*Aquatic Geochemistry* **9:** 87–110, 2003.

# Iron and Sulfur Chemistry in a Stratified Lake: Evidence for Iron-Rich Sulfide Complexes

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(Received 21 July 2003; accepted 4 November 2003)

**Abstract.** A four month study of a man-made lake used for hydroelectric power generation in northeastern Pennsylvania USA was conducted to investigate seasonal anoxia and the effects of sulfide species being transported downstream of the power generation equipment. Water column analyses show that the system is iron-rich compared to sulfide. Total Fe(II) concentrations in the hypolimnion are typically at least twice the total sulfide levels. *In situ* voltammetric analyses show that free Fe(II) as $[Fe(H_2O)_6]^{2+}$ or free $H_2S$ as $H_2S/HS^-$ are either not present or at trace levels and that iron-rich sulfide complexes are present. From the *in situ* data and total Fe(II) and $H_2S$ measurements, we infer that these iron-rich sulfide complexes may have stoichiometries such as $Fe_2SH^{3+}$ (or polymeric forms of this and other stoichiometries). These iron-rich sulfide complexes appear related to dissolution of the iron-rich FeS mineral, mackinawite, because IAP calculations on data from discrete bottle samples obtained from bottom waters are similar to the $pK_{sp}$ of mackinawite. Soluble iron-sulfide species are stable in the absence of $O_2$ (both in lake waters and the pipeline) and transported several miles during power generation. However, iron-sulfide complexes can react with $O_2$ to oxidize sulfide and can also dissociate releasing volatile $H_2S$ when the waters containing them are exposed to the atmosphere downstream of the power plant. Sediment analyses show that the lake is rich in oxidized iron solids (both crystalline and amorphous). Fe concentrations in FeS solids are low ($<5$ $\mu$mole/$gr_{dry\ wt}$) and the pyrite concentration ranges from about equal to the solid FeS to 30 times the solid FeS concentration. The degree of pyritization is below 0.12 indicating that pyrite formation is limited by free sulfide, which can react with the iron-rich sulfide complexes.

## Introduction

Lakes including man-made lakes (reservoirs), which were historically created with dams for power generation, flood control, water supply, and recreation, have a tendency to exhibit stratified conditions particularly during the summer months. During summer stratification, temperature and dissolved $O_2$ decrease with increasing water depth and correlate with the production of reduced chemical species (e.g., iron, manganese and sulfide) in the hypolimnion or anoxic bottom waters of the lake, as a result of the decomposition of organic matter in the hypolimnion and sediments

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(Balistrieri et al., 1992; Davison, 1993; Kuhn and Sigg, 1993). Eutrophication is of significant concern in lake and reservoir systems because of nonpoint and point nutrient releases (Carpenter et al, 1998; Jaworski et al., 1997) from septic systems, wastewater treatment facilities, atmospheric input of $NO_x$ and agricultural fertilizer inputs (runoff), with deep water anoxia as the ultimate result.

Sulfate input into lakes is from both atmospheric sources and natural weathering of soils and minerals within the area (Driscoll et al., 2003). The production of sulfide in the lake hypolimnion during summer stratification can be a significant problem in reservoirs used for power generation, specifically if the facility preferentially withdraws water from the bottom hypolimnion waters of the reservoir. As the sulfide-rich waters flow out of the turbine generation system into the receiving waters, significant odors can result that cause distress to downstream residents. In this study, we document the water chemistry of Lake Wallenpaupack in northeastern Pennsylvania, USA in order to make recommendations concerning the removal of sulfide and to promote green hydropower (Truffer et al., 2003).

Electrochemical work has documented that sulfide forms complexes with Fe and Mn over a wide range of ionic strengths (Al-Farawati and van den Berg. 1999; Luther et al., 1996; Zhang and Millero, 1994). In addition, a soluble multinuclear cluster complex of iron with sulfide ($FeS_{aq}$) has been shown to be present in lake waters (Davison, 1977; Davison et al., 1988; De Vitre et al., 1988) where the total Fe(II) is generally higher in concentration than $H_2S$. In addition, FeS aqueous clusters, $FeS_{aq}$, of unknown stoichiometry have been found in a variety of marine and estuarine environments (Theberge and Luther, 1997; Rickard et al., 1999; Luther et al., 2001; Taillefert et al., 2002a, b; Hebert and Morse, 2003) where dissolved sulfide is higher in concentration than or nearly equal to that of dissolved Fe(II). In laboratory studies, Theberge and Luther (1997) showed that FeS aqueous clusters, $FeS_{aq}$, of unknown stoichiometry form in seawater when equal amounts of Fe(II) are reacted with $H_2S$. The $FeS_{aq}$ species have a unique signal using voltammetry (Davison, 1977; De Vitre et al., 1988; Theberge and Luther, 1997).

It is now possible to measure *in situ* and without sampling artifacts the dissolved $O_2$, Mn(II), Fe(II), $FeS_{aq}$, Fe(III)-organic complexes and $H_2S$ in a single scan simultaneously with solid state voltammetric electrodes (Luther et al., 2001; Taillefert et al., 2000) by deploying the electrodes directly into the lake waters. Previous lake studies using voltammetry (Davison, 1977; De Vitre et al., 1988) have sampled waters with bottles or have pumped waters into a cell aboard a platform or a ship with measurements being made up to 6 h after sample collection. We show that the hypolimnion waters of Lake Wallenpaupack contain dissolved Mn(II), $FeS_{aq}$, Fe(III)-organic complexes, but no or trace amounts of free Fe(II) and $H_2S$. Also, the presence of total Fe(II) is at least twice that of total sulfide and leads to the possible efficient oxidation of sulfide on short-time scales ($<$ 2 h) when $O_2$ is added to the waters. Although there is significant solid phase Fe in the sediments, the production of sulfide from sulfate reduction does not lead to quantitative removal of sulfide via precipitation of FeS and pyrite, $FeS_2$. Thus, both dissolved Fe(II) and $H_2S$ diffuse into the bottom lake waters. The waters are enriched with Fe(II) relative to $H_2S$ by as much as fourfold with formation of $FeS_{aq}$ cluster complexes.

## 1. Experimental

### 1.1. SITE

The Lake Wallenpaupack Hydroelectric Project, owned and operated by Pennsylvania Power and Light Generation, LLC (PPL), is located in the Pocono Mountains of northeastern Pennsylvania (Figure 1). The Project dam and dike structures were constructed to impound Wallenpaupack Creek in 1926 to form what is Lake Wallenpaupack, an important regional tourist destination. The lake is 13 miles long and up to a mile wide, with a surface area of approximately 5,700 acres. Water is drawn from the lake and diverted through a 3.25-mile long 14-ft diameter steel pipeline to the powerhouse for power generation. Flow in the pipeline splits into two 8-ft diameter pipes just below an open-air surgetank on the hillside directly above the powerhouse. The powerhouse is situated along one bank of the Lackawaxen River, approximately 380 feet lower in elevation than the top of the lake surface. The powerhouse discharges water directly into a tailrace constructed to have water leaving the plant flow into the Lackawaxen River, approximately 13 miles upstream of its confluence with the Delaware River.

### 1.2. DISCRETE SAMPLES

Discrete samples were taken from lake waters and from the tailrace with a one-liter Niskin bottle, and from the pipeline via ports and plastic tubing installed to collect water. We used spectrophotometric methods to measure samples for total sulfide, total iron, total manganese and iron(II) from early June to early October 2002 on a weekly basis. We used the methylene blue method (Cline, 1969) for total sulfide, which is defined as free sulfide ($H_2S$, $HS^-$) and sulfide bound to Fe(II) (Luther et al., 2001). We used the $Fe^{2+}$ ferrozine method of Stookey (1972) with and without the use of a reducing agent (hydroxylamine). Both Fe(II) as $[Fe(H_2O)_6]^{2+}$ and Fe(II) bound to sulfide react to form the ferrozine complex with Fe(II) to give total Fe(II). Adding the reducing agent permits total iron analysis so that $Fe^{3+}$ can be determined by difference. Mn was measured by the USEPA method, which uses sodium periodate to oxidize Mn(II) to permanganate. The Mn data determined by this method and by *in situ* voltammetry (see below) agree well.

Not all samples were filtered before measurement onboard the boat with a portable spectrophotometer. However, comparison of analyses between filtered and non filtered samples showed that all total Fe(II) and total sulfide passed through a 0.2 $\mu$m filter and are dissolved (operationally defined).

