) with high iron concentrations corresponding to rises in lake level throughout the time period represented by the core. These data support the notion that little to no Fe remobilization occurs in these sediments.

Iron normalized profiles (Fig. 5a) show considerable enrichment of Pb and lesser

enrichment of Zn and Cu. Normalized Pb, Zn, and Cu profiles show a peak at 10-11 cm, representing 1955 to 1959 (Fig. 5a), which are most likely due to sewage discharges as the Cu and Zn profiles decrease sharply after approximately 1960. This is about the time the sewage treatment plant was constructed on Creel Bay. Cu, Pb, and Zn are commonly deposited in sediments due to sewage inputs (Nriagu et al, 1979; Hershelman, et al, 1981). Engstrom (1987) found that P concentrations in Creel Bay sediments had increased considerably after 1900 due to anthropogenic activities and presently are about 50% above background concentrations. The Pb profile also shows a peak at 6-7 cm which corresponds approximately to the early 1970's (shown in Fig. 5a), when the use of leaded gasoline in the United States was at its maxima.

The general decline in Pb emissions from gasoline combustion in North America has been documented in the atmosphere (Eisenreich et al, 1986) and in a variety of sedimentary environments (Trefry et al, 1985; Christensen and Goetz, 1987; Finney and Huh, 1989). Figure 6 (after Eisenreich et al, 1986) shows the Pb concentration as measured in the atmosphere over Minnesota. The atmospheric Pb profile seems to correspond well with the normalized Creel Bay Pb profile. It is interesting to note that the small depression in the Pb profile in Creel Bay between 20 cm and 16 cm corresponds approximately to 1940, when automobile and boat use would have been severely curtailed due to fuel rationing during World War II. Although this decrease is within the analytical variation for Pb in this study, the profile suggests that the sediments of Creel Bay may be very sensitive to

environmental changes within the basin.

Normalized Cu and Pb concentrations returned to near background in the upper intervals of the Creel Bay core, but Zn did not. The source of this Zn is not known, but since Zn compounds are common in many products including motor oils, fuels, and rubber, it is probable that the Zn is from a local source. The normalized Cu profile shows a peak at the surface. This source of this increase is not known, but may be related to the As increase and hence possible sediment solubilization and remobilization as discussed below.

The sharp increase in the arsenic profile from Creel Bay at 2-3 cm indicates that this metal has probably been remobilized into the sediments here. The arsenic concentration at 2-3 cm is far greater than observed elsewhere in the profile. Komor (1992) observed bidirectional sulfate diffusion in the upper 10 cm of sediments from Creel Bay and Main Bay and found that sulfate reduction was at a maximum between 1 and 3 cm. In this interval, pore water was found to be saturated with AsS, PbS, FeS, and FeS, (Komor, 1992).

Many other studies have dealt with arsenic mobility and speciation in a variety of sedimentary environments (Creceilus et al, 1975; Brannon et al 1976; Belzile, 1988; Masscheleyn, et al, 1991). Under reducing conditions, As (III), is quite soluble, and is the dominant As species. Callender (1968) found the Eh in Main Bay surface sediments ranged from -50 to -150 mV and pH was approximately 8.1. At a pH above 7.5, in Hyco Reservoir, North Carolina, Masseurleyn et al (1991) found that dissolved As concentrations increased substantially. The low As

concentrations below the zone of maximum sulfate reduction may indicate that As is not being removed as a sulfide in Creel Bay. Belzile (1988) found a strong correlation between As and pyrite in anoxic sediments of the Laurentian Trough of Canada. However, Brannon et al (1976) suggested that in marine anoxic environments, sulfides are ineffective in immobilizing As. In the surface sediments, As may be associated with Fe-oxyhydroxides which are reduced by bacteria in the top few centimeters (Lent, 1992). When the reduction of these oxides occurs, the As is then solubilized into the pore waters where it can diffuse upward or downward in the sediment profile depending on the chemical gradient.

The normalized Cu profile at Main Bay shows an increase from 5 cm to the surface which may also be due to remobilization. Van der Weijden et al (1977) has reported that desorption into seawater occurs in the order $Zn > Cu$, but different removal mechanisms are responsible for desorption of each metal (Nriagu and Coker, 1980; Salomons and Mook, 1980). Van der Weijden et al found that Fe and Pb were not desorbed. Slight differences in the Zn and Cu profiles may be due in part to the different geochemical behavior of the metals in this environment.

Main Bay- Sedimentation rates determined for Main Bay were approximately 0.2 cm/yr. This is slightly lower than the sedimentation rates determined by Jacobson and Engstrom (1989) and Lent (et al, in review) of 0.3 and 0.25 cm/yr respectively. Jacobson and Engstrom (1989) found that sediments in Main Bay had been mixed to considerable depths (10-12 cm) and sediment ages obtained via

^{210}Pb and pollen dating did not correlate well. Unlike at Creel Bay, the iron profile from Main Bay (Fig. 4) does not correspond well with the profile of lake level (Fig. 2), again suggesting considerable wind-induced sediment mixing has occurred.

Iron normalized metal profiles show the onset of trace metal enrichment occurring in about 1875 (Fig. 5b). This is prior to permanent European settlement of the Devils Lake Basin. In Fig. 5a, notice that the normalized Creel Bay profiles show the onset of enrichment occurring in approximately 1940. The discrepancy is again due to wind-induced mixing.

Metal concentrations observed in Main Bay were almost as high as in Creel Bay (Table 1). From the iron normalized profiles (Fig. 5b), only Pb shows considerable enrichment, but the enrichment is much less than that observed in Creel Bay. The highest Pb concentration at 3-4 cm, corresponding to approximately the mid-1970's, again indicates that much of the Pb in Main Bay has probably come from gasoline combustion. The short term variations in Pb concentration are due to an unknown cause, but may be due to analytical variation (i.e. $\pm 13\%$ certainty), sediment mixing, lake level fluctuations, or sediment chemistry. The arsenic profile shows an increase between 20 cm in depth (~80 ybp) and the present which may be connected with fossil fuel consumption, but the sharp increase to the surface indicates that As has probably undergone a considerable amount of remobilization as mentioned in the section on Creel Bay. Sewage discharges may be reflected in all of the Main Bay profiles as the peak marked in Fig. 5b may indicate, but the Pb, Cu, and Zn profiles do not support assigning this source to any of the

observed peaks.

