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Manganese redox buffering limits arsenic release from contaminated sediments, Union Lake, New Jersey

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Abstract

The sediments of Union Lake in Southern New Jersey are contaminated with arsenic released from the Vineland Chemical Company Superfund site 11 km upstream. Seasonal anoxia has been shown to release arsenic from sediments to similar lakes; this process was hypothesized as a major arsenic source to Union Lake. Data indicate, however, that releases of arsenic to bottom waters from the sediments or from pore waters within the sediments are relatively minor: bottom water arsenic concentrations reached ~30 ppb (~12 μM) at most, representing <13% of the dissolved arsenic content of the lake. Manganese concentrations increase more quickly and to higher levels than arsenic and iron concentrations; maximum $[\text{Mn}] = \sim 13 \text{ ppm}$ (~250 μM), maximum $[\text{Fe}] = \sim 6 \text{ ppm}$ (~120 μM). Incubation experiments support the hypothesis that manganese acts as a redox buffer and prevents large arsenic releases. Under the observed conditions, little of the arsenic in the water column is from contaminated sediment. This study also suggests that arsenic release from sediment to lake water may be more important in lakes that remain anoxic more continuously.

1. Introduction

Arsenic is a toxic metalloid found widely dispersed throughout the earth's crust and concentrated in some locations due to both human and geological factors. Arsenic is of particular concern in the aqueous phase, where it is mobile, bioavailable, and hazardous to human and ecological health. Arsenic dissolved in lake water has been widely investigated, e.g. (Kuhn and Sigg 1993, Martin and Pedersen 2002, Senn and Hemond 2002). Because it is well understood that arsenic mobility varies with redox conditions (Masscheleyn, Delaune et al. 1991), arsenic concentrations vary during lakes' seasonal stratification and related variations in dissolved oxygen levels with higher arsenic concentrations generally found in low-oxygen waters (Hamilton-Taylor and Davison 1995, Hasegawa, Rahman et al. 2009, Barringer, Szabo et al. 2011).

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Numerous mechanisms can be responsible for increased aqueous arsenic concentrations under more reducing (lower Eh) conditions. These mechanisms include direct reduction of As(V) to As(III) (Masscheleyn, Delaune et al. 1991); biotic (Lovely, Holmes, et al. 2004) or abiotic reductive dissolution of iron and manganese minerals to which arsenic is sorbed (Dixit and Hering 2003); a decrease in the number of sorption sites available for arsenic on both oxide (Bowell 1994) and sulfide (Bostick and Fendorf 2003) minerals; complexation of organic matter, itself driving low Eh conditions, with As (Mladenov, Zheng et al. 2015); and increased aqueous sulfide concentrations stabilizing As-S species (Wilkin, Wallschläger et al. 2003, Couture, Gobeil et al. 2010). Conversely, related mechanisms can also be responsible for limiting the release of arsenic to waters or sequestering released As. These mechanisms can include insufficient reducing agents, such as organic carbon (Gillispie, Andujar et al. 2016) and/or redox interactions between metals controlling speciation (Han, Li, et al. 2011, He and Herring 2009). In particular, manganese oxides have been shown to oxidize aqueous As(III) and Fe(II), enhance sorption of the oxidized As(V), and enhance sequestration of arsenic in the solid phase (Ehlert, Mikutta et al. 2014, He and Herring 2009, Manning, Fendorf et al. 2002). The first goal of this study is to examine which mechanisms of arsenic release and/or arsenic sequestration may be relevant to the during seasonal (summer) anoxia or suboxia in Union Lake, New Jersey.

A 1993 study at Union Lake (Ficklin, Balistrieri et al. 1993) showed bottom water concentrations of dissolved arsenic up to $\sim 1.75 \mu\text{M}$ and porewater concentrations $\sim 22\times$ higher. At Lake Mohawk in Northern New Jersey, seasonal anoxia leads to dissolved arsenic concentrations of up to $\sim 0.4 \mu\text{M}$ (Barringer, Szabo et al. 2011) although this represents a very small fraction of the arsenic found in the highly contaminated sediments. Studies of Spy Pond, MA (Senn, Gawel et al. 2007) have indicated that persistent seasonal anoxia is responsible for $>95\%$ of dissolved arsenic by release from contaminated sediments. The second goal of this study is to construct a rough mass balance for arsenic in Union Lake, and use this information to determine the importance of seasonal/anoxia-related arsenic release to lake waters.