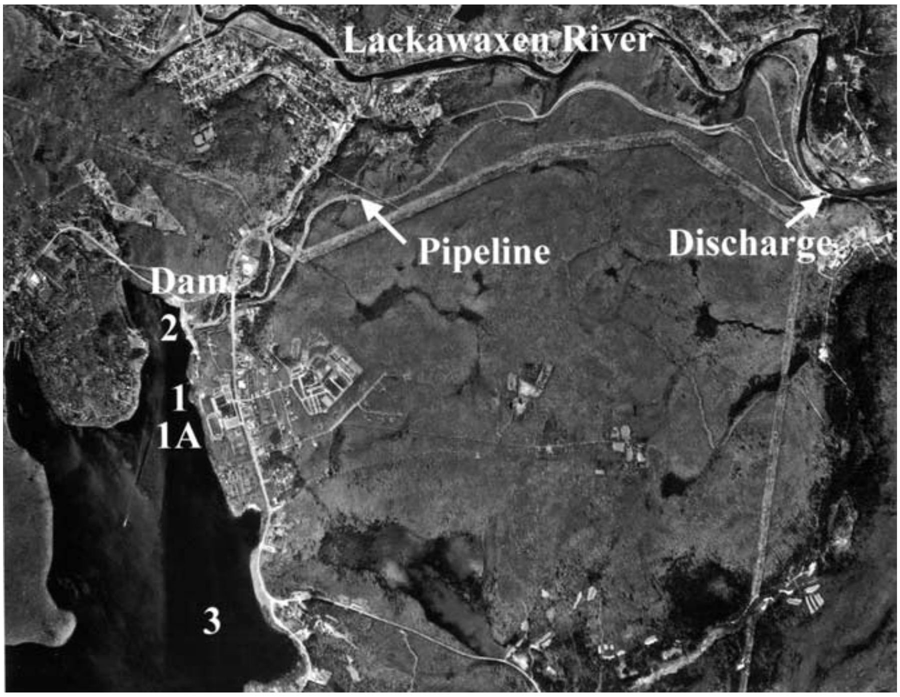

*Figure 1.* The Lake Wallenpaupack area in northeast Pennsylvania (41°25′29.0"N; 75°13′16.7"W). Photograph courtesy of the USGS.

### 1.3. IN SITU MEASUREMENTS

Real time analyses were performed on a total of two separate days on each of the two one-week field trips during August and September between 9:30 AM to 5:00 PM. Temperature and salinity were obtained with a YSI-30 T-S meter with a 16 m cable. pH was measured by a portable Digi-Sense pH meter using a Sensorex pH electrode with a 15 m cable that was calibrated with NIST (NBS) pH standards. *In situ* voltammetry measurements were also taken at all locations using a 30 meter cable (see below). For the pipeline, a flow cell with electrodes (Luther et al., 2002) was mated to the port to perform real time measurements. Dissolved $O_2$, Mn(II), Fe(II), Fe(III) organic complexes, $FeS_{aq}$ and $H_2S$ were measured using a solid-state gold-amalgam (Au/Hg) PEEK$^{TM}$ voltammetric microelectrode with a solid state Ag/AgCl reference and a counter (Pt) electrode that constituted a three-electrode system (Brendel and Luther, 1995; Luther et al. 1999; Luther et al. 2001). Table I shows the electrode reactions for the chemical species that can be measured. The specifics are detailed below. The waterproof wires for the T-S sensor, pH sensor and the voltammetry cable were tied together and mounted in a stainless steel metal CTD cage attached to a hand winch for lowering through the water column. The electrodes were placed into a Delrin housing that was mounted into the center of the metal cage. Data were obtained in real-time from the surface (0.2 m) of the

*Table I.* Electrode reactions at the mercury electrode for oxygen, sulfur, iron and manganese species. Potentials are given for lake water and can vary with medium

| | $E_p$ (V vs Ag/AgCl) |
|---|---|
| $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ | −0.30 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | −1.30 |
| $HS^- + Hg \rightarrow HgS + H^+ + 2e^-$ | Adsorption onto Hg $< -0.7$ |
| $HgS + H^+ + 2e^- \leftrightarrow HS^- + Hg$ | −0.7 |
| $S^0 + Hg \rightarrow HgS$ | Adsorption onto Hg $< -0.7$ |
| $HgS + H^+ + 2e^- \leftrightarrow HS^- + Hg$ | −0.7 |
| $Hg + S_x^{2-} \rightarrow HgS_x + 2e^-$ | Adsorption onto Hg $< -0.7$ |
| $HgS_x + 2e^- \leftrightarrow Hg + S_x^{2-}$ | −0.7 |
| $S_x^2 + xH^+ + (2x - 2)e^- \rightarrow xHS^-$ | −0.7 or more negative (varies with scan rate) |
| $Fe^{2+} + Hg + 2e^- \leftrightarrow Fe(Hg)$ | −1.43 |
| $Mn^{2+} + Hg + 2e^- \leftrightarrow Mn(Hg)$ | −1.55 |
| $FeS + 2e^- + H^+ \rightarrow Fe(Hg) + HS^-$ | −1.2 |
| $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ | −0.25 to −0.9 |

water column to the bottom of the lake, ranging from 11 to 19 meters in depth. *In situ* determination eliminated the possibility of chemical speciation artifacts or errors during sampling, sample storage and transport back to the laboratory.

### 1.4. MICROELECTRODES AND ANALYTICAL METHODS

Gold amalgam PEEK™ electrodes were made by fixing 100 $\mu$m-diameter Au wire soldered to the conductor wire of BNC cable within a body of 0.125″-diameter PEEK™ tubing, which is commercially available as standard HPLC high-pressure tubing. The metal is fixed within the tubing with the West System 105 epoxy resin and 206 hardener to form a high-purity, optical-grade, nonconductive fill. The epoxy was injected into the tip of the PEEK™, which contained the gold wire that was previously soldered to the conductor wire of the BNC cable. The epoxy comes out the end where the BNC cable is and the BNC cable is then pushed flush to make contact with the PEEK™ tubing because the PEEK™ tubing is slightly smaller than the diameter of the BNC cable. The epoxy has a moderate setting time (~1 h). On setting, the epoxy seals the gold into the tip, which can be refilled with epoxy if necessary. Then the BNC cable end is coated with Scotchkote (3M) electrical coating and Scotchfil (3M) electrical insulation putty. After final setting of the epoxy, the tip is sanded and polished. We have tested this design in the lab at a pressure of 200 atm without failures. PEEK™ and high-purity epoxy fill permits the determination of metal concentrations without risk of contamination, and at temperatures as high as 150 °C. Once constructed each electrode surface was polished and plated with Hg by reducing Hg(II) from a 0.1 N Hg/0.05 N $HNO_3$ solution, for 4 minutes at a potential of $-0.1$ V, while purging with $N_2$. The mercury/gold amalgam was conditioned using a 90 second $-9$ V polarization procedure in a 1 N NaOH solution. The electrode was then run in linear sweep mode from $-0.05$ to $-1.8$ V versus a Saturated Calomel Electrode (SCE) or Ag/AgCl electrode several times in oxygenated seawater to obtain a reproducible $O_2$ signal.

### 1.5. IN SITU VOLTAMMETRIC ANALYSES

All voltammetric analyses were carried out in real-time using an Analytical Instrument Systems, Inc. (AIS) DLK-100 electrochemical analyzer, which was controlled by a microcomputer aboard ship or off the pipeline, using software provided by the manufacturer. The analyzer and computer were connected to a 12 V D.C. marine deep cycle battery. A Long Cable Receiver, AIS Model DLK-LCR-1, was connected directly to the analyzer as an interface with a 30-m waterproof cable. The cable contained three shielded wires [center conductor with shield] for the working (Au/Hg), reference (solid state Ag/AgCl; see Luther et al., 1999) and counter (Pt) electrodes as well as DC power (+15 V, $-15$ V) and ground. The other end of the cable was connected to a transmitter, AIS Model DLK-LCT-1, enclosed in a pressure housing and mounted on a stainless steel frame connected to a winch with durable rope. The transmitter was connected via 1-meter lengths of shielded cable directly to the working, reference and counter electrodes mounted on the stainless steel frame. The working electrode acted as the virtual ground for the system. This setup allows signals to be transmitted through 30 m of cable without signal degeneration. We typically used linear sweep voltammetry and cyclic voltammetry (1000 mV/s) waveforms for the *in situ* analyses. Any other electrochemical waveform can also be applied to this electrode system. The potential range scanned was typically $-0.05$ to $-1.8$ V.

To maintain reproducibility during analysis, a conditioning step was used between each potential scan. When $O_2$ is present, conditioning is not necessary and a value more negative than $-0.1$ V will result in partial consumption of $O_2$. We have found that a potential of $-0.05$ V for a period of $<5$ seconds restores the electrode surface when measuring Fe and/or Mn in anoxic environments in the absence of $H_2S$. If $H_2S$ or a soluble Fe(III) species is present, a potential of $-0.8$ V is used to remove any Fe, Mn and sulfide deposited on the electrode, since none of these species is electroactive at this potential. Standardization of the electrodes is described in Brendel and Luther (1995) and Luther et al (2002). In this study, we collected and filtered both surface and bottom waters in order to perform standardizations.