High As, Cu, Fe, and Zn concentrations at depth are coincident with a zone of high pore water sulfide concentrations reported by Komor (1992).

East Bay- The sedimentation rate determined for East Bay was 0.4 cm/yr. It is likely that winds and organisms have mixed the sedimentary profile considerably since East Bay is shallower than Main Bay (water depth at sampling location < 2 m) and is likewise not protected from winds. In addition, East Bay was dry during the 1940's and parts of the 1950's and 60's.

Metal concentrations observed in East Bay were lower than those observed in Creel and Main Bays (Table 1). Waters in East Bay have undergone a large amount of evaporation (Lent, 1992) and the low metal concentrations may be due in part to the metals being removed up the hydrologic gradient in the Devils Lake Basin. The Fe profile (Fig. 4) did not correlate with the lake level profile (Fig 2), but did correlate well with factor 1 (Fig. 3b). No relationship between loss on ignition and Fe concentrations was evident. The lack of relationship is probably due in part to sediment mixing.

Iron normalized profiles (Fig. 5b) show an increase only for Pb, which shows a peak at 6-7 cm and As which has a peak at 3-5 cm. The increase in Pb may be related to automobile and boat traffic in the Devils Lake area as discussed previously. Cu and Zn profiles do not show evidence of enrichment in these metals and both show a peak at 4-5 cm. The Se profile shows a large peak at 2-3

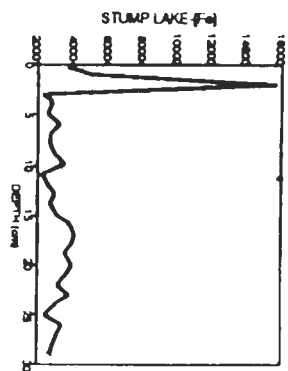
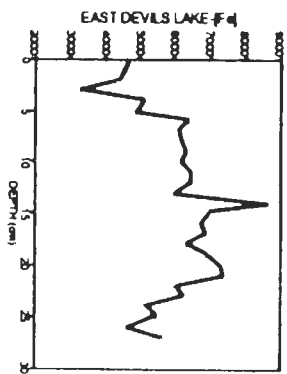
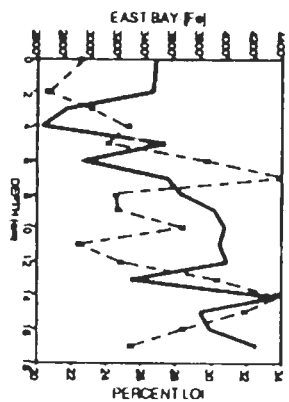
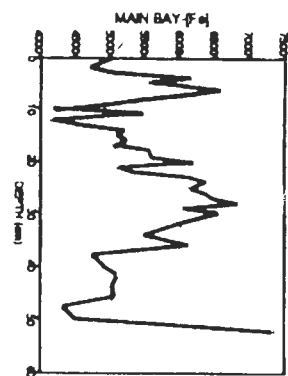
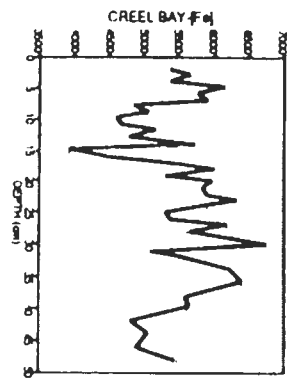
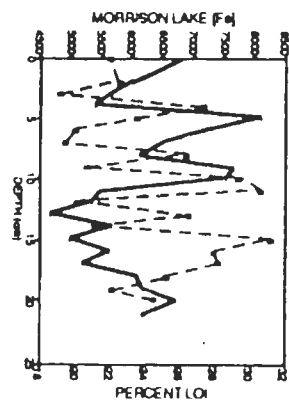


Fig. 4: Plots of Fe concentration versus depth for all cores. Percent loss on ignition included for Morrison Lake and East Bay cores. (concentrations in $\mu\text{g/g}$)