2. Materials and Methods

2.1 Field Site

Union Lake is located in the town of Millville NJ (39.473W, -75.063N) in the coastal plain and Pineland ecosystem of southern NJ (Figure 1). Surficial deposits are comprised mainly of sand of late Miocene origin. The Vineland Chemical Company manufactured arsenical biocides in Vineland, NJ from 1950 to 1994 during which time arsenic salts were stored improperly. This storage introduced large-scale arsenic contamination to soils and groundwater, which subsequently contaminated the Black Water Branch stream located next to the superfund site. The Black Water Branch flows into the Maurice River, which feeds Union Lake. Sediments in Union Lake are contaminated with up to 15 mmol As/kg (1125 mg/kg) on a dry weight basis. Union Lake is a man-made lake $\sim 3.6 \text{ km}^2$ in area, with an average depth of $\sim 3 \text{ m}$ and a total volume of $\sim 1 \times 10^7 \text{ m}^3$; Union Lake is located in a residential area and is used for fishing and swimming (EPA 2002, Wovkulich, Mailloux et al. 2010).

By 1994 hazardous materials had been removed from the Vineland Chemical Company site. In 2000, a high-volume pump and treat operation for contaminated groundwaters began; this operation is ongoing. Between 2003–2007 a soil washing plant processed over 400,000 tons of arsenic contaminated soil and sediments (Wovkulich, Mailloux et al. 2010). Fieldwork for this study was conducted in 2007, 2008, and 2010. Sediments along the Blackwater Branch (from the chemical plant to the confluence with the Maurice River) were cleaned and/or removed in ~2009–2011. The EPA has not yet decided if or how to remediate sediments of the Maurice River and Union Lake (EPA 2014).

2.2 Field Methods

At the beginning of the summer in 2007 and 2008, a buoy was placed in the lake at a depth of 7.5 meters, close to the deepest point in the lake, using bathymetry maps (Figure 1), GPS, and an electronic depth finder. All samples and measurements were taken adjacent to this buoy from a small boat. Continuously logging temperature sensors were placed at 1, 5 and 7.5 m depth in Union Lake during August–October 2007 and June–September 2008 (Figure 2). Samples were collected at three depth intervals: 0–1 m, 4–5 m, and 6–7.5 m. At the time of sampling, temperature, pH, and dissolved oxygen were analyzed by a YSI 6600 multimeter at 0.25 m intervals by lowering the YSI to the bottom of the lake. Dissolved oxygen levels were also checked with Chemets ampoules (<http://www.chemets.com>). Water was obtained using a Niskin bottle and from this samples were saved for chemical analyses. Metals were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS); for ICP-MS samples, water was withdrawn from the Niskin bottle and immediately syringe filtered (Whatman 0.2 μ m) and acidified to 1% with Optima grade nitric acid. Major anions were analyzed by ion chromatography (IC); samples for IC analysis were syringe filtered immediately and frozen within 3 hours.

2.3 Microcosm Incubations

Microcosm incubations were performed with sediment and water collected on October 13, 2010. Water samples were collected right above the sediment/water interface layer at a depth of 6.4 m using a Niskin bottle; water was not filtered for the incubations. Sediment was collected from the same location using an Ekman bottom grab sampler and stored in plastic container. Incubations were begun within 24 hours of sediment and water sampling; during that period materials were kept in closed but not impermeable containers. Gas impermeable microcosm bottles (Wheaton Serum bottles), 60 mL each, were filled with 5 g of Union Lake sediment and 50 mL of water, leaving a minimal (air) headspace. All bottles were capped with impermeable septa (VWR part number 100483-774) and stored in a closed box at room temperature. Any oxygen was quickly consumed by microbial activity within the sediments; previous experiments show this occurs within 1–3 hours. Incubation conditions were (1) sediment/untreated water and (2) sediment/high Mn water with total [Mn] = 0.53 mM. Mixed ACS grade Mn(II) and Mn(IV) oxides (approximately 1:1 ratio) were added as solids to create the high Mn condition.

At the time of collection of microcosm materials from Union Lake, water samples were obtained and preserved, as above, for ICP-MS and IC analysis. Water samples were also taken from microcosms at 0, 3, 6, 10, 13, 20, 27, 34, 41, 56, 68, and 96 days. Each sampling

event obtained duplicate samples from both conditions. Water was extracted from bottles using a sterile needle and syringe that had been purged with N₂ gas to prevent oxygenation of samples. Samples were obtained for analysis of metals and anions, and preserved as described above.