### 1.6. SEDIMENT SAMPLING

Sediment samples were collected with a gravity core sampling device from a pontoon boat. The sediment was sliced onboard ship into 2 cm slices, placed in acid-washed 50 ml centrifuge tubes so that there was no headspace in the tube and immediately frozen for subsequent analysis. The porewaters were then extracted by centrifugation under a $N_2$ atmosphere in the lab but were not analyzed.

### 1.7. SOLID PHASE EXTRACTION AND MEASUREMENTS

For each depth interval, the centrifuged sediment was sub-sampled to provide three replicates for separate determinations of amorphous iron (ASC-Fe), total amorphous and crystalline iron [$Fe(III)_T$], FeS, and pyrite. The ASC-Fe is defined as the material leached from ascorbic acid solution (Anschutz et al., 1998) and includes some FeS (Kostka and Luther, 1994). Crystalline iron ($Fe_{crys}$) was defined as the reactive Fe leached during a dithionite extraction minus the ASC-Fe fraction (Kostka and Luther, 1994). $Fe_{crys}$ has been shown to contain large portions of crystalline and amorphous Fe(III)oxides, and traces of reactive Fe silicates (Canfield 1989; Kostka and Luther, 1994).

Dissolved Fe(II) was analyzed by colorimetry using a Spectronic 601 (Milton Roy). Samples were immediately stabilized in the ferrozine after filtration under a $N_2$ atmosphere. The ferrozine solution consisted of 50% of a 2.5 M ammonium acetate buffer and 50% of 0.01 M ferrozine. Samples were allowed to stand for less than 30 min for color development, followed by an absorbance measurement at 562 nm. For FeT determination, 0.1 M HCl-hydroxylamine was added to the samples to reduce any dissolved Fe(III) to Fe(II). FeT samples were allowed to stand for 24 h at room temperature to ensure complete Fe(III) reduction had taken place. Then the FeT samples were reacted with ferrozine solution for subsequent Fe analysis.

For amorphous iron (ASC-Fe), 10 ml of ascorbic acid solution were added to 0.4 g of sediment according to the method of Anschutz et al. (1998). The ascorbic acid solution consisted of 10 g Na-citrate and 10 g bicarbonate in 200 ml of de-aerated DI water to which 4 g of ascorbic acid were slowly added to obtain a pH of 8. The samples were then put into a water bath (50 °C) and shaken at 200 rpm. After 24 h, the samples were filtered (0.2 $\mu$m) and measured for Fe to give ASC-Fe.

To determine total Fe(III) as [Fe(III)]oxide (amorphous + crystalline), approximately 0.25 g of sediment was mixed with 10 ml of dithionite solution. The dithionite solution was prepared daily by dissolving 20 g of dithionite into a 200 ml mixture of 0.35 M Na-acetate/0.2 M Na-citrate, which had been de-aerated by purging with $N_2$ for 1 h. The samples were then shaken at 200 rpm for 2 days at room temperature. The extract was filtered (0.2 $\mu$m) and measured for FeT by the ferrozine method as indicated above.

Pyrite ($FeS_2$) and acid volatile sulfide (AVS) were extracted from wet sediments in a sequential extraction. First FeS was extracted with 3 M HCl. $FeS_2$ determination was accomplished by reduction with acidified Cr(II) and AVS determination by acidification with 3 M HCl according to the methods described in Luther et al. (1992). A Jones reduction column was used daily to reduce 1 M $CrCl_3$ (in 1 M HCl) to Cr(II). The sulfide produced by these two extraction schemes was purged with $N_2$ and trapped in 1 M NaOH prior to measurement by cathodic square wave voltammetry with a hanging mercury drop electrode system (model 303A, EG&G Princeton Applied Research coupled to a DLK-100A electrochemical analyzer from Analytical Instrument Systems, Inc.).

### 1.8. DEFINITION OF SOLID PHASE FRACTIONS EXTRACTED

Fe-ASC is defined as the amorphous iron(III) (oxy)hydroxide, which reacts most quickly with sulfide to form FeS (Fe-AVS). Fe-dithionite [Fe(III)T] is the iron(III) in both amorphous and crystalline iron(III) (oxy)hydroxide fractions. The total reactive Fe ($Fe_{total}$ or $Fe_{reactive}$) is defined as the iron extracted from the dithionite leach plus the sulfide from the AVS leach plus one-half the sulfide from the $FeS_2$ leach (Equation (1)). This is the iron that can eventually form pyrite or has already been converted to pyrite.

$$\mathrm{Fe}_{\mathrm{total}} = \mathrm{Fe}_{\mathrm{reactive}} = \text{Fe-dithionite} + \text{Fe-AVS} + \text{Fe-pyrite}. \tag{1}$$

The crystalline iron ($Fe_{crys}$) is defined as the Fe-dithionite minus the Fe-ASC (Equation (2)).

$$\mathrm{Fe}_{\mathrm{crys}} = \text{Fe-dithionite} - \text{FeASC}. \tag{2}$$

Mn-dithionite and Mn-ASC are defined similar to the Fe-dithionite and Fe-ASC, except the Mn can be in +3 and +4 oxidation states not just +3 as with Fe.

## 2. Results

### 2.1. WATER COLUMN DATA

Figure 2 shows the total Fe(II), total sulfide, total Fe and Mn data from the hypolimnion at 14.5 to 17 m water depths at site 1 (Wilsonville area) over the four month period in 2002. In early June, total Fe(II) comprises a small amount of the total Fe whereas it is the major form of Fe in July, August and September. Total Fe increases from 15 $\mu$M to 60 $\mu$M in mid July, remains constant till late August and September when it increases again. Fe(II) increases from about 1 $\mu$M to about 40 $\mu$M in July and then remains nearly constant till the end of the sampling. Mn increases from 15 $\mu$M in early June to 30 $\mu$M in late June and early July after which it steadily decreases during the summer and is not detectable in late September and October. Total sulfide is not detectable in early June, then becomes measurable in late June/early July followed by a steady increase from 1 to 22 $\mu$M in late August. The

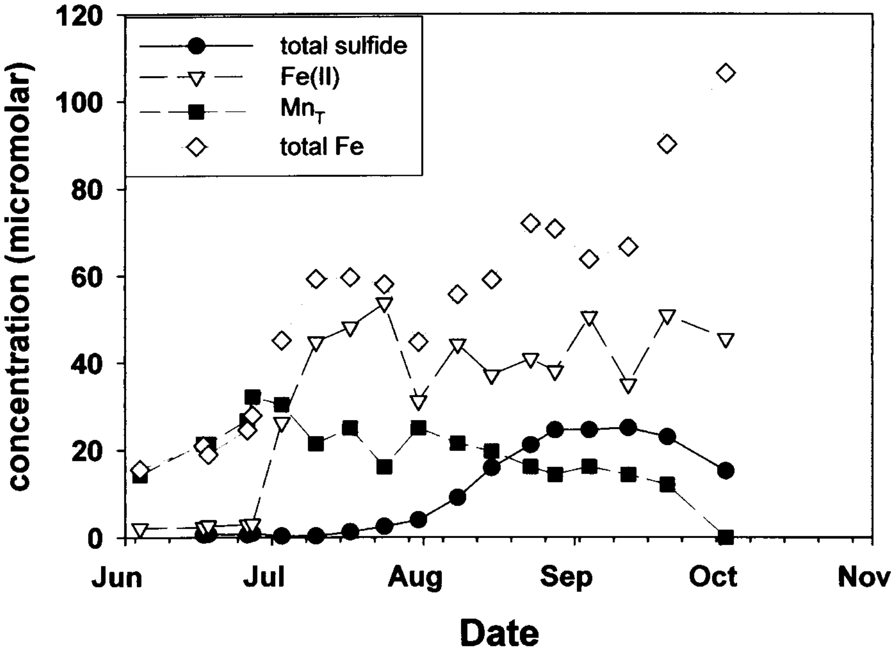

*Figure 2.* Seasonal data for Fe, S and Mn in the bottom waters of Lake Wallenpaupack at Wilsonville site 1.

total sulfide concentration remained constant until late September when it began to decrease. These data show that the hypolimnion is seasonally anoxic and that the formation of reduced chemical species occurs in the order Mn(II), Fe(II), and $H_2S$ in accordance with the decomposition of organic matter by alternate electron acceptors (Froelich et al., 1979).