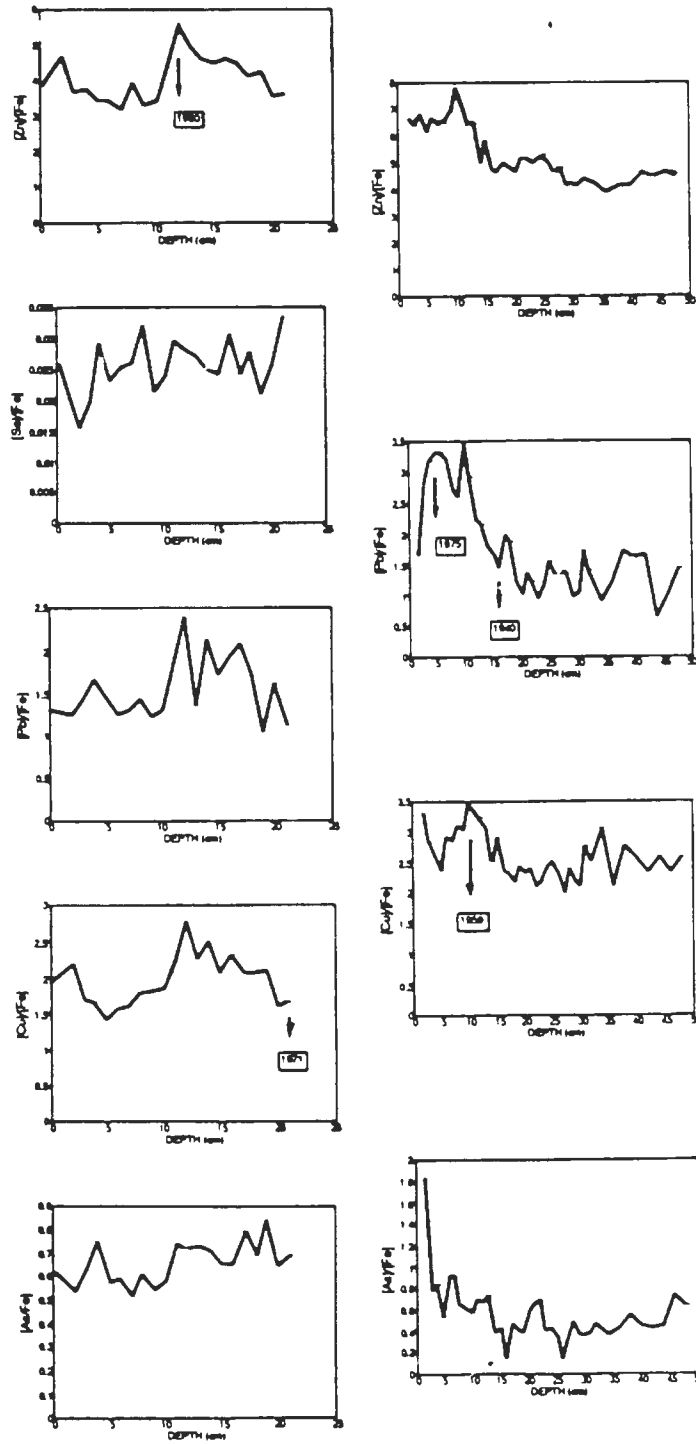


Fig. 5a: Iron normalized metal profiles for Morrison Lake (top) and Creel Bay (bottom).
(concentrations iron normalized $\cdot 1000$)

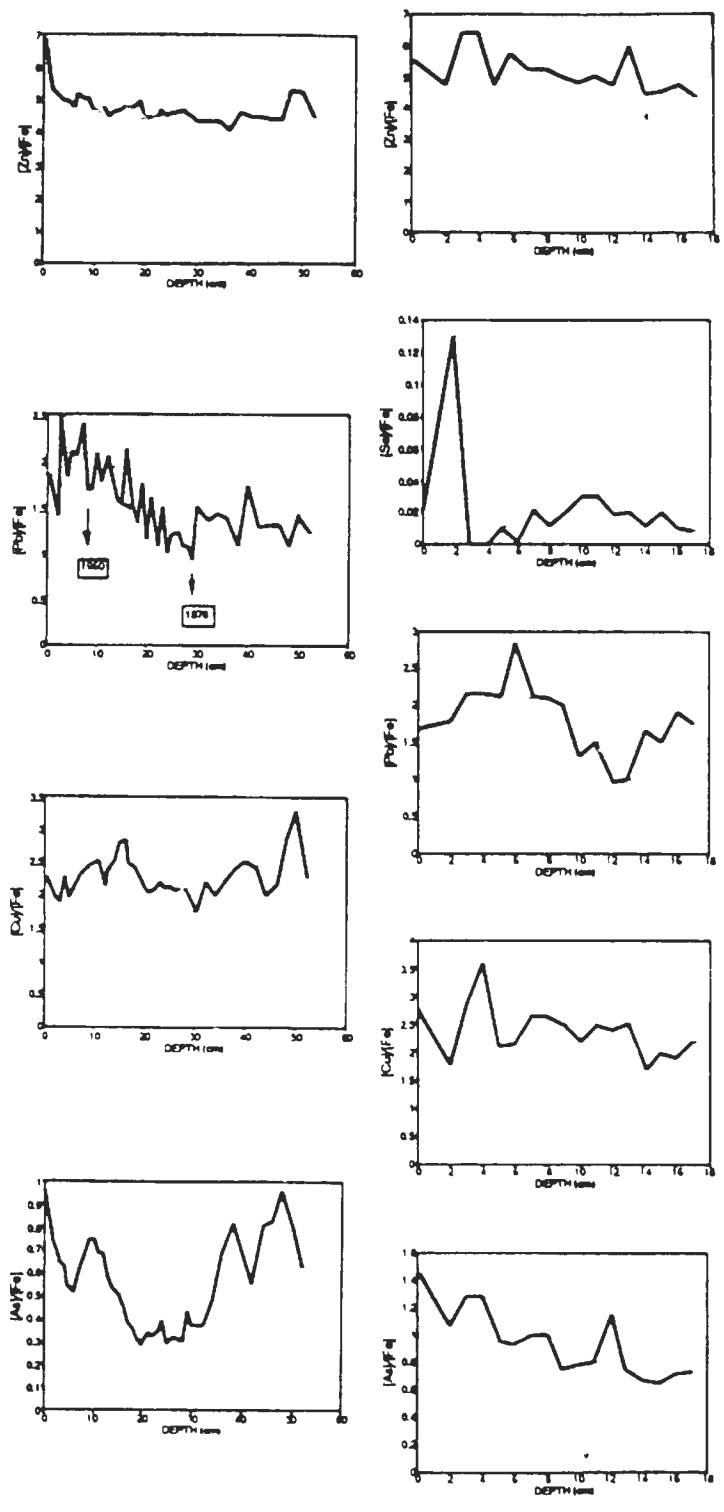


Fig. 5b: Iron normalized metal profiles for Main Bay (top) and East Bay (bottom).
(concentrations iron normalized * 1000)

