5.0 PHYSICOCHEMICAL PROPERTIES OF LAKE DEPUE

The first portion of this research project focused on profiling the physical and chemical properties of Lake DePue. In order to understand what may control the detailed chemical properties of the sediments, it is crucial to first look at the whole system and its dynamic properties. The variables selected for this survey include the pH, temperature, specific conductivity, alkalinity, metal concentrations, and anion concentrations. These results lead to the profiling of the plume of zinc contamination from the source into the water column. Additionally, the visible characteristics (size, color, wetness) of the sediment cores are described from each site. X-ray diffraction of sediment from the deltaic site (C_2) was performed to see if crystalline zinc-bearing mineral phases in the sediments were detectable.

5.1 WATER COLUMN PROPERTIES

The concentrations of inorganic contaminants are the primary difference between the three sampling sites at Lake DePue. Table 5.1 shows the general surface water characteristics at each of the collection sites. The different depths at each of the sampling locations reflect the differences in the lacustrine environments between the sites. Site M_1 is located in the middle of the lake, and thus has the greatest depth. Site C_1 is located in the bed of a stream where the contaminants enter the lake, and as a result, has an extremely shallow depth. Site C_2 is a deltaic interface between C_1 and M_1 and has a water depth intermediate of that of C_1 and M_1.

Table 5.1: Chemical composition for relevant species in Lake DePue water at the various sampling locations. (Webb, *et. al.*, 2000)

Property	**C_1**	**C_2**	**M_1**
Depth	3 cm	50 cm	200 cm
Temp. (°C)			27.6
D.O. (μM)			166
Conductivity (μS)			0.598
pH	7.32	7.78	7.84
Alkalinity	3.8/9.0 meq	5.3 meq	4.1 meq
$[Zn]_d$	275 ± 14 μM	298 ± 26 nM	87 ± 15 nM
$[SO_4^{2-}]$	19.4 ± 0.3 mM	563 ± 30 μM	536 ± 6 μM
$[Cl^-]$	1.09 ± 0.10 mM	1.13 ± 0.03 mM	1.15 ± 0.01mM

In addition to the surface water samples at each of the sites, water column profiles from the middle of the lake have been measured. These measurements were taken approximately 25 to 40 m from the M1 location. Figure 5.1 shows the seasonal changes of temperature, dissolved oxygen (D.O.), and pH, over the course of May through September 1998.