Figure 3 shows two representative depth profiles determined with traditional bottle sampling and spectrophotometric analyses at the deepest water depth site (Wilsonville site 1) during August and September. Fe, Mn, and $H_2S$ are detectable at about 8 m and increase with depth. The Fe(II) is typically two to three times higher than the total sulfide at all depths indicating that Fe(III) reduction (from both direct microbial reduction and chemical reduction by sulfide, etc.) is more significant than sulfate reduction. Other sites show similar characteristics.

Figure 4 shows representative *in situ* voltammetry data at a 8 meter depth on August 21, 2002 for the Wilsonville site1. Similar voltammograms occur in deeper waters, but the current increases or decreases according to the concentration of the species present. Dissolved Mn(II) (−1.6 V) and $FeS_{aq}$ (−1.2 V) are detectable. However, dissolved free Fe(II) as $[Fe(H_2O)_6]^{2+}$, which gives an "s" shaped signal between the $FeS_{aq}$ and Mn(II) peaks at −1.40 V, is not detectable. The broad "s" shaped signal at −0.7 V indicates the reduction of Fe(III) to Fe(II) in soluble Fe(III)-organic compounds (Huettel et al., 1998; Taillefert et al., 2000; 2002a, b). Although this signal cannot be quantified with a standard because all

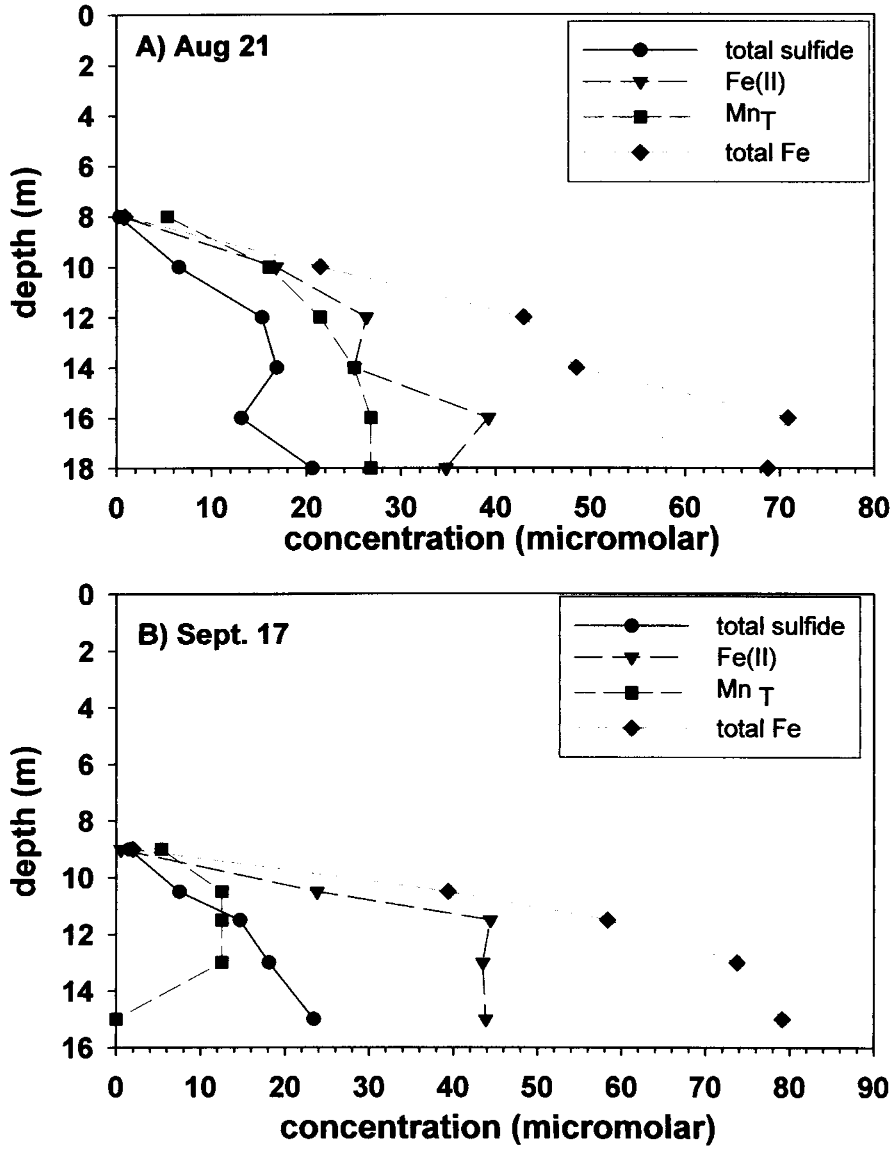

*Figure 3.* Representative profiles from analyses of discrete water samples taken from the Wilsonville site 1.

Fe(III) organic complexes give a different current versus concentration curve as well as different potential for the reduction of Fe(III) to Fe(II) (Taylor et al., 1994; Lewis et al., 1995), the signal shows that Fe(III) is present and corresponds with the measurement of total Fe, which is higher than Fe(II) from traditional bottle samples (Figure 2). No sharp peak signal at –0.7 to –0.8 V for $H_2S$ (Brendel and Luther, 1995) is observed and indicates that all sulfide is bound to Fe (Luther et al.,

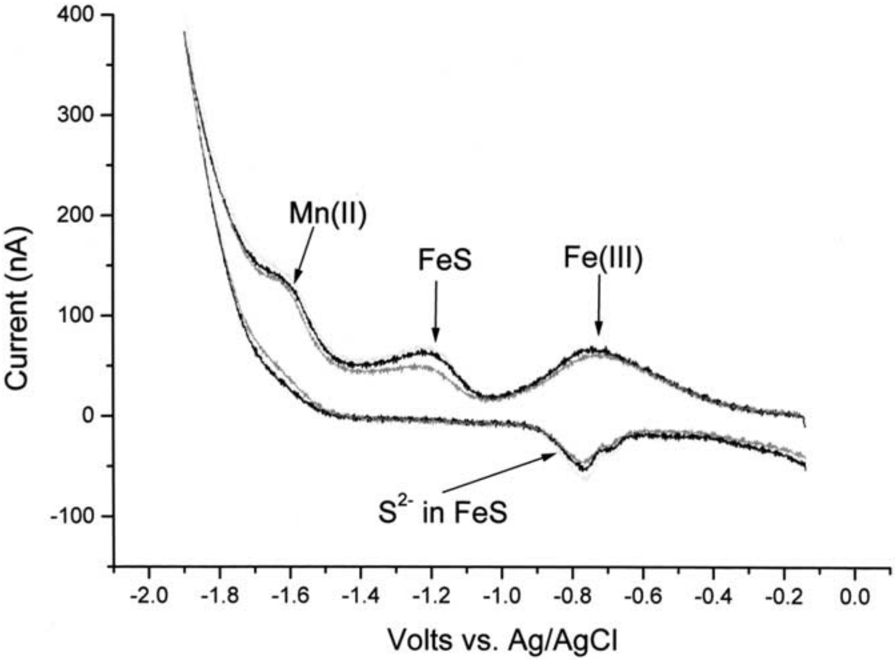

*Figure 4.* Cyclic voltammetric scans taken in Lake Wallenpaupak waters on Aug. 21, 2002 at site 3. Scan direction is from positive to negative then back to positive; scan rate is 1 V/sec. $Mn^{2+}$, FeS is observed, but free $H_2S$ and $Fe^{2+}$ are not detected.

1996; Taillefert et al., 2000). Because free or hydrated Fe(II) was not observed, the Fe(II) was also bound entirely to sulfide (see discussion below).

Figure 5 shows *in situ* voltammetry data from September 17, 2002. At 8.7 m from the surface, trace amounts of $O_2$ and Fe(III) were present. Fe(III) increased in current (and concentration) as $O_2$ decreased at 9.1 m. At these depths, Mn(II) also gave a peak shifted from −1.6 V presumably due to organic complexation. At 10.2 m, $FeS_{aq}$ was present at −1.2 V as was Fe(III) bound to different organic compounds, giving broad peaks at both −0.35 V and −0.8 V. Taillefert et al. (2000) showed that Fe(III) organic complexes can be observed over the potential range from −0.2 to −0.9 V. The sharper edge for the −0.9 V signal indicates that $H_2S$ or soluble S(0) is present because both give a similar signal at the Hg electrode (Rozan et al., 2000). The scan at 10.2 m is similar to the laboratory studies of Taillefert et al. (2000), who added small amounts of sulfide to high concentrations of an Fe(III) organic complex. Thus the sharp edge for the peak at −0.9 V is likely S(0) at all depths and sites because Fe(III) is detectable by voltammetry and discrete methods (Figures 2 and 3). Similar to the August data, both free Fe(II) and free sulfide [S(0) is likely present] were not observed or were in trace amounts. Detection limits for soluble Mn(II) and Fe(II) are 1.5 micromolar, whereas free sulfide is 200 nanomolar (Luther et al., 1991).