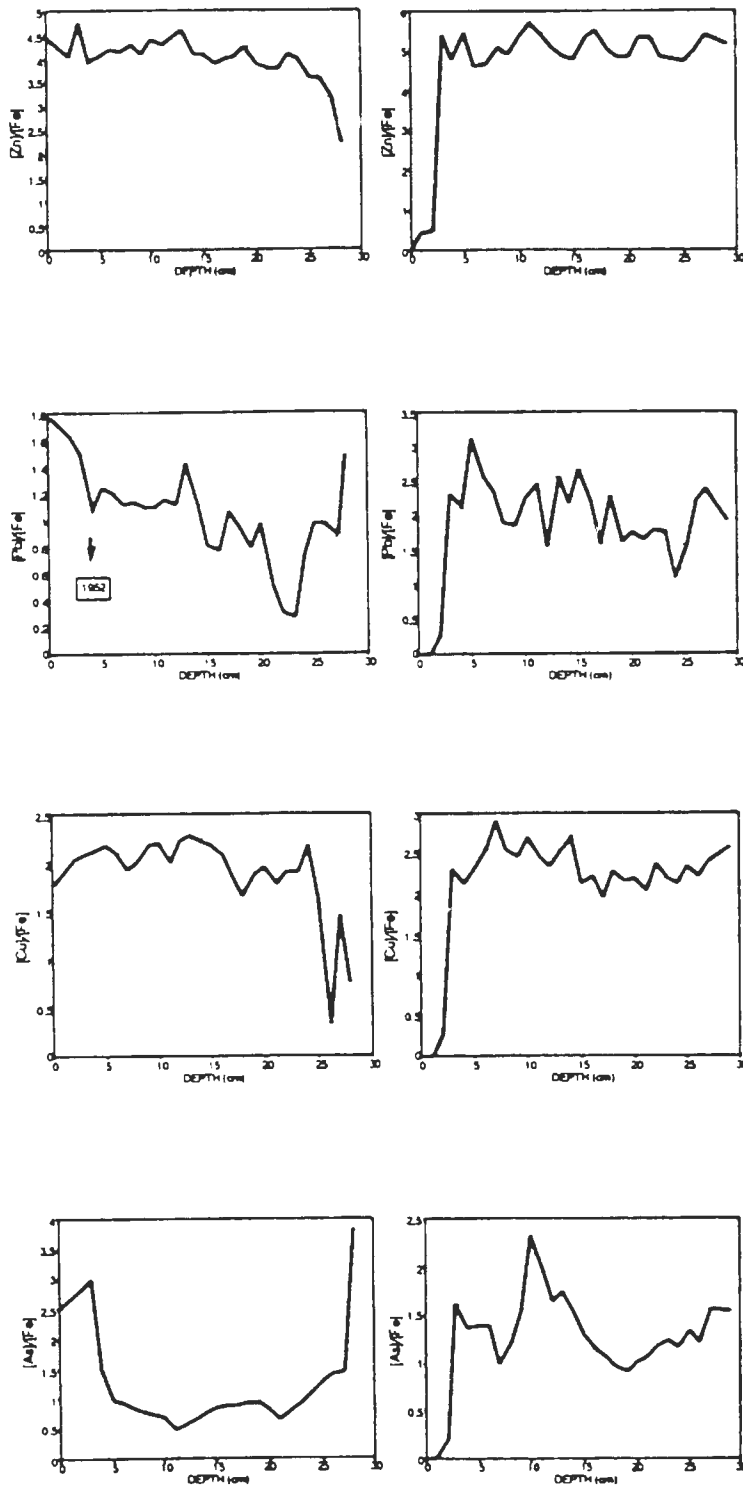


Fig. 5c: Iron normalized metal profiles for East Devils Lake (top) and Stump Lake (bottom).
(concentrations iron normalized \bullet 1000)

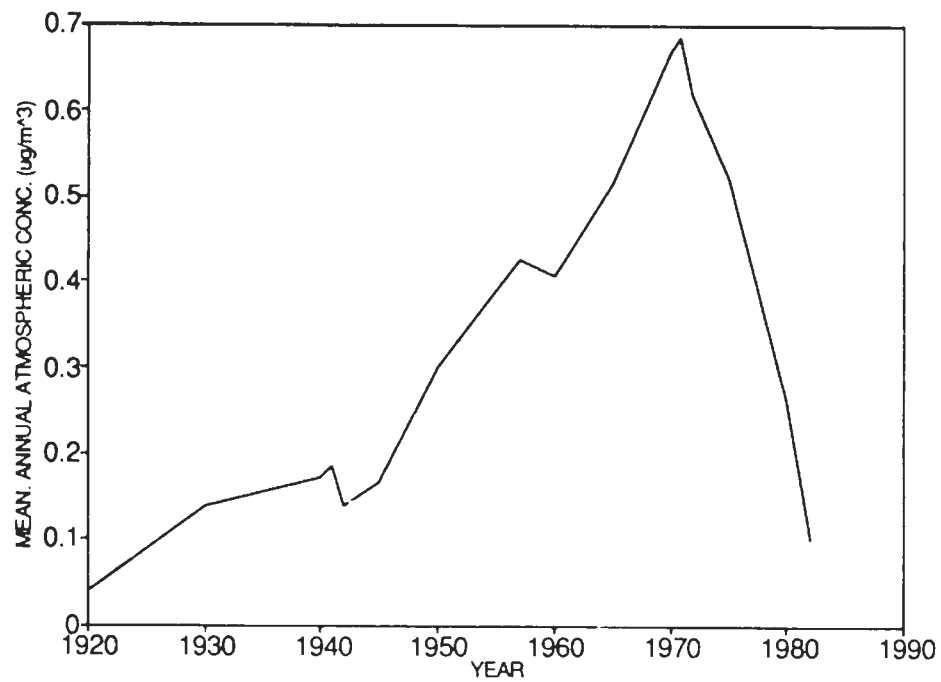


Fig. 6 (after Eisenreich et al, 1986): Pb concentrations in atmosphere over Minnesota.

cm, but relatively little selenium is observed elsewhere in the profile. The Se peak is coincident with the porewater S maximum reported at similar depths in Devils Lake by Komor (1992).

East Devils Lake- The sedimentation rate determined for East Devils Lake was approximately 0.10 cm/yr. The depth of the lake should prevent wind related mixing of sediments, but at such a low sedimentation rate, some metals could be significantly remobilized within the sedimentary profile.

Metals in East Devils Lake showed a wide variation in range (Table 1). Between Morrison Lake and East Bay, background trace metal concentrations generally decrease downgradient, but background metal concentrations in East Devils Lake are among the highest observed in this study. These high metal concentrations probably reflect a nearby source to East Devils Lake. The Fe profile (Fig 4) from East Devils Lake shows a relationship with factor 3 (middle grain sizes) (Fig 3c), but this may be coincidental since the middle grain size fraction accounted for so little of the total variance. However, sediments at East Devils Lake were slightly coarser than those from Morrison Lake or East Bay and the profile may indicate that much of the metals enter East Devils Lake at the same time as the coarser sediments and are deposited during storm events.

Iron normalized metal profiles (Fig. 5c) show a near surface increase in Pb extending from 4 cm (~1950) (Fig. 5c) in depth to the surface. This is consistent with the Pb enrichment observed in the Creel Bay core. Again the As profile shows

a sharp increase in the same time frame as does the Pb profile and there may be a relationship between these metals. As concentrations, however, are highest in East Devils Lake (Tab. 1) and also may be related to agricultural activities. Neither metal shows a large increase over average background concentrations, however. The low sedimentation rate in East Devils Lake would not allow for the appearance of a large decrease in Pb concentrations within the time frame indicated by the top 2 cm as this interval represents 20 years. The normalized Zn and Cu profiles do not show an appreciable increase with time for these metals. Cu and Zn concentrations decrease at depth as As and Pb increase. The reason for this is unknown.