2.4 Laboratory Analyses

Inductively coupled plasma mass spectrometry (ICP-MS) was performed using a high resolution Axiom Single Collector instrument (Thermo Elemental, Germany) to examine manganese, iron, and arsenic; methods have been described in full elsewhere (Cheng, Zheng et al. 2004, Keimowitz, Zheng et al. 2005). Runs were accepted only if R² values of internal curves were > 0.97 and relative standard deviations between triplicates were < 10% (typically < 5%). Ion chromatography was performed with a Dionex ICS-3000 ion chromatograph to quantitate sulfate, nitrate, and chloride. Samples were injected onto an AS-18 4×150 mm column using 39 mM KOH eluent. Runs were accepted with R² values > 0.99 for external standard curves. Two samples from each of two cores obtained from Union Lake (Keimowitz, Zheng et al. 2005) were analyzed by loss on ignition (Ball, 1964) at 550° C for organic matter content.

3. RESULTS AND DISCUSSION

Historical data from Union Lake (Ficklin, Balistrieri et al. 1993) and from Lake Mohawk (Barringer, Szabo et al. 2011) suggested that anoxic conditions might develop in bottom waters over the summer months. Anoxic conditions can be disrupted by lake inversion events which would mix oxic surface waters with anoxic bottom waters; summer overturning was not observed in Lake Mohawk. Temperature logging data from Union Lake indicate that in 2007 lake mixing was observed twice by the middle of September; during the same time period during 2008, no mixing events were detected (Figure 2). Mixing events in 2007 were concurrent with storms with high wind speeds, however higher wind speeds in 2008 did not lead to mixing. Wind directions were comparable for these two years, and predominantly from the North. These data suggest that storm events may be necessary but not sufficient to mix Union Lake; other necessary factors are not known. Lake Mohawk and Union Lake have similar length, width, and depth measurements, but Lake Mohawk was not observed to regularly overturn (Barringer, Szabo et al. 2011). Reasons for this difference between these two lakes is not known, but this suggests that sampling over more years would be helpful at both sites; the absence of this data at Union Lake is a limitation of this study.

Measurements by YSI multimeter were made regularly during the summer months of 2007 and 2008 in Union Lake in order to explore the formation of a thermocline and oxycline and any associated release of metals. In neither summer did a sharply defined thermocline develop in Union Lake (Figure 3a, 3b), consistent with the temperature sensor data (Figure 2). In 2007 the DO concentrations decreased at depths below 2m. The decreases were short lived, however, and a strong oxycline did not develop. Only during one sampling period were the bottom waters anoxic. In contrast in 2008 a more defined oxycline developed and dissolved oxygen concentrations were at or near zero over a greater depth interval (Figure

3c, 3d), consistent with less frequent lake mixing during 2008 (Figure 2). These data imply more strongly reducing conditions during 2008. These data contrast with the 1993 results of Ficklin et al (Ficklin, Balistrieri et al. 1993), in which more complete anoxia and larger metal release was observed. Data from more summers would provide a fuller exploration of conditions at this lake.

During observed periods of anoxia, metals were released from the contaminated sediment into the water column (Figure 3e–j); during summer 2008, higher Mn and Fe concentrations were seen concurrent in time and space with prolonged anoxia. Previous work has shown that concentrations of these elements are consistently high in (anoxic) pore waters, but oxic bottom waters trap these elements below the sediment-water interface (Keimowitz, Zheng et al. 2005). Elevated dissolved metal concentrations could expand their extent into lake waters via diffusion or advection. In the summer of 2007 and especially 2008, sufficient anoxia occurred in the bottom waters of Union Lake to allow appreciable upward diffusion of dissolved species from pore waters into the lake waters. Much of Union Lake is perched above the water table, limiting advection of pore waters or ground waters, however the deeper parts of the lake occupy the former river channel of the Maurice River and advective groundwater seeps may occur in those areas.

A plot of dissolved manganese, iron, and arsenic concentrations as a function of time highlights manganese's increase prior to increases in arsenic and iron (Figure 4) in 2008 and in the absence of an appreciable spike in [Fe] and [As] in 2007. The presence of elevated manganese concentrations in the absence of or prior to elevated iron and arsenic concentrations suggests that conditions are, for a time, reducing enough to reduce and mobilize manganese, but not iron and arsenic. This is consistent with the generally accepted redox ladder (Stumm and Morgan 1996) as well as the sediment reduction experiments of Miao and colleagues (Miao, DeLaune et al. 2006). In Miao's experiments, manganese concentrations rose gradually as sediment was reduced from an Eh of ~400 mV to ~0 mV whereas iron concentrations only began to rise at ~0 mV and continued to increase until -100 mV.