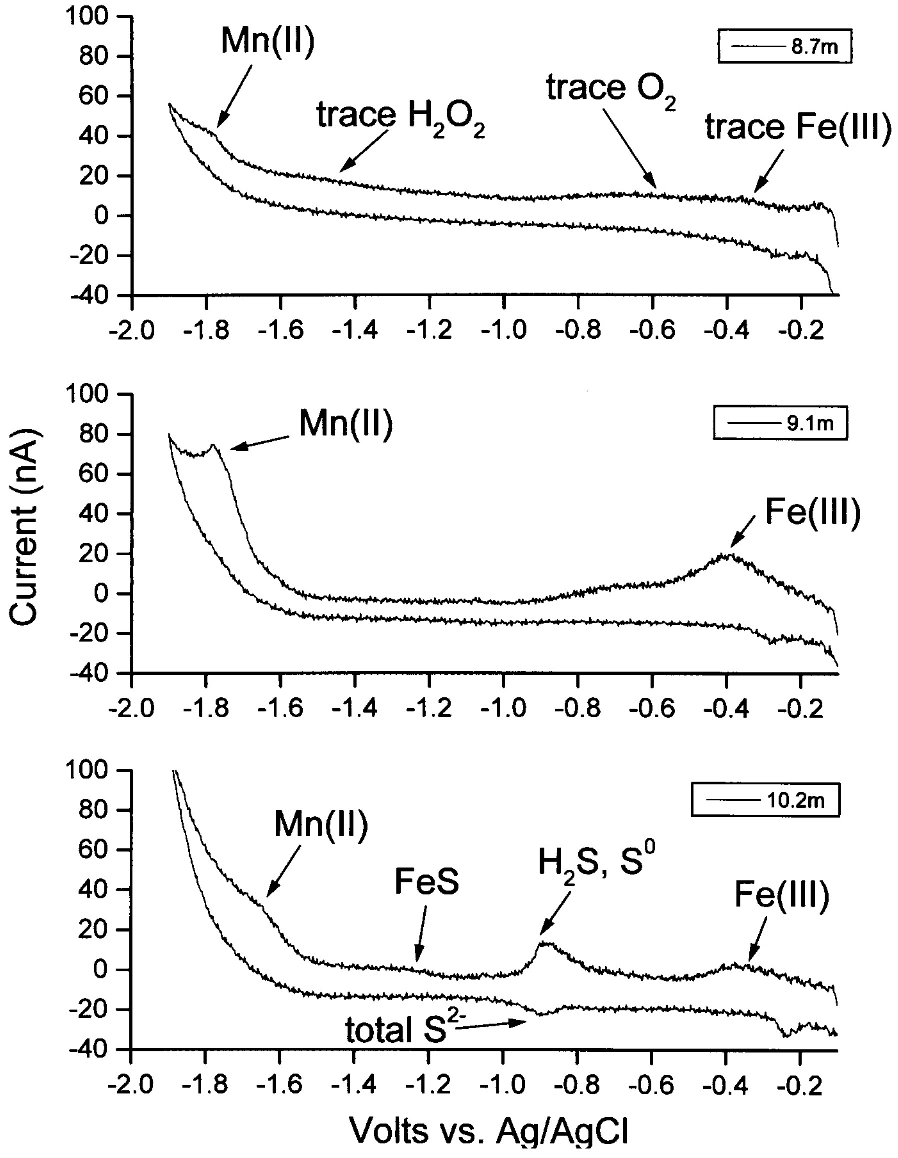

*Figure 5.* Cyclic voltammetric scans taken at the oxic-anoxic interface of Lake Wallenpaupak waters on Sept. 17, 2002 at site 2 at the dam forebay. Scan direction is from positive to negative then back to positive; scan rate is 1 V/sec. $Mn^{2+}$, FeS, Fe(III)-organic complexes and S(0) (traces of $H_2S$) are observed, but $Fe^{2+}$ is not detected.

Our *in situ* voltammetry data show different speciation characteristics than previous voltammetry data on samples from discrete bottles and from pumping water into a cell aboard ship (Davison, 1977; De Vitre et al., 1988). In those studies, both free sulfide and Fe(II) were measurable, but loss of current for free sulfide and increases in current for free Fe(II) were noted over time. Also, those measurements were not performed immediately after sampling but hours ($< 6$) after sample collection so the iron-sulfide system may have reached a different state of equilibrium after sampling and during storage (Davison et al., 1988). Measurement of samples aboard ship at atmospheric pressure and temperature versus *in situ* measurement at higher pressures and lower temperatures with depth can shift the equilibrium from iron-sulfide complexes to the free ions (Luther et al., 2002).

Figure 6 is a profile from the *in situ* data obtained on August 21, 2002. Temperature decreases sharply from 22 to 12 °C (surface to bottom), and pH decreases with depth systematically from a surface high of 7.0 to about 6.2 near the bottom. Note that Mn(II) is found at the interface, where overlap of $O_2$ with Fe(III) organic complexes can occur. Mn(II) shows a subsurface maximum, then a decrease with depth to a constant concentration in the hypolimnion. Fe(III) shows a similar profile as Mn(II). $FeS_{aq}$ and $H_2S/S^0$ (see above) also increase with depth and this is the only profile that shows a possible sharp peak for $H_2S/S^0$. For the two profiles in August and four in September, $O_2$, Fe(III) organic complexes and Mn(II) were all detectable in trace amounts at the oxic-anoxic interface. $FeS_{aq}$ also appeared to be present in trace amounts at or just below the interface.

## 2.2. SEDIMENT DATA

Figures 7 and 8 show the results for Fe and Mn solid phase speciation for Lake Wallenpaupack sites 1, 1A and 2 (samples collected August 2002). Total solid phase Fe ranges from 250 to 420 $\mu$mole/$gr_{\text{dry wt}}$ and is an order of magnitude higher than the total solid phase Mn. Fe in FeS or acid volatile sulfide (FeAVS) is less than 5 $\mu$mole/$gr_{\text{dry wt}}$, whereas pyrite generally has a higher concentration but is typically less than 40 $\mu$mole/$gr_{\text{dry wt}}$. The $FeS_2$ values are reported on the basis of Fe not S so doubling the values gives the total S stored in the sediments, which are in the range reported by Giblin et al. (1990) for a large number of lakes.

Table II shows all the Fe solid phase data including the percentages of the crystalline and amorphous Fe(III) phases. In Figure 7 and Table 2, the sites show that there is a large excess of total and amorphous iron(III) that can react with sulfide to form pyrite and FeS. These data are consistent with the soluble iron in the lake bottom waters always exceeding the sulfide, which indicates that there is more Fe binding to sulfide and that sulfide concentration is limiting iron-sulfide mineral or solid formation. Based on these solid phase results and the water column results, Fe(III) reduction appears more significant than sulfate reduction.

The degree of pyritization (DOP) is calculated with Equation (3), which is an indicator of the utilization of iron(oxy)hydroxide and sulfide for pyritization (DOP).

*Table II.* Solid phase data from sediments sampled on August 21, 2003

| Site | Depth (cm) | Fe ASC ($\mu$mol/gr$_{\text{dry wt.}}$) | Fe Dithionite ($\mu$mol/gr$_{\text{dry wt.}}$) | Fe AVS ($\mu$mol/gr$_{\text{dry wt.}}$) | Fe Pyrite ($\mu$mol/gr$_{\text{dry wt.}}$) | Fe Total ($\mu$mol/gr$_{\text{dry wt.}}$) | Fe Crys ($\mu$mol/gr$_{\text{dry wt.}}$) | % Fecrys | % FeASC |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0–2 | 114.2 | 233.8 | 0.99 | 17.52 | 252.32 | 119.57 | 47.39 | 45.28 |
|  | 2–4 | 140.7 | 351.7 | 3.31 | 30.74 | 385.78 | 210.98 | 54.69 | 36.48 |
| 1A | 0–2 | 110.4 | 243.1 | 1.08 | 28.22 | 272.38 | 132.72 | 48.73 | 40.52 |
|  | 2–4 | 129.7 | 342.4 | 1.78 | 34.08 | 378.24 | 212.67 | 56.23 | 34.29 |
|  | 4–6 | 97.7 | 333.4 | 1.73 | 40.82 | 375.97 | 235.72 | 62.70 | 25.99 |
| 2 | 0–2 | 206.9 | 399.2 | 6.05 | 3.77 | 408.99 | 192.27 | 47.01 | 50.59 |
|  | 2–4 | 133.8 | 346.4 | 6.88 | 7.57 | 360.83 | 212.62 | 58.93 | 37.07 |

Definitions are: FeASC = amorphous Fe from the ascorbate extraction; FeAVS = acid volatile sulfide; Fetotal = Fedithionite + FeAVS + Fe pyrite; Fecrys = Fedithionite-FeASC.