Stump Lake- No sedimentation rate could be determined by ^{210}Pb for Stump Lake. An approximate sedimentation rate of approximately 0.06 cm/yr was, however, estimated using biogenic silica data from Devils and Stump Lake and stratigraphic interpretation from Devils Lake, where sedimentation rates are known (Lent and Lyons, unpublished data).

The first three intervals in the Stump Lake core were primarily organic matter (algae and macrophyte roots). It was difficult to determine where the sediment-water interface was in the core due to the precipitation of ~5 cm of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) on the lake bottom and the large amount of organic matter in the surface sediments. A wide range in iron concentrations in the first few cm is shown in Fig. 4. Crystalline pyrite was abundant in the filtrate of all of the intervals

below 5 cm and the metal concentrations observed for the Stump Lake sediments are probably low due to the inability of the amount of acid added to dissolve all sulfide minerals present in the highly anoxic and sulfate rich sediments. Ranges of concentrations for metals are shown in Table 1.

Iron normalized profiles (Fig. 5c) do not show any trends with depth, nor a great range in concentration. Normalized Cu and Pb profiles show a very small increase near the surface. The normalized As profile shows much more variation than the other normalized metal profiles. This further suggests that pyrite formation is an ineffective mechanism for immobilizing As in the lakes studied here.

Comparison to Crustal Abundances

With the exception of Creel Bay and Main Bay, the trace metals discussed in this study do not appear to be significantly enriched above natural background concentrations. However, As, Se, and Pb do appear to be enriched relative to crustal abundances in all cores. Table 2 displays the average crustal concentrations for As, Cu, Pb, Se, and Zn (Wedepohl, 1971). Cu concentrations have been used to normalize As, Pb, Se, and Zn concentrations for crustal concentrations, soils, and average metal concentrations for all cores. The rationale for this is that Cu concentrations have changed less over time in the Devils Lake Basin than the other trace metals discussed in this study. We have interpreted this to indicate that little anthropogenically introduced Cu has entered the Devils Lake

Basin.

In reading Table 2, notice that larger metal/Cu ratios for the cores indicate greater enrichment relative to crustal abundance. It can be seen that As concentrations in the Devils Lake Basin are greatly enriched above crustal abundances and Se and Pb less enriched (Table 2). The source of most of these trace metals is certainly the Pierre Shale, which is known to contain high concentrations of the trace metals discussed in this study (Tab. 1) (Schultz et al, 1984). Zn/Cu ratios, however, in the cores are equivalent to crustal abundances. Metal/Cu ratios for As, Pb, and Zn in the cores are very similar to metal/Cu ratios for the shales and soils. The Se/Cu ratio is much lower than in the soil and shale and may indicate that the Se in the soil and shale is less environmentally available than the other metals discussed in this study.

Other Studies

Metal concentrations determined for this study (Tab. 1) are similar to those found in other trace metal studies in the northern plains and prairie of the United States and Canada. Martin and Hartman (1984) analyzed pothole and riverine sediments from national wildlife refuges on the northern plains for concentrations of As, Cd, Pb, Hg, and Se. Ranges of concentration for pothole sediments were As (1.4-9.3 $\mu\text{g/g}$), Pb (7.4-22 $\mu\text{g/g}$), and Se (0.13-2.1 $\mu\text{g/g}$) respectively. As and Se were analyzed on mixed HNO_3 - HClO_4 digestates and Pb was analyzed on HNO_3 ,

Table 2: Comparison of crustal metal concentrations and core concentrations as well as metal to copper ratios for crust and cores

I. Crustal Abundances	Cu	As	Pb	Se	Zn
Concentration	30	1.7	15	.09	60
		[As]/[Cu]	[Pb]/[Cu]	[Se]/[Cu]	[Zn]/[Cu]
Ratio		0.6	0.5	0.003	2
II. Pierre Shale					
Concentration	28	9.2	20	0.74	96
Ratio		0.33	0.71	0.026	3.4
III. Soils					
Concentration	20	6.5	15	1.0*	45
Ratio		0.33	0.75	0.05	2.3
IV. Cores					
Morrison Lake					
Concentration	12	4	9	0.16	25
Ratio		0.33	0.75	0.013	2.1
Creel Bay					
Concentration	14	3	10	---	29
Ratio		0.21	0.71	---	2.1
Main Bay					
Concentration	12	3	8	---	26
Ratio		0.25	0.67	---	2.2
East Bay					
Concentration	8	3	6	0.08	18
Ratio		0.38	0.75	0.01	2.3
East Devils Lake					
Concentration	11	6	6	---	23
Ratio		0.55	0.55	---	2.1
Stump Lake					
Concentration	7	4	6	---	15
Ratio		0.57	0.86	---	2.1

Concentrations in ug/g

*-estimated

Sources: Crustal Abundances, Wedepohl, 1971; Shale, Schultz et al 1980; Soils, Shacklette and Boerngen, 1984.

reflux digestates.

In Lake Winnepeg, Allan and Brunskill (1976) measured total trace metal concentrations in sediment cores. Ranges of concentrations were As (1-9 $\mu\text{g/g}$), Pb (8-36 $\mu\text{g/g}$), and Zn (134-224 $\mu\text{g/g}$). Cu concentrations ranged between 17 and 998 $\mu\text{g/g}$, but only one sample showed such a high concentration. Surface enrichment was evident only near the Red River outlet.

In the midwest United States, Iskandar and Keeney (1974) analyzed lake sediments for Cu, Pb, and Zn concentrations in six rural lakes from northern Wisconsin. Analysis was performed using mixed HNO_3 - HClO_4 digestates. Cu and Zn concentrations in sediments ranged from between 7 and 64 $\mu\text{g/g}$ and 12 and 165 $\mu\text{g/g}$ respectively. Background Pb concentrations ranged from below detection limits to 9 $\mu\text{g/g}$. High surface Pb concentrations were attributed to fossil fuel input from both boat and automobile traffic.