These data suggest that in Union Lake, arsenic releases from bottom waters are limited by manganese acting as a redox buffer. This buffering may occur either because (1) large amounts of manganese in the sediments hold the Eh above the iron/arsenic reducing zone or (2) the lake is not becoming more strongly reducing due to lack of reducing agents (primarily organic carbon, though also nitrogen, phosphorous, reduced iron, or sulfides) or excess of other oxidizing agents. These mechanisms could operate independently or in conjunction with one another. In particular, if reducing agents are present but recalcitrant (kinetically slow) the sediment manganese could be sufficient to serve as the dominant electron acceptor without the sediments necessarily being unusually Mn-rich. Data are consistent with these mechanisms operating together.

Iron:manganese ratios in Union Lake sediment are approximately 75:1 (Keimowitz, Zheng et al. 2005), as compared to a more typical ratios of 50:1. This argues against mechanism (1) operating alone, as manganese levels are not exceptionally high. Loss-on-ignition values are $34 \pm 3\%$ for the fine-grained sediment core from the deepest part of Union Lake, and $20 \pm 4\%$

for the sandier core obtained closer to shore (Keimowitz, Zheng et al. 2005). These values are associated with “very eutrophic” lakes in a study of the relationship between trophic level and sediment composition (Hakanson 1984) but Union Lake is only weakly eutrophic. This suggests that mechanism (2), absence of reducing agents, is not dominating the system. It is possible, however, that the organic carbon present is too recalcitrant to contribute to eutrophication or that N, P or other nutrient levels are insufficient to support eutrophication. Between 1993 and 2007, efforts to reduce fertilizer runoff in Union Lake’s watershed may have contributed appreciably to reducing available N or P (Guida, 1989). The absence of TOC or DOC data, as well as more sophisticated characterizations of organic matter, limit our ability to more thoroughly investigate this issue using only field data, so we turn to laboratory manipulations.

Preliminary microcosm experiments (data not shown) and previous studies (Keimowitz, Mailloux et al. 2007) indicate that all dissolved oxygen and nitrate are consumed in microcosms within the first three days. In our incubations, direct Eh measurements in microcosm incubations were not possible, but nitrate was absent by day three and sulfate concentration never decreased; this fixes the Eh of the system between ~350 and -250 mV. This range contains the Eh values consistent with manganese, iron, and arsenic reduction and consistent with manganese redox buffering. This mechanism suggests that Eh initially dropped rapidly and subsequently stabilized in the Mn-oxide reducing zone; only when most or all manganese oxides were reduced could the Eh continue to drop. Those incubations with “artificial” manganese oxides added would be expected to have a longer Eh plateau in the context of manganese-mediated redox buffering.

Arsenic release relies on a combination of processes that generally occur as Eh decreases; these processes include direct As reduction, reductive dissolution of arsenic-hosting minerals, decrease in As sorption sites on oxide minerals, decrease in As sorption sites on sulfide minerals, and stabilization of As-S species by high concentrations of aqueous sulfide. The data indicate that Eh is ~0 mV (both in the field and in the laboratory incubations), allowing the mechanisms that require sulfur transformations to be eliminated, as these transformations occur at lower Eh values. The data do not permit determination of the relative importance of desorption, reductive dissolution of As-hosting minerals, and decrease in sorption sites; all three are expected to play a part. Mechanisms of arsenic sequestration are also crucial, and may include a host of sorption and precipitation pathways (He and Herring 2009; Manning, Fendorf et al. 2002).

The addition of manganese to one set of microcosms did not change the reducing agents available in the sediment but decreased arsenic and iron release (Figure 5). This suggests that the absence of sufficient reducing agents is not limiting arsenic release on its own although the balance between reducing agents and manganese (or other electron acceptors) is shifted in these experiments. The presence of additional manganese may have exhausted the supply of nitrogen or phosphorous in the sediments, preventing further use of the rather abundant (as measured by LOI) carbon. Alternately, decomposition of the carbon present may have been kinetically limited after a pool of more labile carbon was oxidized. Although it is not possible to entirely specify the mechanism, the appreciable difference in iron and arsenic concentrations in high manganese and low manganese waters support the concept of

manganese as a redox buffer, fixing the Eh of the system slightly too high to permit iron reduction, arsenic reduction, and reductive dissolution of relevant arsenic bearing minerals.