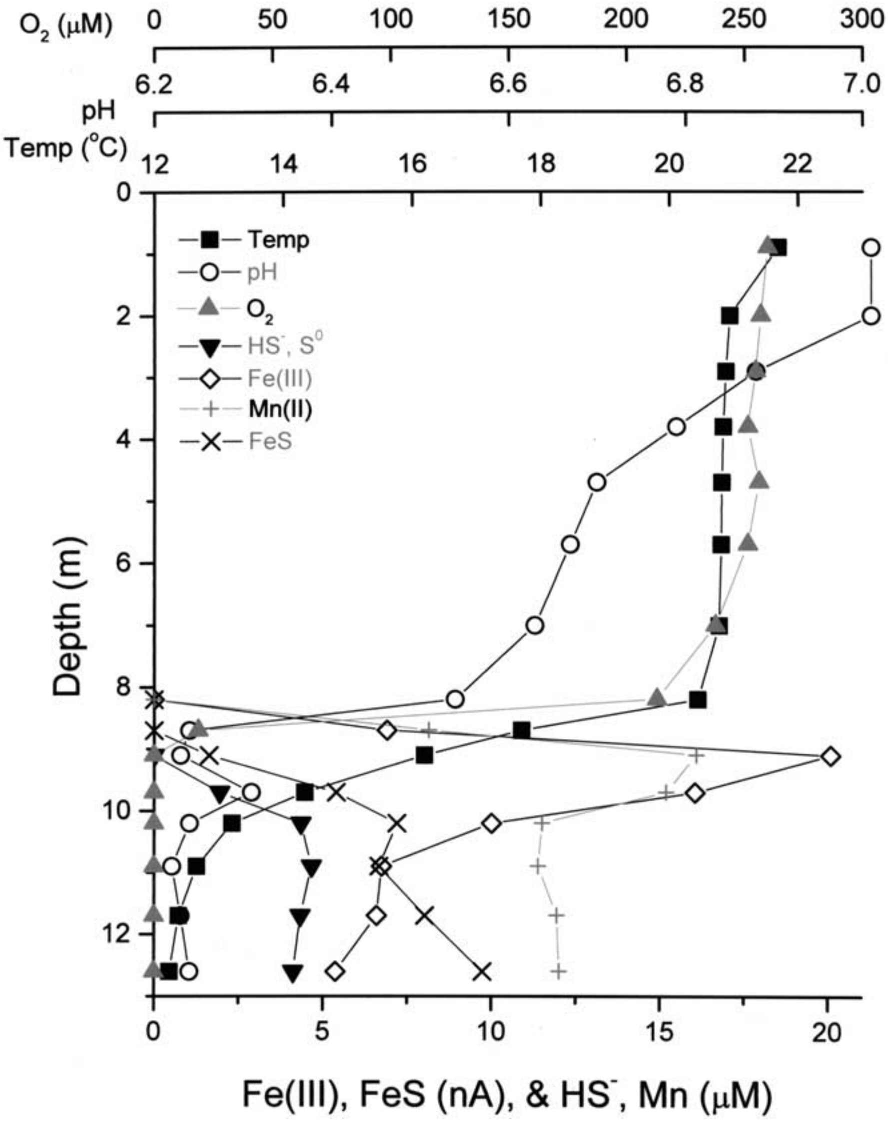

*Figure 6.* *In situ* profile for site 2 at the dam forebay on Sept. 17, 2002. $O_2$ and FeS overlap at the oxic/anoxic interface with a peak of $Mn^{2+}$ below the interface.

The DOP scale is from 0 to 1 and is an operational definition based on leaching experiments. Lake Wallenpaupack sediments are typically below 0.1 indicating that there is much more oxidized Fe available to form pyrite as has been found in continental slope sediments (Morse et al., 2002).

$$\mathrm{DOP} = \frac{[\mathrm{FeS_2}}{[\mathrm{FeS_2}] + [\mathrm{AVS} - \mathrm{Fe}] + [\mathrm{Dithionite} - \mathrm{Fe}].} \tag{3}$$

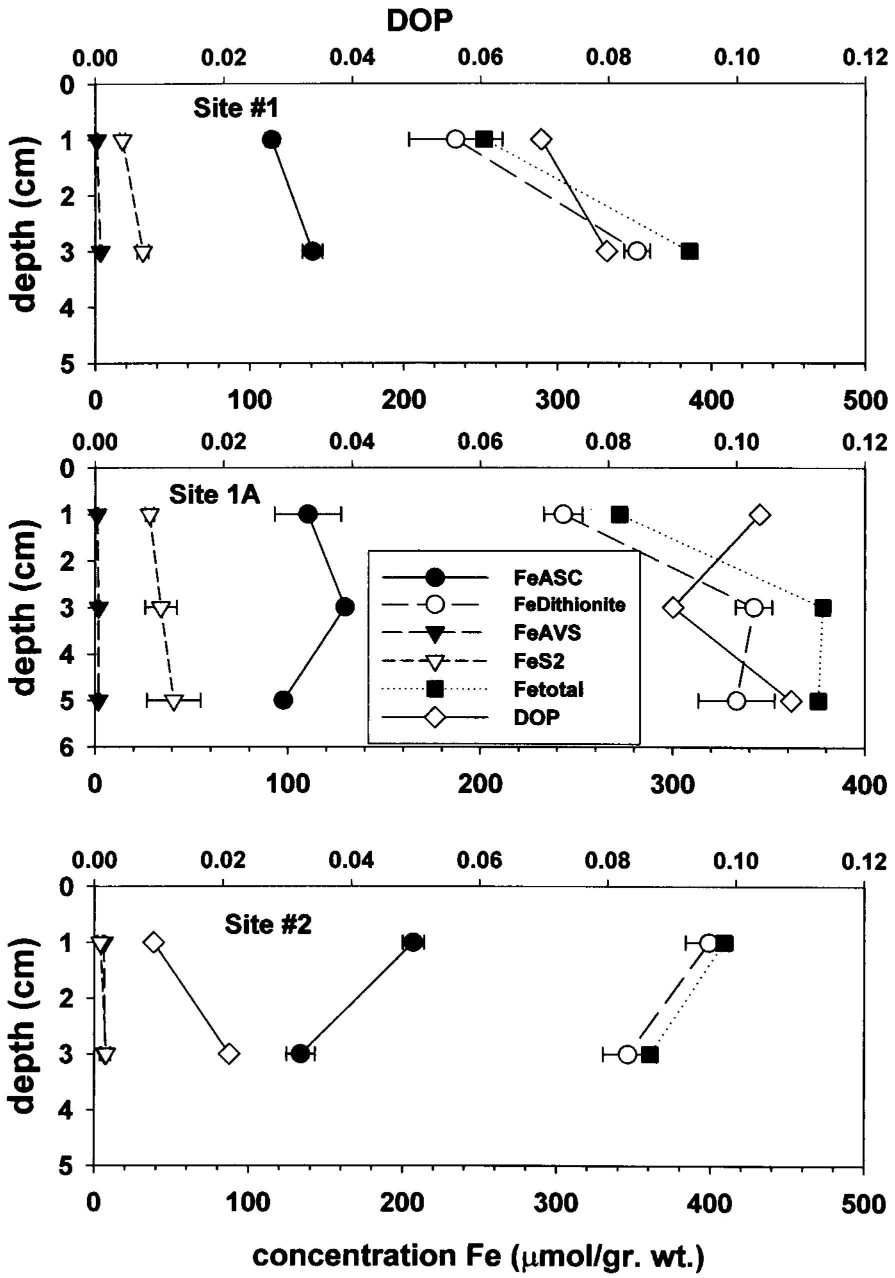

*Figure 7.* Solid phase Fe analyses and DOP versus depth. Depth is averaged since all cuts were 2 cm slices; i.e., 1 cm is the average from 0–2 cm.