Calculation of Fluxes

In order to determine how trace metal loadings in the Devils Lake Basin have changed since precultural times, natural and total fluxes were calculated for surface sediments from Creel Bay and total fluxes calculated for surface sediments from the other sampling locations. Measured fluxes were calculated using the formula $F(\mu\text{g/cm}^2\text{yr}) = R(1-w)\rho C$ where R is the sedimentation rate in cm/yr, w is the water content of the sample (%), ρ is the sediment density (g/cm^3), and C is

Table 3: Comparison of fluxes for Creel Bay sediments and calculated fluxes for other cores

i) Creel Bay flux comparison

Element	As	Cu	Pb	Zn
Bkgnd. Conc.	3	13	7	24
Natural Flux	0.22	0.95	0.52	1.77
Surface Conc.	5.5	17	19	35
Total Flux	0.38	1.15	1.31	2.41
Enrichment Factor	1.7	1.2	2.5	1.3

ii) Calculated fluxes for surface sediments from other cores

Core	Element	As	Cu	Pb	Se	Zn
Morrison Lake		2.0	6.2	4.2	0.085	12.5
Main Bay		0.2	0.4	0.3	1.3
East Bay		1.5	2.9	1.7	0.024	5.8
East Devils Lake		0.5	0.4	0.4	0.9
Stump Lake		0.1	0.2	0.2	0.3

All concentrations in ug/g

All fluxes in ug/cm²*yr

the metal concentration ($\mu\text{g/g}$). Sediment density was calculated as 2.33 g/cm^3 from data provided in Jacobson and Engstrom (1989).

Table 3i shows the calculated total and natural fluxes from Creel Bay and Table 3ii displays calculated total fluxes for the other lakes. Background concentrations for Creel Bay were estimated by averaging the precultural metal concentrations. Surface concentrations of the metals were used for these calculations, except for As in Creel Bay for which an average near-surface concentration was estimated due to probable remobilization of this metal as discussed previously. Background metal concentrations are much lower than those listed for soils in northeastern North Dakota by Shacklette and Boerngen (1984) (Tab. 1). It must be remembered, however, that our metal concentrations do not reflect total metal concentrations as do the soil concentrations.

Total metal loadings (Table 3) generally appear quite high when compared to previous studies (e.g. Galloway and Likens, 1979; Hamilton-Taylor, 1979), but the high loadings probably reflect high sedimentation rates in Morrison Lake and Devils Lake rather than high metal concentrations in the surface sediments.

Except for Pb which shows an enrichment factor (total flux/natural flux) of 2.5, the enrichments seen in Creel Bay are not large. In studies of lakes which are known to have experienced large recent increases in trace metal influxes (e.g. Galloway and Likens, 1979, Hamilton-Taylor, 1979), total metal fluxes may be well over ten times natural fluxes and are dominated by anthropogenic input. Arsenic shows an enrichment factor of 1.7 and both Zn and Cu show an enrichment factor

of slightly greater than one.

Conclusions

Possible routes for trace metals to enter lakes in the Devils Lake Basin include deposition and runoff of regionally or locally discharged airborne particles (power plant emissions, automobile and boat emissions, wind blown soil particles), inflow of waters containing large amounts of metals such as street runoff and storm drainage, sewage discharges, and runoff from agricultural lands, and weathering of soil and rock materials (Nriagu, 1988; 1989)

The sampling sites for this study were so located in order to allow for a comparison of the different possible routes for trace metals to enter lakes in the Devils Lake Basin. If trace metal enrichments are due to a regionally important source of metals, then high concentrations of each trace metal would be expected in surface sediments of all lakes in the Devils Lake Basin and highest in Main Bay and East Bay where much of the water in the basin terminates. Trace metals originating in agricultural runoff would be expected to produce high concentrations in all locations except in Creel Bay where runoff from the city of Devils Lake enters Devils Lake through Main Bay.

In this study, only in Creel Bay and Main Bay were large trace metal enrichments observed. Even so, surface concentrations of metals in these locations were much lower than obtained from other studies of trace metals in lake

sediments (e.g. Iskandar and Keeney, 1974; Galloway and Likens, 1979; Hamilton-Taylor, 1979; Davis and Galloway, 1980). Possible anthropogenic trace metal contaminant sources of local origin to both Creel Bay and Main Bay are sewage discharges (prior to the installation of sewage treatment plant), municipal runoff emanating from the city of Devils Lake and vicinity, and boat and automobile emissions. High Cu, Zn concentrations probably originate in sewage effluent while the primary Pb source is most likely emissions from boats and automobiles. Cu and Pb concentrations have returned to near background concentrations in surface sediments, but Zn concentrations remain quite high although concentrations are below a maximum reached in approximately 1960.

Although the Pb profile in Creel Bay closely matches the atmospheric Pb profile in Figure 7. The primary source of Pb in Creel Bay is probably not regional in nature as the high Pb concentrations in Creel and Main Bays (Table 1.), relative to other locations, indicate. The Pb concentrations in Morrison Lake, where boating is not common, are also relatively high and may indicate that a small proportion of the Pb did not originate within the Devils Lake Basin and that automobiles are more important Pb emitters than boats. The slight Pb increase in surface sediments in East Devils Lake reflects an increase in gasoline consumption during the last forty years, but it is unknown if the source is boating or if runoff may be transmitting atmospherically deposited Pb into the lake from the surrounding area. The decrease in Pb concentrations in near-surface sediments in both Creel Bay and Main Bay is encouraging and is indicative of the positive effect of decreasing

Pb content of gasoline in the United States (Eisenreich et al, 1986).

Fertilizers and pesticides do not appear to be a major source of metals to the lakes discussed in this study, except possibly at East Devils Lake where relatively high As concentrations are seen.

Distant sources of trace metal contaminants, including coal combustion, may contribute metals to the Devils Lake Basin, but have apparently not yet caused a significant change in near-surface metal concentrations.

Except in Creel Bay and Main Bay, the results of this study are consistent with a natural source being the primary source of most of the trace metals discussed in this study. The source of these metals is almost certainly the Pierre Shale which is known to contain very high concentrations of trace metals (Shultz, et al, 1984). As, Se, and Pb concentrations in lake sediments from the Devils Lake Basin appear to be far above crustal abundances, however. It is probable that total metal content in most of the sediments from the basin would yield concentrations similar to those reported for soils in northeastern North Dakota by Shacklette and Boerngen (1984).

Diagenetic remobilization of metals in sediments may occur for all of the metals discussed in this study except for Pb (McKee et al, 1989; Andreae, 1979). However, the very high sulfate concentrations in the pore waters and active sulfate reduction close to the sediment-water interface (Komor, 1992; Lent, 1992), probably limit large scale remobilization via sulfide mineral fixation. The exception to this is As and Se, which appear to have been mobile in our sediment profiles.

Remobilization could make metals available to benthic and pelagic organisms including fish and may be a serious concern in Devils Lake. Formation of sulfide metal complexes in the near-surface sediments as reported by Komor (1992) may, however, prevent uptake by organisms (Belzile, 1988).