A rough mass balance of arsenic in Union Lake was performed to determine what fraction of arsenic in the lake originates from release from sediment as compared to flowing in via the Maurice River. Release from sediment would likely occur via diffusion of high-As pore waters into bottom waters.

This mass balance was performed by dividing the lake into three depth layers: 0–3 m, 3–6 m, and 6–7.5 m, shown in Figure 3. The concentration of arsenic in each layer was assumed to be uniformly the concentration of arsenic measured within that layer, i.e. at 1 m, 4–5 m, and 7–7.5 m. All arsenic in the bottom layer of the lake was assumed to originate from release from sediments; and no arsenic in the middle and upper layers was assumed to originate from sediment release, but was assumed rather to originate from dissolved and colloidal arsenic entering the lake via the Maurice River. The date of maximum arsenic concentration in the bottom waters (0.34 μM or 28 ppb on 7/30/08) was selected in order to get an upper bound on the fraction of arsenic from sediment release. Average concentrations of arsenic measured in the upper two layers were used. Although sediment at the entry point of the Maurice River might contain higher arsenic concentrations, it would be less likely to become anoxic and therefore was deemed a less likely source of *dissolved* arsenic. Additionally, our sampling point was one of the few locations in Union Lake thought to be depositional. Much of the sediment-bound arsenic entering Union Lake may also exit Union Lake without being deposited.

The mass balance indicates that release of arsenic from sediment accounts for less than 13% of total dissolved arsenic. This is in sharp contrast to Spy Pond, MA and other studied lakes in which re-release processes account for >90% of total arsenic concentrations (Lattanzi, Senn et al. 2007, Senn, Gawel et al. 2007). This difference occurs for two reasons: (1) Union Lake overturns frequently, preventing the strong and persistent anoxia observed in Spy Pond; and (2) no ongoing arsenic inputs are present for Spy Pond, whereas small but significant masses of arsenic are entering Union Lake via the Maurice River. Differences in sediment and water chemistry may also exert some control on the timing and amount of arsenic re-release. Higher levels of dissolved arsenic were observed in 1993 (Ficklin, Balistrieri et al. 1993) prior to efforts to decrease fertilizer runoff in the watershed; at that time, higher levels of nutrient pollution presumably facilitated more persistent anoxia and therefore greater metal release (Guida 1989).

Concentrations of dissolved As in Lake Mohawk are ~30 ppb (0.4 μM) in summer months, similar to the highest concentrations observed in this study despite higher sediment concentrations of As in Union Lake (~1125 mg/kg) as compared to Lake Mohawk (91–462 mg/kg in core tops). The 1993 conditions of Union Lake (Ficklin, Balistrieri et al. 1993) may have had higher concentrations of reducing agents, more similar to current conditions observed in Lake Mohawk (Barringer, Szabo et al. 2011), which is bordered by unsewered residential development. The smaller amounts of reducing agents and/or greater recalcitrance of reducing agents in today's Union Lake, in combination with the larger amounts of arsenic in the sediment (as compared to Lake Mohawk) may be giving rise to the

similar concentrations of arsenic in both lakes. Fewer lake overturning events are observed in Lake Mohawk for reasons not well-understood; data in (Barringer, Szabo et al. 2011) did not allow examination of the role manganese might play in Lake Mohawk. Further comparisons of the geochemical processes cycling arsenic in these lakes is warranted.

4. Conclusions

The chemical data indicate that chemical and geographic factors may limit arsenic releases from sediment and control the cycling of arsenic within this lake. The lake geometry (shallow and large) allows frequent overturning, thereby limiting arsenic releases, although the contrast between 2007 and 2008 as well as comparisons with Lake Mohawk indicates that weather may play a role beyond the scope of this study. The elevation of manganese concentrations prior to elevation of iron and arsenic concentrations in the field, in conjunction with lower arsenic and iron concentrations in the presence of high manganese in incubations, indicates that manganese prevents Eh values low enough sufficient to permit large arsenic releases, possibly due to recalcitrance of reducing agents present or absence of N or P. Under the observed conditions, little of the arsenic in the water column is from contaminated sediment. Arsenic contaminated lakes are common throughout the US, and this study suggests that reducing agents, potential redox buffers, and lake overturning frequency should be considered together when considering the importance of arsenic release from lake sediments.