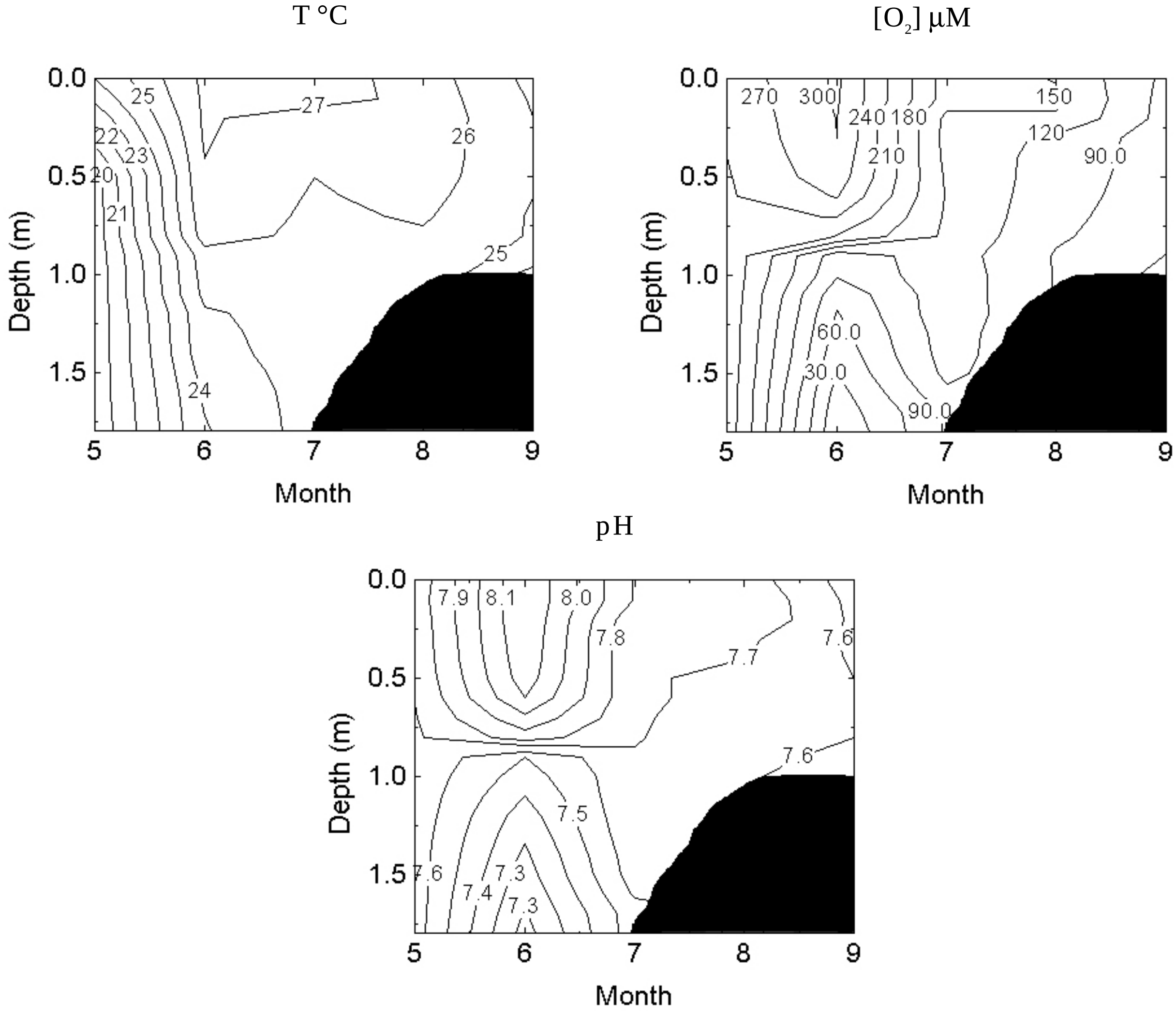

Figure 5.1: Seasonal evolution of physiochemical properties of Lake DePue from May to September 1998. Only the upper 2 m of the water column is displayed (in May the lake was 4.2 m deep in flood stage). The darkened areas represent the bottom of the lake, *i.e.* stages where the lake was shallower than the graph axis. Top left: temperature in degrees Celsius. Top right: D.O. in μM. Bottom: pH.

The temperature in Lake DePue is relatively constant at any given time throughout the water column, although the lake does warm rapidly once the summer months begin. This observation is expected, as temperature stratification would not be expected to occur in this lake because of the shallow depth. However, in the summer months there appears to be some chemical stratification of the water, particularly evident in the month of June. This is seen in the pH and D.O. profiles, which show a rapid difference in the span of 2 m from completely saturated with O_2 and high pH to nearly anoxic and lower pH. The profiles follow the classical trends of primary productivity causing super-saturation of D.O. and an increase in pH whereas at depth, respiration of organic matter consumes D.O. and lowers the pH (Stumm and Morgan, 1996). In the autumn, these gradients subside due to the diminished volume of the lake which likely increases mixing induced by the wind.

This "chemocline" may be induced by a dense nepheloid layer that has been observed at the sediment-water interface. This layer has been observed by a significant rise in the conductivity that occurs at the bottom 50 cm of the lake. Additionally, direct sampling of the water column in this region shows an increase in turbidity and particle concentration. This phenomena of a non-settling layer at the sediment interface is observed year round in the lake, although it becomes less pronounced in the late fall. The presence of this layer may help sustain the observed chemocline in pH and dissolved oxygen.

5.2 PROPERTIES AT C1

The C1 site is the location at which the zinc contamination apparently enters Lake DePue. As noted in Table 5.1, both the dissolved zinc and sulfate concentrations are extremely high, nearly 300 μM and 20 mM respectively. Additionally, voltammetry was performed on samples from C1 that were collected during and shortly after a flood event in the spring of 1998. These results show that nearly all of the dissolved Zn at this location is present as labile Zn^{2+}, even when the surface water has a high influence of lake water. Dissolved and labile zinc concentrations during the flood were 860 nM and 615 nM respectively and after the flood 275 μM and 250 μM respectively. A