It is unfortunate that Creel Bay is the only location in the Devils Lake Basin where a high sedimentation rate is combined with a sheltering from winds. The East Devils Lake core may not have been disturbed by winds, but the low sedimentation rate prevents a high temporal resolution and a lack of knowledge about the hydrology of East Devils Lake hinders any interpretation on the source of metals to this lake. Given the problem of sediment mixing in most of the lakes in the Devils Lake Basin, the usefulness of a sediment "unmixing" method, such as the one presented in Christensen and Klein (1991), in such lakes should be developed. In addition, the trace metal influx to other smaller lakes in the northern plains warrants study and may lead to a better understanding as to what contribution, if any, various anthropogenic trace metal sources make to the region's aquatic environments.

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Appendix

CREEL BAY TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Zn (ug/g)
2-3cm	5373	9.9	17.9	9	35.8
3-4	5668	4.5	16.2	16	36.4
4-5	5382	4.5	14.2	17	36.8
5-6	6158	3.2	14.7	21	38.1
6-7	5774	5.3	16.8	19	38.5
7-8	5928	5.5	16.9	19	38.1
8-9	4866	3.2	15.0	13	31.8
9-10	5040	3.1	15.3	13	35.1
10-11	4600	2.6	16.0	16	36.0
11-12	4675	3.3	15.6	14	33.1
12-13	5144	3.5	16.6	12	33.2
13-14	4785	3.5	14.6	10	31.2
14-15	5718	2.2	14.3	10	28.6
15-16	3919	1.6	11.4	7	22.9
16-17	4427	0.6	10.5	6	21.1
17-18	5538	2.6	12.9	11	25.8
18-19	6019	2.4	13.2	11	30.1
19-20	5297	2.1	12.8	6	25.7
20-21	5992	3.6	14.0	6	28.0
21-22	5835	3.8	14.1	8	30.2
22-23	5932	4.1	12.6	7	30.6
23-24	6324	2.6	13.8	6	31.6
24-25	5928	2.5	14.4	7	30.5
25-26	5316	1.8	13.3	8	28.2
26-27	5392	0.7	12.6	7	27.0
27-28	6181	2.3	12.4	8	28.8
28-29	5646	2.7	13.6	8	27.3
29-30	6330	2.3	13.9	6	26.2
30-31	6758	2.5	14.2	7	28.5
31-32	5103	1.9	14.1	9	21.1
32-34	5516	2.6	13.8	8	24.5
34-36	6226	2.3	19.0	6	26.4
36-38	6412	2.7	13.6	8	25.3
38-40	5595	3.1	15.4	10	23.2
40-42	5647	2.6	14.6	9	23.7
42-44	4800	2.1	11.2	8	22.4
44-46	5065	2.3	13.1	3	22.9
46-48	4915	3.6	11.5	5	22.9
48-50	5483	3.4	14.1	8	25.1

EAST BAY TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Se (ug/g)	Zn (ug/g)
0-2cm	3468	5.0	9.6	6	0.08	19.3
2-3	3446	3.6	6.1	6	0.45	16.2
3-4	2823	3.6	8.1	6	0.00	18.1
4-5	2632	3.4	9.4	6	0.00	16.9
5-6	3547	3.4	7.5	7	0.04	16.8
6-7	2939	2.7	6.3	8	0.00	16.8
7-8	3565	3.6	9.4	8	0.08	18.8
8-9	3654	3.7	9.6	8	0.04	19.2
9-10	3906	2.9	9.8	8	0.08	19.5
10-11	3995	3.1	8.7	5	0.12	19.1
11-12	3950	3.2	9.9	6	0.12	19.7
12-13	3997	4.6	9.5	4	0.08	19.0
13-14	3297	2.5	8.2	3	0.07	19.8
14-15	4358	2.9	7.3	7	0.05	19.4
15-16	3802	2.5	7.6	6	0.08	17.1
16-17	3877	2.8	7.4	7	0.04	18.5
17-18	4212	3.1	9.2	7	0.04	18.3

EAST DEVILS LAKE TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Zn (ug/g)
0-2cm	4643.1	11.736	8.2	8	20.6
2-3	4391.1	12.500	8.9	7	17.9
3-4	3286.1	9.817	6.9	5	15.7
4-5	5125.6	7.683	11.0	5	20.1
5-6	4867.0	4.853	10.6	6	19.7
6-7	6381.5	5.973	13.5	8	27.0
7-8	6082.9	5.245	11.8	7	25.4
8-9	6180.3	4.950	12.4	7	26.5
9-10	6328.2	4.663	13.8	7	25.9
10-11	6176.7	4.417	13.6	7	27.2
11-12	6413.3	3.321	12.9	7	27.7
12-13	6503.6	3.636	14.5	7	29.1
13-14	6001.7	3.954	13.8	9	27.5
14-15	8665.8	6.652	19.5	10	35.7
15-16	6945.1	6.061	15.2	6	28.4
16-17	6734.2	6.148	14.1	5	26.3
17-18	6900.9	6.239	12.8	7	27.5
18-19	6326.8	5.997	10.5	6	25.5
19-20	6877.6	6.610	12.9	6	29.4
20-21	7279.1	6.032	14.2	7	28.4
21-22	7342.4	4.661	13.1	4	28.0
22-23	6005.7	4.971	11.5	2	22.9
23-24	6219.3	5.949	11.9	2	25.5
24-25	5155.0	5.834	11.3	4	20.7
25-26	5506.3	7.181	9.0	5	19.7
26-27	4645.6	6.522	1.5	5	16.7
27-28	5662.1	8.242	8.2	5	18.1
28-29	2022.5	7.784	1.5	3	4.5