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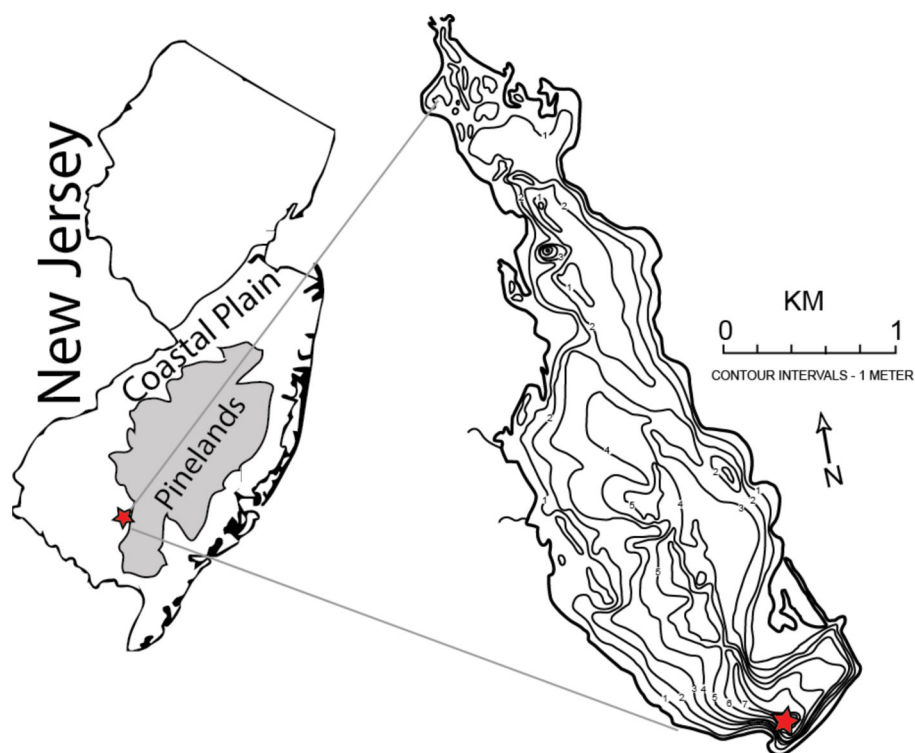


Figure 1. Bathymetric map and location of Union Lake, Millville, NJ. Larger map shows New Jersey, including boundaries of the coastal plain and the Pinelands, with the lake at the border of the Pinelands. In the lake bathymetry map, contour intervals are 1 m; buoy and sampling location is shown with the red star.