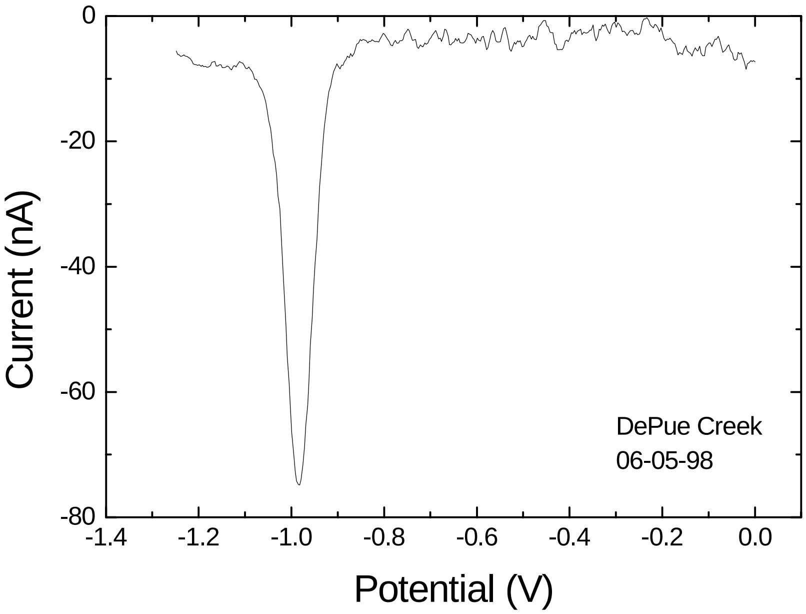

Figure 5.2: Voltammogram from the June 1998 sampling trip at Lake DePue. The sample originates from the C1 location and corresponds to a labile zinc concentration of approximately 250 μM.

voltammogram of water from C1 at the 250 μM concentration showing the peak of labile zinc is shown in Figure 5.2.

To examine the extent at which the effluent influences the lake, a plume study was conducted in July of 1998. Surface water was collected at 14 sites at various distances from the outlet of the creek and the location of each sample recorded by differential GPS. The concentrations of the effluent in the stream from Table 5.1 show that there are elevated levels of both Zn and SO_4^{2-} present. Thus these species were both monitored in the plume profiling. Concentrations of both Zn_d and SO_4^{2-} decreased rapidly, with 5% of the zinc present in the effluent remaining in the water column only 30 m away. However, significant zinc (3 times above lake "background" concentrations) was present in the surface water over 400 m away from the source of contamination. The concentrations of Zn_d and SO_4^{2-} are strongly correlated. This correlation is shown in Figure 5.3. This suggests that both dissolved species behaved similarly upon entering the lake. Since SO_4^{2-} is expected to primarily act conservatively in the water column (i.e., only be diluted, as opposed to participate in chemical reaction or sorption), the aqueous zinc concentration is also reduced primarily by dilution with lake water. Note that this conservative behavior of sulfate would not be expected in sediment pore water, where significant sulfate reduction occurs.

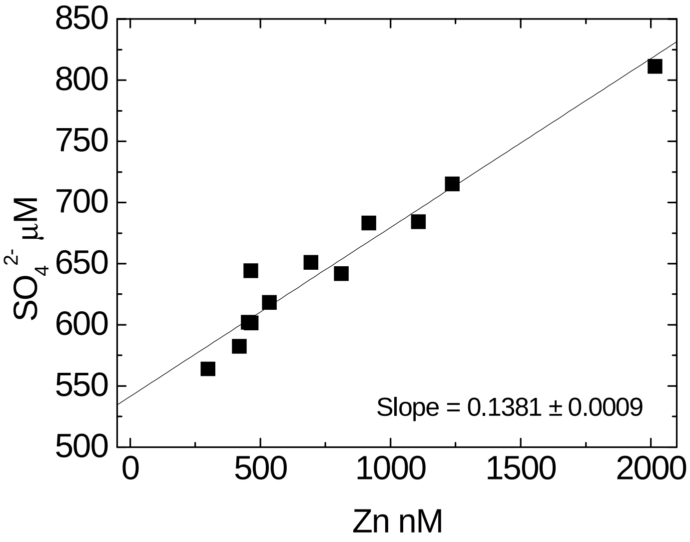

Figure 5.3: Correlation of the concentrations of Zn_d and SO_4^{2-} at each point in the plume study. The source concentrations are included in the regression, but are not displayed on the graph for clarity of the more important values. The correlation has a R^2 value of 0.9998.

5.3 SEDIMENT CHARACTERIZATION

The sediments of Lake DePue are generally characterized as loose, unconsolidated, and fine-grained silts and clays. The M_1 site is comprised of the thinnest layer of unconsolidated sediment. The stratigraphy consists of approximately 5 cm of light green-gray colored unconsolidated sediment, and 15 cm of darker brown to black colored consolidated sediment. The water content of the upper, unconsolidated layer is approximately 55% and drops to 25% in the consolidated region. These layers lie on top of a clay lens that could not be penetrated by the coring device. The core sampled from the C_2 site consisted of 80 cm of generally unconsolidated sediments, showing no significant consolidation or loss of water throughout the entire depth profile examined. The sediments are composed mainly of light green-gray silts and clays as in the upper unconsolidated sediments of M_1. At several depths (15, 22, and 33 cm), there are lenses that consist of fine sands grading to silt. These lenses also have a high content of organic plant material.