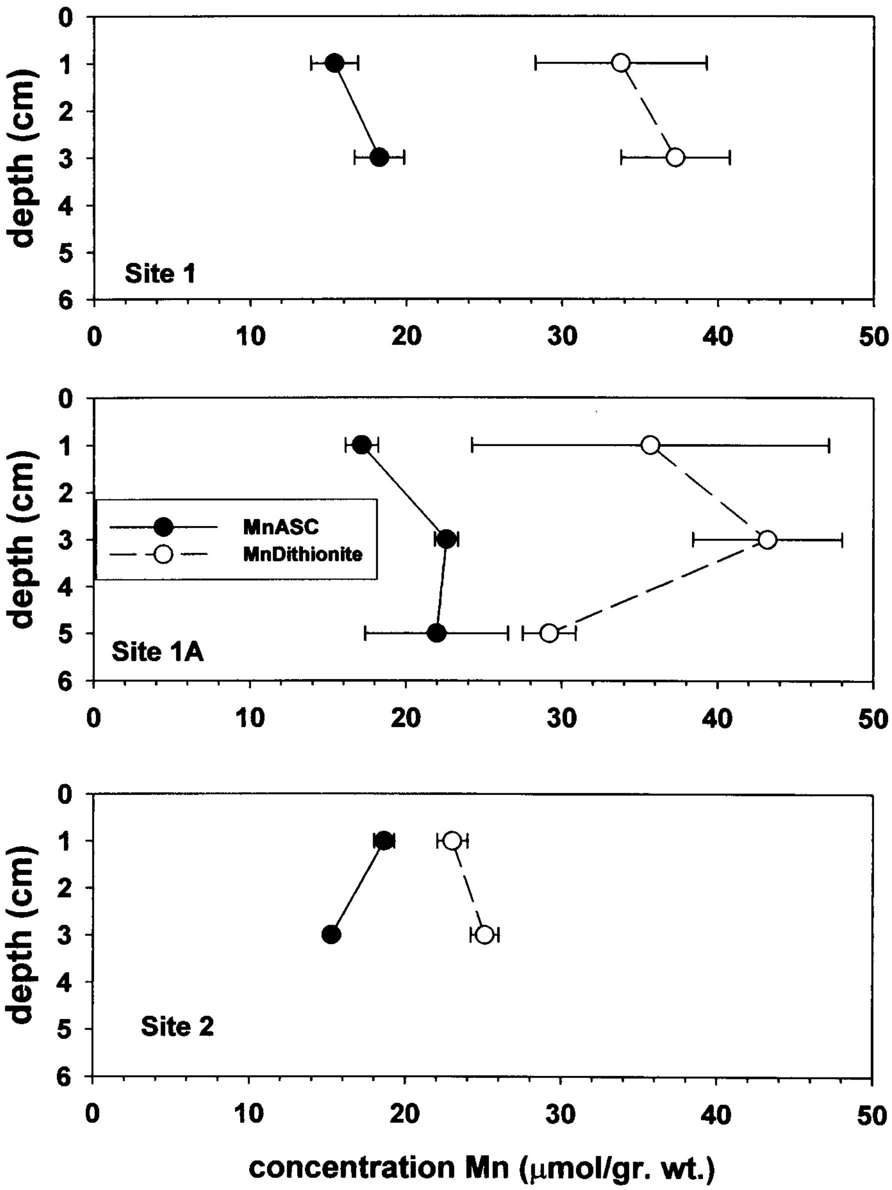

*Figure 8.* Solid phase Mn analyses versus depth. Depth is averaged since all cuts were 2 cm slices.

## 3. Discussion

In Figures 7 and 8, the total Mn(III,IV) phases as Mn-dithionite are an order of magnitude lower than the corresponding Fe phases. The same is true for Mn-ASC and indicate that Mn(III,IV) phases react with both free sulfide and sulfide bound to Fe; i.e. oxidize the sulfide as in Equations (4) and (5) (Aller and Rude, 1988).

Free Fe(II), although not measured in our samples, can also react with Mn(III, IV) to form Mn(II) and Fe(III) phases. These reactions contribute to the significant amount of soluble Mn in the lake's bottom waters most of the summer.

$$MnO_2 + H_2S + 2H^+ \rightarrow Mn^{2+} + 1/8\ S_8 + 2H_2O, \tag{4}$$

$$MnO_2 + FeS + 2H^+ \rightarrow Mn^{2+} + 1/8\ S_8 + Fe^{2+} + 2OH^-. \tag{5}$$

Figure 7 and Table II show that the solid phase Fe-ASC is about 50% of the total iron(III) in the sediments. The FeAVS and FeS2 are very low in concentration, and the low DOP values vary between 0.009 to 0.108 (the maximum value is 1 if all reactive Fe converts to $FeS_2$). However, the solid phase data suggest that FeS solids could control the solubility of iron and sulfide in the lake bottom waters. To assess this possibility, we calculated the ion activity product (IAP) for FeS in the bottom waters based on Equations (6) and (7),

$$FeS_{(s)} + H^+ \rightarrow Fe^{2+} + HS^-, \tag{6}$$

$$IAP = \{Fe^{2+}\}\{HS^-\}/\{H^+\}, \tag{7}$$

where { } indicate the activities of the dissolved components. To be consistent with earlier work, we did not correct for any complexation of Fe(II) with sulfide. The results of the calculations are shown in Table III, and indicate that the pIAP value approaches 3.6 in the deep waters, which is similar to the $pK_{sp}$ of 3.6 ± 0.2 for mackinawite (Davison, 1991; Morse et al., 1987). In most bottom anoxic freshwaters studied to date, the pIAP data typically approach 2.95 (amorphous FeS) but a couple of values as high as 3.8 have been reported (Davison, 1991). These calculations indicate that the $FeS_{aq}$ phases found in this study are in equilibrium with the iron-rich sulfide mineral mackinawite ($Fe_{1+x}S$; Morse et al. 1987). Table III shows that almost all samples contain Fe(II) at least twice the level of sulfide. These data along with the IAP calculations are consistent with the *in situ* voltammetry data (Figures 4 and 5), which show no free Fe(II) or sulfide. From these data, we conclude that the $FeS_{aq}$ phases, which give a voltammetric signal at $-1.2$ V and are found in the waters at or below the oxic-anoxic interface in these lake waters, are iron-rich sulfide complexes. These complexes can react with $O_2$ (see below).

In a laboratory study, Luther et al (1996) showed that sulfide complexes enriched with Fe are possible over a wide range of ionic strengths (I) as in Equations (8a) and (8b). These

$$2Fe^{2+} + H_2S \rightarrow [Fe_2(HS)]^{3+} + H^+ \quad \log K = 10.17 (I = 0.07), \tag{8a}$$

$$3Fe^{2+} + H_2S \rightarrow [Fe_3(HS)]^{5+} + H^+ \quad \log K = 16.82 (I = 0.07), \tag{8b}$$

complexes have reasonable stability constants. The hypolimnon water column data show that there is always an excess of Fe(II) to sulfide of 2:1 or greater and that

*Table III.* Sample depths for which IAP calculations for FeS were performed and where a signal for $FeS_{aq}$ was found

| Depth (m) | Total S(-II) ($\mu$M) | Total Fe(II) ($\mu$M) | pH | pIAP |
|---|---|---|---|---|
| Wilsonville 9/17/2002 | | | | |
| 9 | 1.56 | 0.537 | 6.47 | 6.23 |
| 10.5 | 7.50 | 23.82 | 6.37 | 4.07 |
| 11.5 | 14.69 | 44.41 | 6.32 | 3.60 |
| 13 | 18.12 | 43.52 | 6.30 | 3.56 |
| 15 | 23.44 | 43.88 | 6.23 | 3.57 |
| Wilsonville 8/21/2002 | | | | |
| 8 | 0.312 | 0.716 | 6.03 | 7.61 |
| 10 | 6.56 | 18.83 | 6.02 | 4.88 |
| 12 | 15.31 | 26.32 | 6.10 | 4.21 |
| 14 | 16.88 | 25.07 | 6.15 | 4.10 |
| 16 | 13.12 | 39.22 | 6.18 | 3.96 |
| 18 | 20.62 | 34.74 | 6.20 | 3.78 |
| Dam forebay 9/16/02 | | | | |
| 9 | 0.625 | 0.358 | 6.28 | 7.14 |
| 10 | 6.09 | 30.79 | 6.26 | 4.25 |
| 11 | 16.09 | 49.24 | 6.22 | 3.70 |
| 12.5 | 24.06 | 48.70 | 6.22 | 3.53 |
| Caffrey Pt 8/21/2002 | | | | |
| 9 | 5.93 | 15.75 | 6.17 | 4.72 |
| 11 | 17.81 | 32.94 | 6.21 | 3.85 |
| 13 | 20.01 | 35.63 | 6.25 | 3.69 |

these iron-rich complexes may exist. This ratio of iron to sulfide is different from marine systems where the sulfide is usually in excess to the Fe(II) (Luther et al., 1991; Passier et al., 1997). Formation of iron-rich sulfide complexes (Equations (8a) and (8b)) indicate that there is not enough sulfide to react readily with Fe(II) and FeS phases to form $FeS_2$, shown in Equation (9) (Rickard, 1997). Figures 4 and 5 show that a soluble $FeS_{aq}$ phase (molecular cluster of unknown stoichiometry; Theberge and Luther (1997)) was observed using *in situ* voltammetry in the lake bottom waters (hypolimnion) as well as in the pipeline and the tailrace (data not shown) and that free Fe(II) is not detected using *in situ* voltammetry. These data also indicate that the $FeS_{aq}$ phase is iron-rich in these samples. In addition, these data from the lake and pipeline indicate that $FeS_{aq}$ complexes are stable in the absence of air ($O_2$) and can be transported long distances (several miles from the lake hypoliminion through the pipeline to the tailrace). Although $FeS_{aq}$ phases can also react with polysulfides ($S_x^{2-}$; eq. 10; Luther, 1991; Rickard, 1975), the voltammetric signal for polysulfides (Rozan et al., 2000) was never observed in any waters in the lake or in the pipeline/tailrace.