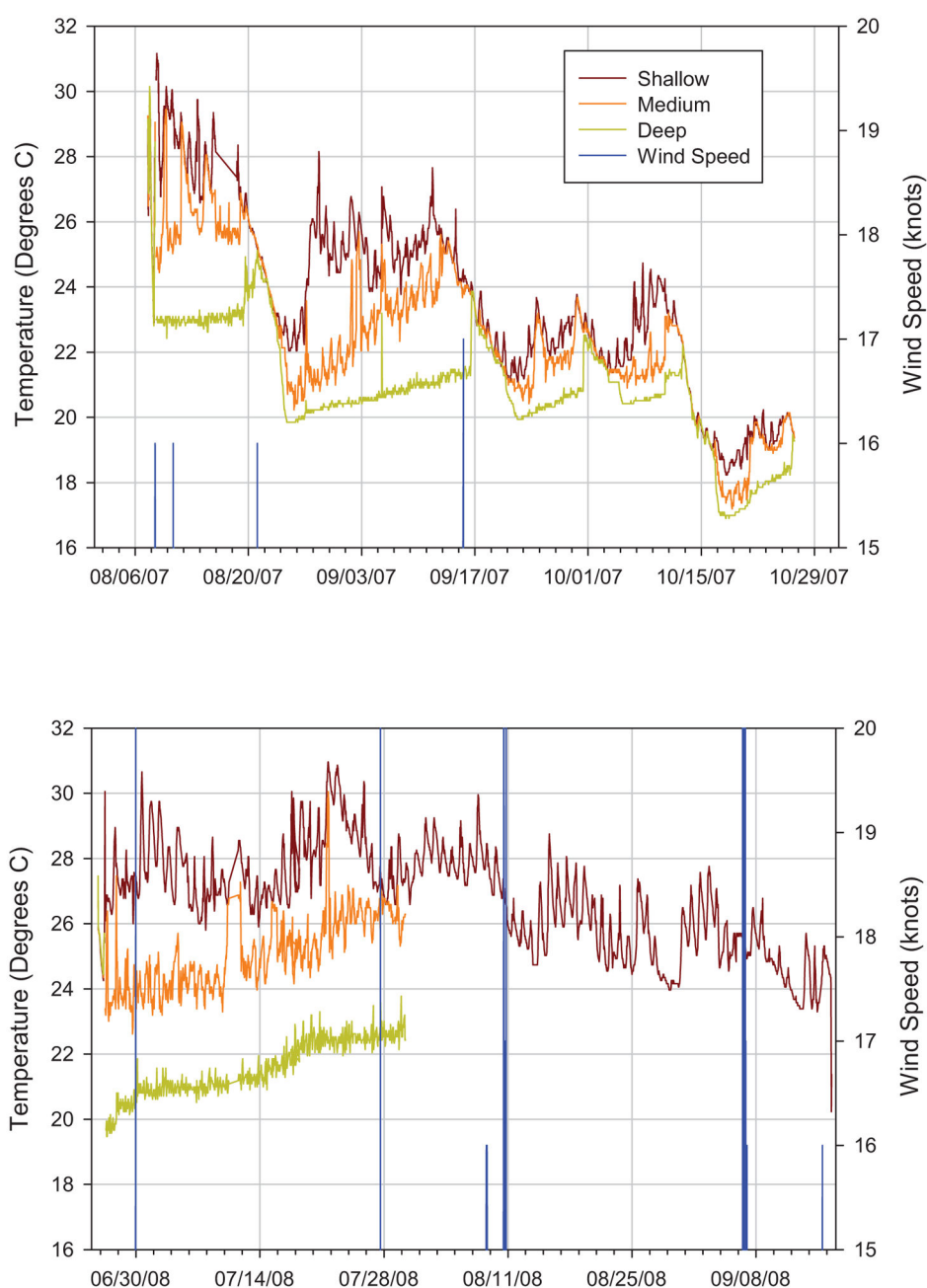


Figure 2.

Data from temperature sensors placed in the lake in summer 2007 and 2008; data downloaded from <http://www.weather.noaa.gov> for the Millville Airport weather station shown, indicating that high wind events occur immediately before lake mixing in summer 2007. Two sensors malfunctioned in 2008.

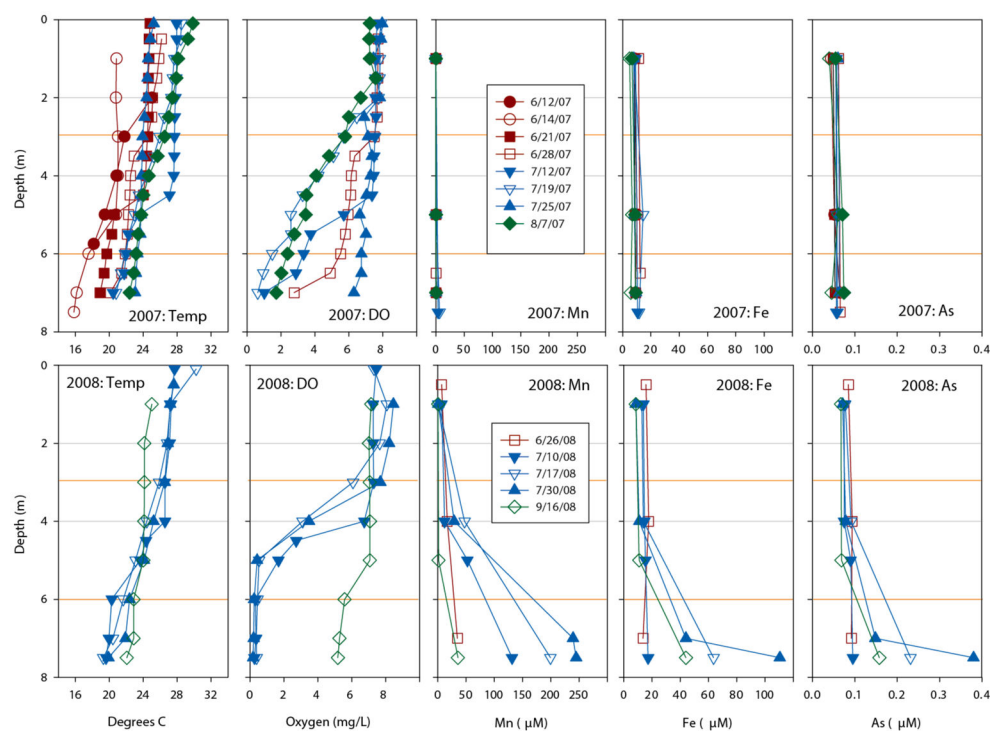


Figure 3. Depth profiles in Union Lake in the summers of 2007 and 2008. Dissolved oxygen and temperature were measured by YSI; arsenic, iron, and manganese were measured by ICP-MS.