EAST DEVILS LAKE TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Zn (ug/g)
0-2cm	4643.1	11.736	8.2	8	20.6
2-3	4391.1	12.500	8.9	7	17.9
3-4	3286.1	9.817	6.9	5	15.7
4-5	5125.6	7.683	11.0	5	20.1
5-6	4867.0	4.853	10.6	6	19.7
6-7	6381.5	5.973	13.5	8	27.0
7-8	6082.9	5.245	11.8	7	25.4
8-9	6180.3	4.950	12.4	7	26.5
9-10	6328.2	4.663	13.8	7	25.9
10-11	6176.7	4.417	13.6	7	27.2
11-12	6413.3	3.321	12.9	7	27.7
12-13	6503.6	3.636	14.5	7	29.1
13-14	6001.7	3.954	13.8	9	27.5
14-15	8665.8	6.652	19.5	10	35.7
15-16	6945.1	6.061	15.2	6	28.4
16-17	6734.2	6.148	14.1	5	26.3
17-18	6900.9	6.239	12.8	7	27.5
18-19	6326.8	5.997	10.5	6	25.5
19-20	6877.6	6.610	12.9	6	29.4
20-21	7279.1	6.032	14.2	7	28.4
21-22	7342.4	4.661	13.1	4	28.0
22-23	6005.7	4.971	11.5	2	22.9
23-24	6219.3	5.949	11.9	2	25.5
24-25	5155.0	5.834	11.3	4	20.7
25-26	5506.3	7.181	9.0	5	19.7
26-27	4645.6	6.522	1.5	5	16.7
27-28	5662.1	8.242	8.2	5	18.1
28-29	2022.5	7.784	1.5	3	4.5

MAIN BAY TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Zn (ug/g)
0-2cm	5042	4.9	11.5	9	34.7
2-3	4714	3.5	9.4	7	25.3
3-4	5018	3.2	9.6	12	26.0
4-5	6158	3.9	14.0	11	30.9
5-6	5576	3.1	11.0	12	27.6
6-7	6600	3.4	13.8	14	31.7
7-8	6150	3.6	14.2	15	32.1
8-9	5518	3.6	13.2	9	28.0
9-10	5053	3.8	12.4	9	25.5
10-11	4186	3.1	10.5	9	19.7
11-12	5469	5.7	13.8	10	25.2
12-13	4158	2.8	8.9	9	19.7
13-14	4572	2.7	10.9	9	20.6
14-15	5199	2.8	13.2	8	24.1
15-16	5107	2.6	14.3	8	24.0
16-17	5234	2.4	14.8	11	25.3
17-18	5036	1.9	12.6	8	24.0
18-19	5572	2.0	13.5	7	27.0
19-20	5592	1.7	12.8	10	27.8
20-21	6198	1.8	13.3	7	27.5
21-22	5108	1.8	10.4	8	23.1
22-23	5307	1.7	11.1	6	24.0
23-24	6109	2.1	13.4	9	28.6
24-25	6391	2.5	13.4	6	28.8
25-26	6148	1.8	13.2	7	28.2
26-27	6379	2.0	13.1	8	29.6
27-28	6501	2.0	13.8	7	30.8
28-29	6835	2.1	14.4	7	31.2
29-30	6068	2.6	12.1	6	27.3
30-32	6534	2.5	11.5	10	28.3
32-34	6022	2.2	13.3	8	26.4
34-36	5502	2.7	11.1	8	23.8
36-38	6109	4.2	13.7	8	25.0
38-40	4742	3.9	11.5	5	22.1
40-42	4938	3.4	12.5	9	22.0
42-44	5104	2.8	12.4	7	23.1
44-46	5027	4.1	10.1	7	22.1
46-48	5044	4.2	10.9	7	22.3
48-50	4342	4.2	12.5	5	23.3
50-52	4511	3.6	14.8	6	23.8
52-54	7356	4.7	16.9	9	33.2

MORRISON LAKE TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Se (ug/g)	Zn (ug/g)
0-2cm	6783	4.2	13.1	9	0.18	26.3
2-3	6008	3.2	13.1	8	0.09	28.2
3-4	5670	3.6	9.7	8	0.11	21.1
4-5	5385	4.0	9.0	9	0.16	20.2
5-6	8121	4.6	11.6	12	0.19	27.8
6-7	7278	4.3	11.4	9	0.18	25.0
7-8	6513	3.4	10.5	8	0.17	21.0
8-9	6140	3.7	11.0	9	0.20	24.1
9-10	7645	4.2	13.9	9	0.16	25.5
10-11	7555	4.4	13.9	10	0.18	25.8
11-12	5469	4.1	12.2	10	0.16	24.3
12-13	5361	3.9	15.0	13	0.15	30.0
13-14	4664	3.4	10.6	6	0.13	23.3
14-15	5653	4.0	14.1	12	0.14	26.2
15-16	4980	3.3	10.3	9	0.12	22.3
16-17	5636	3.7	13.0	11	0.17	26.0
17-18	5191	4.1	10.7	11	0.13	23.3
18-19	6075	4.2	12.6	10	0.17	25.1
19-20	6176	5.2	13.0	7	0.13	26.0
20-21	6749	4.4	10.9	11	0.17	23.9
21-25	6196	4.3	10.3	7	0.21	22.4

STUMP LAKE TRACE METAL DATA

SAMPLE	Fe (ug/g)	As (ug/g)	Cu (ug/g)	Pb (ug/g)	Zn (ug/g)
0-1cm	3749	0.0	0.0	0	0.0
1-2	5188	0.0	0.0	0	2.3
2-3	15728	3.1	4.1	4	8.2
3-4	2290	3.7	5.3	5	12.4
4-5	2830	3.9	6.0	6	13.5
5-6	2550	3.6	5.9	8	13.9
6-7	3247	4.5	8.4	8	15.0
7-8	2697	2.7	7.9	6	12.6
8-9	2760	3.3	7.0	5	14.0
9-10	3062	4.7	7.5	6	15.1
10-11	3475	8.1	9.4	8	18.7
11-12	2228	4.4	5.5	5	12.8
12-13	2517	4.1	5.9	4	13.8
13-14	2979	5.2	7.6	8	15.3
14-15	2776	4.2	7.6	6	13.6
15-16	3173	4.1	6.8	8	15.2
16-17	3790	4.4	8.4	8	20.2
17-18	4053	4.3	8.0	6	22.4
18-19	4001	3.9	9.2	9	20.2
19-20	3609	3.3	7.8	6	17.6
20-21	3969	4.0	8.7	7	19.2
21-22	3732	4.0	7.7	6	19.9
22-23	3119	3.7	7.4	6	16.7
23-24	3834	4.7	8.4	7	18.6
24-25	3177	3.7	6.8	3	15.3
25-26	2458	3.3	5.8	4	11.6
26-27	3479	4.2	7.7	8	17.3
27-29	3219	5.0	7.7	8	17.4
29-31	2820	4.4	7.3	5	14.5