The core sample from C_1 was comprised of 50 cm of unconsolidated, watery sediment. The water content of these sediments averaged approximately 50% and reached a maximum of 70% by weight. However, the particles in this core showed more variation in their appearance and composition than at the other sampling locations. The first 6 cm of sediment are composed of green-gray silt and clays, similar to the upper sediments at the other locations. Cores from the 6-15 cm region of the core are composed of similar material, but also have orange-red-ochre masses present. These pieces range from 1 mm up to 1 cm in diameter and have a maximum in number at a depth of 10-12 cm. These pieces grade to finer particles at either end of the sediment depth range. The core sections from 16-24 cm are composed primarily of silts and clays, with pronounced lenses of organic plant detritus. Sediment stratigraphy from 24-38 cm is composed of finer, darker clays and silts, which contain light tan-colored clay inclusions. The inclusions are slightly more compacted than the surrounding sediment and compose up to 35% of total sediment at 32 cm depth. Adjacent to these clays is a porous gravel lens of sediment from 40-48 cm. The sediment contains small dark brown to black gravel grading to fine sands and containing some silt. Many of the sand grains in this region are red and orange in color. The lens contains more fine-grained particles toward the bottom and grades into mostly silts with some sands at 48 cm. The last 2 cm of the core (48-50 cm) is composed of more compacted, dark green clays.

The presence of crystalline mineral phases in the sediments was also examined by X-ray diffraction (XRD). This method relies on the diffraction of X-rays from crystalline lattice planes in the sample to provide a fingerprint. The results can then be compared to the diffraction lines of known minerals. However, mineral phases that are amorphous or in small quantities will not be detected by this technique. The X-ray diffractogram of sediment near the C_2 location from the summer of 2000 is given in Figure 5.4. Nearly all of the major peaks present can be attributed to the presence of either quartz, dolomite, or calcite. Although there are some minor, broad peaks that are difficult to assign, the XRD does not show the presence of any major crystalline zinc bearing phases. Since the sediment has a zinc concentration of approximately 10,000 ppm, any major zinc phases should easily be seen. Thus, characterization of the zinc in the lake sediments must be accomplished utilizing an alternate approach.

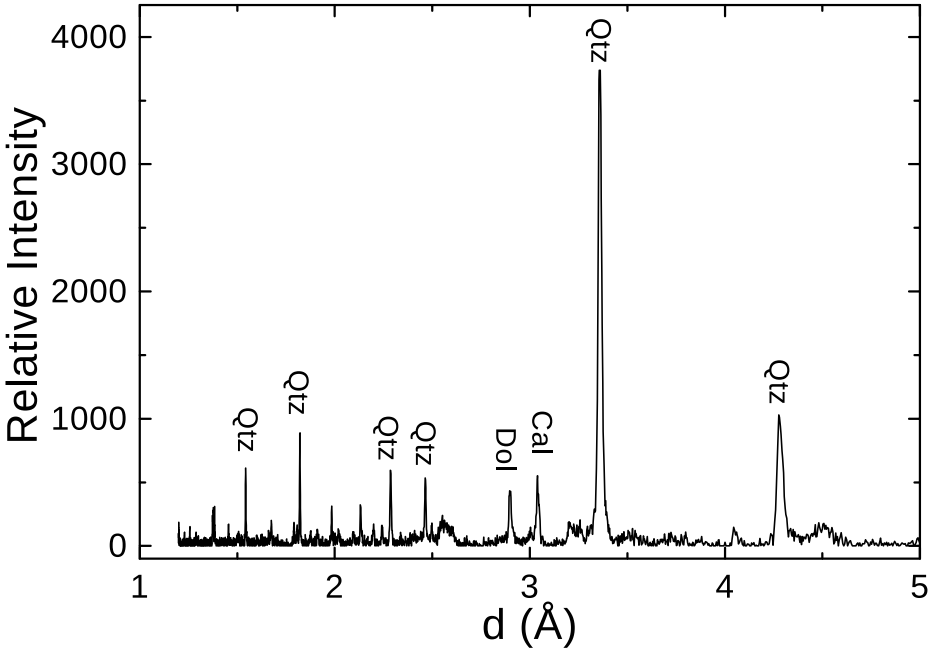

Figure 5.4: X-ray difractogram of Lake DePue sediments collected near the C_2 sampling site. Well-crystalline components consist primary of quartz (qtz), with some calcite (cal) and dolomite (dol).