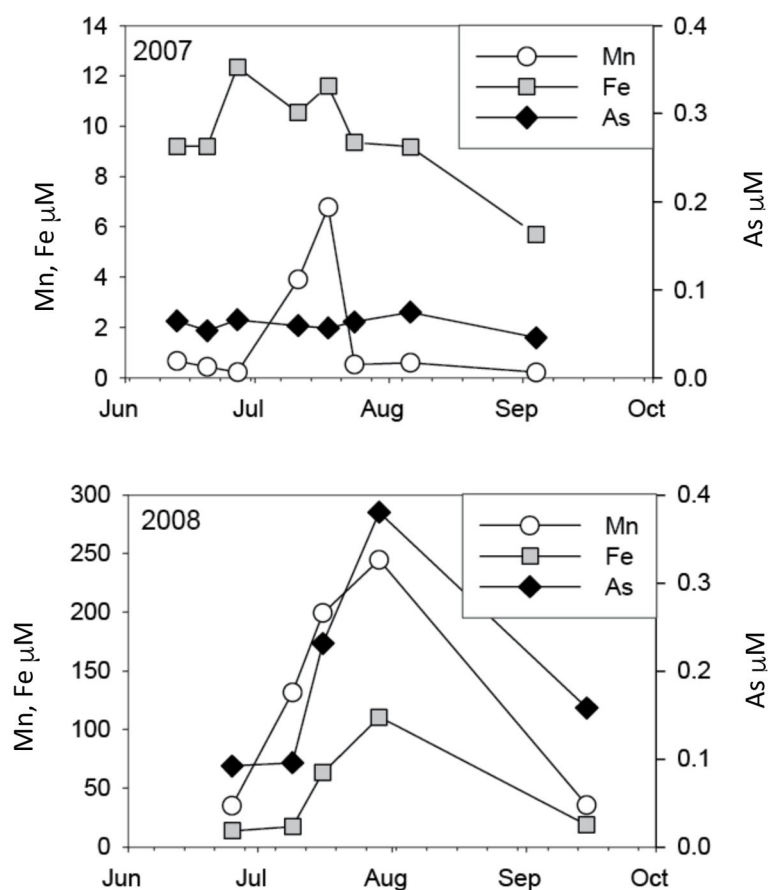


Figure 4. Dissolved manganese, iron, and arsenic concentrations as a function of time in summers 2007 and 2008; note the different axes in the two years.

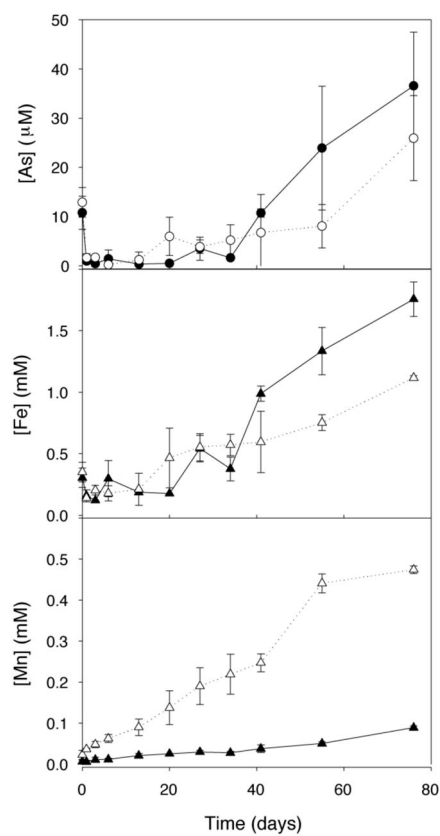


Figure 5. Concentrations of arsenic, iron, and manganese with time during microcosm incubations. Closed symbols are untreated sediment and water; open symbols are sediment, water, and additionally Mn oxides. DO <1 mg/L for all points measured.