$$FeS_{aq} + H_2S \rightarrow FeS_2 + H_2, \tag{9}$$

$$FeS_{aq} + S_x^{2-} \rightarrow FeS_2 + S_{x-1}^{2-}. \tag{10}$$

We performed laboratory experiments where Fe(II) and sulfide were added together in deionized water or filtered lake water. The $FeS_{aq}$ cluster complex forms at low concentrations as the $-1.2$ V voltammetry signal is present, immediately after the addition of Fe(II) and sulfide. In a normal voltammetry cell that has argon flushing over the solution, the signal for free Fe(II) increases and that of free sulfide decreases with time. Addition of Mn(II) to these solutions can broaden the $FeS_{aq}$ signal. However, addition of Mn(II) to sulfide does not give the $-1.2$ V signal, but addition of Fe(II) to solutions containing Mn(II) and sulfide does result in the $-1.2$ V signal confirming $FeS_{aq}$ formation. Thus, Fe(II) forms sulfide cluster complexes better than Mn(II). Although $FeS_{aq}$ is formed at high Fe(II) to sulfide ratios, we cannot indicate what the exact stoichiometry of these complexes formed in the lake is.

Once lake waters go through the pipeline and exit into the tailrace from the turbines, they are exposed to the atmosphere (no longer a closed system). Thus, sulfide can dissociate from the Fe(II) at these pH values of 6.5 or less in the bottom waters to produce volatile $H_2S$ as in Equations (11)–(12).

$$FeS_{aq} + 2H^+ \rightarrow H_2S \uparrow + Fe^{2+}, \tag{11}$$

$$Fe_2SH^{3+} + H^+ \rightarrow H_2S \uparrow + 2Fe^{2+}. \tag{12}$$

$Fe_2SH^{3+}$ indicates an iron-rich cluster, which is likely polymeric. The resulting $Fe^{2+}$ can be oxidized by $O_2$ to form Fe(III) aqueous species and precipitates, which can oxidize any $H_2S$ that does not volatilize. Reddish-orange Fe(III) precipitates are observed on the creek bed downstream from the tailrace.

Previous work (Vazquez et al., 1989) has demonstrated that $O_2$ oxidizes the sulfide faster in the presence of Fe(II) by oxidizing $Fe^{2+}$ to $Fe^{3+}$, which in turn oxidizes sulfide (Fe catalysis). This reaction can occur via an inner sphere complex between oxygen, iron (II) and sulfide (Luther, 1990). Adding air to these lake waters during incubation experiments, producing $O_2$ concentrations of 20 to 100 $\mu$M, confirms that the total sulfide is oxidized with a half-life $<1.5$ h at concentrations of 40 $\mu$M total Fe(II) and 20 $\mu$M total sulfide. Figure 9 shows kinetic data and a pseudo-first order plot of log total sulfide versus time after air addition.

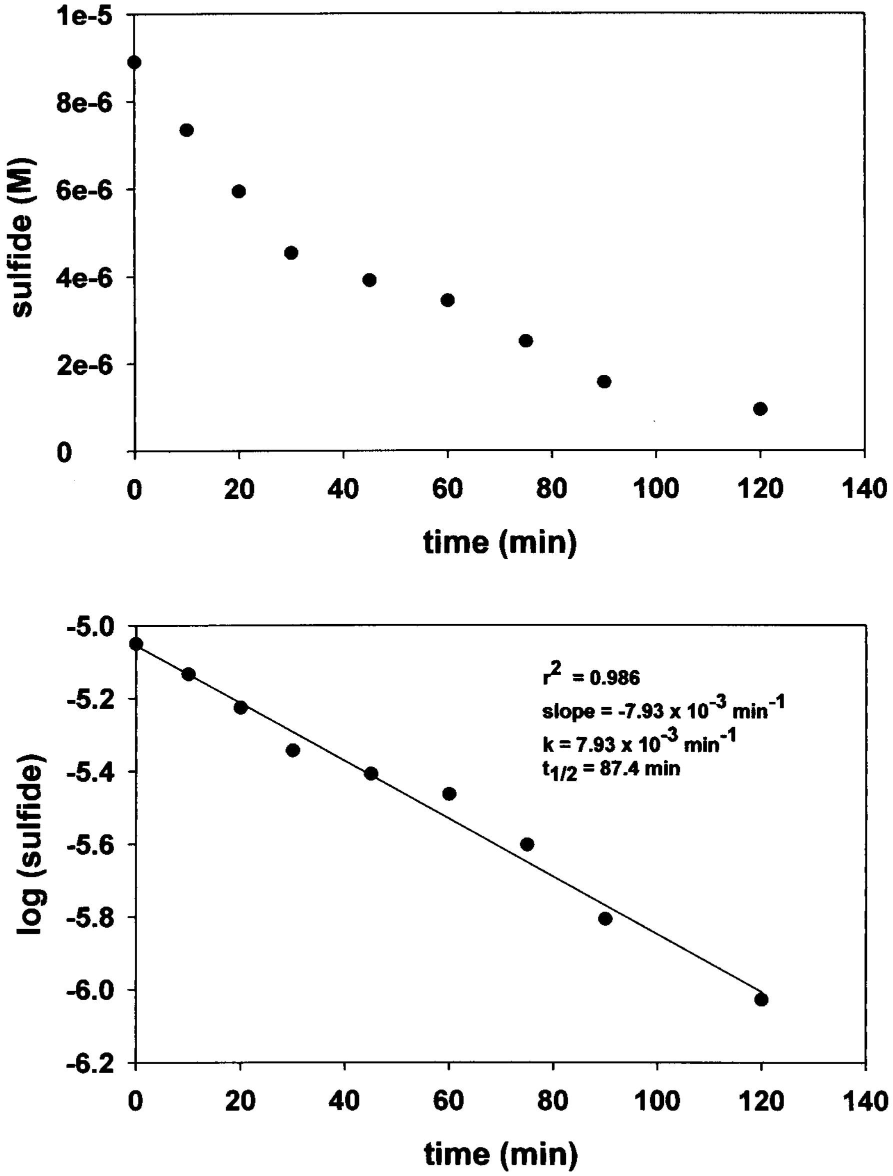

*Figure 9.* Kinetic data for waters sampled from the dam forebay on Sept. 19, 2002.

## 4. Conclusions

These data indicate that there is plenty of solid phase iron in Lake Wallenpaupack to affect iron sulfide precipitation as pyrite and remove sulfide. However, more Fe(III) is being reduced to Fe(II) than sulfate is being reduced to sulfide because more Fe(II) is present in lake waters than total dissolved sulfide. In addition, no free Fe(II) or sulfide ($H_2S$) are found in these lake waters using *in situ* voltammetry.

Thus, the increased soluble Fe(II) is preventing fast reaction with and removal of sulfide via $FeS_2$ formation, due to the formation of iron-rich sulfide complexes such as $Fe_2SH^{3+}$ (or polymeric forms of this and other stoichiometries). These iron-rich soluble sulfide complexes of unknown stoichiometry appear to be in equilibrium with the iron-rich sulfide mineral, mackinawite. The iron-rich soluble sulfide complexes are also stable in the absence of $O_2$ and can be transported several miles from the hypolimnion through the pipeline and to the tailrace when hydroelectric power is generated during the summer anoxic period. Because there are many man-made and natural lakes throughout the world that experience anoxic conditions, similar processes are likely to be found in other systems.

## Acknowledgments

The authors would like to thank PPL Generation, LLC for their support of this work. We would also like to thank Captain George Welker for assisting with sample collection. G.W.L. also acknowledges partial support from the National Oceanographic and Atmospheric Administration (NA16RG0162-03) and the National Science Foundation (OCE-0096365).

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