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Effects of Eutrophication and Runoff on Arsenic Cycling in an Urban Lake

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Abstract

Urban lakes are important recreational and natural resources that add to the quality of life for city residents. Unfortunately, urban watersheds often contribute contaminants to these lakes, including organic chemicals, metals, nutrients, and pathogens. Nitrogen and phosphorus are very high in urban and suburban runoff, mostly as a result of animal waste and fertilizers, although leaky sewage systems may also contribute. These nutrients promote plant and algal growth in urban lakes, ultimately resulting in hyper-eutrophic conditions. Eutrophication, in turn, may affect the cycling and mobility of contaminants, such as arsenic and other toxic metals. Spy Pond, located in Arlington, Massachusetts, was recently discovered to be heavily contaminated with arsenic of unknown origin. Surface sediment concentrations above 2,500 ppm have been measured. Subsequent investigations have also revealed that total arsenic levels in the overlying hypolimnetic waters reach over 150 ppb. However, the two interconnected basins that constitute Spy Pond have been found to differ by an order of magnitude in the concentrations of arsenic found in hypolimnetic waters. The goal of this study is to determine the mechanisms responsible for the differences in arsenic mobility in the two basins of Spy Pond, and how this may impact the potential for minimizing human and ecological arsenic exposure. Based on differences in the concentrations of chemical constituents (e.g. iron, sulfur, conductivity, etc.) measured in each basin, we hypothesize that the greater arsenic concentrations found in the bottom waters of the South Basin of Spy Pond are caused by the combined effects of eutrophication, differences in the Fe/S ratio of the two basins, and the physical and chemical impacts of salts in highway runoff.

Introduction

Cultural eutrophication (the process by which human-induced loads of nutrients and organic matter increase the productivity of a water body) has been an issue in Spy Pond, in Arlington, MA (located 5 miles northwest of Boston), at least since 1871, when complaints regarding nuisance vegetation were first recorded by local water authorities (Jason M. Cortell and Associates 1973). Soon thereafter the water was declared unfit for human consumption and the ice harvesting industry on the Pond was forced to shut down. Nitrogen and phosphorus inputs from lawn fertilizers, pet waste, and waterfowl continue today to result in noxious algal blooms and macrophyte growth. The decomposition of aquatic vegetation in the sediments causes the loss of loss of oxygen in the bottom waters of Spy Pond from April to November each year. One of the direct effects of this anoxia has been the significant decline of cold-water fish species in the Pond. In addition, anoxia has affected the cycling, and subsequently the mobility, of many metals in the hypolimnetic waters and sediments. This has become an important issue in the Pond, where arsenic contamination was discovered less than two years ago.

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Spy Pond is a glacially-formed “kettle-hole” lake in the Mystic River watershed [Figure 1]. The lake has a surface area of 41 hectares, a volume of approximately 470 million gallons, and an average depth of 4.4 m. It is split into two distinct basins by Elizabeth Island (a 1.05 ha glacial kame) and its surrounding shallows, which reach approximately 2 m in depth. The North Basin has a maximum depth of 11.5 m while the South Basin is 6.5 m at its deepest point.

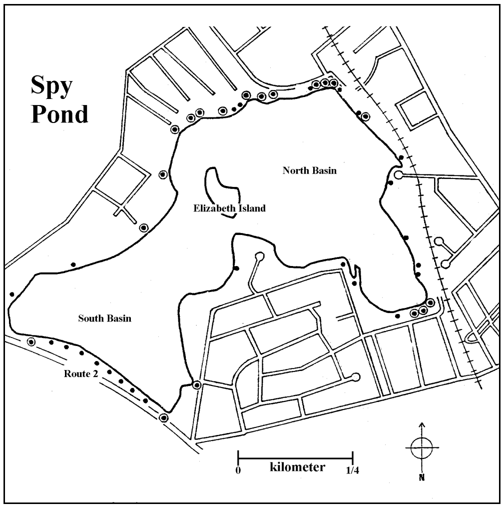

Figure 1: Spy Pond, Arlington, Massachusetts.

Spy Pond is the receiving body for drainage from a 350 hectare urban watershed. Although the Spy Pond watershed is primarily residential, a small commercial area and an eight lane state highway are also located near the Pond boundaries. The North Basin receives runoff from the commercial development, whereas the South Basin receives runoff from the highway. No natural surface water inflows remain, and water is emptied into the lake through more than 40 storm drains of various sizes and shapes. The lake’s single outlet is a drop inlet control structure located near the southeast corner of the South Basin that empties into Little Pond on the south side of the highway (see Figure 1; Environmental Design and Planning Inc. 1982; Shanahan 1997).

Arsenic contamination in Spy Pond was discovered in 1997 by Ivushkina (1999), while conducting a survey of metals contamination in surface sediments of the streams and lakes of the Alewife Brook and Mill Brook watersheds (the Spy Pond watershed is located within the Alewife Brook watershed). Subsequently, extensive mapping of the surface sediments by Lukacs and MacLaughlin (MacLaughlin 1999) showed maximum total arsenic concentrations of 2,600 and 1,100 ppm As in the North and South Basins, respectively. Although arsenic contamination in the Aberjona River (the headwaters of the Mystic River system) is well known (Aurilio et al. 1995), no significant sources of arsenic have been documented for the Spy Pond watershed (MacLaughlin 1999). An investigation is ongoing to determine the source of this contamination, but sediment arsenic profiles collected by Durant and Senn (unpublished data) suggest that a discrete, rather than a long-term or continuous, release of arsenic may be the most likely scenario.

Although the determination of the source of arsenic to Spy Pond may be important for remediating the problem. More immediate concerns include reducing the potential for human exposure to arsenic in the Pond, as well as reducing the impacts that the arsenic may be having on the biota there. This study was conducted to determine the forms and concentrations of arsenic in the pond water and thereby gain insight as to how to reduce the potential for human exposure and environmental impacts. Specific emphasis was given to understanding the chemical cycling and mobility of arsenic in Spy Pond, and the impact of urban runoff on the limnology and chemistry of this recreational resource.

Methods

Sampling stations were established at two locations within Spy Pond, near the areas of maximum depth for each basin. Water samples were collected on various dates from June to October 1998 from a boat moored with two anchors placed at least 10 m to either side of the sampled water column. A sampling tube was attached to an *in situ* water quality probe that records on a ship-board computer the depth, temperature, specific conductivity, dissolved oxygen, pH and the oxidation/reduction potential (ORP) at each depth selected. All probe measurements were calibrated in the lab with standards prior to each sampling run. Water was pumped to the surface using a low-flow peristaltic pump with acid-washed tubing and collected in acid-washed high-density polyethylene bottles and vials, with the exception of water for sulfide and methane analyses, which was collected in acid-washed BOD bottles. Filtered samples (30 ml) were pushed through 5 µm and 0.4 µm syringe filters (Gelman Sciences Acrodisc) in series immediately upon pumping to the surface. Ferrous iron (Fe-II) concentrations were carried out on-board using a field spectrophotometer and vacuum vials containing pre-measured reagents (CHEMetrics), which were placed directly in the pumping water. All samples for later analysis were stored on ice for transport to the laboratory.

Sulfate, nitrate, and chloride measurements were made by separation via ion chromatography with a conductivity detector (Dionex 16). Sulfide measurements utilized the methylene blue method, and phosphate measurements the molybdenum blue method. Methane concentrations were separated on a purge-and-trap gas chromatograph and measured by flame-ionization detector (Carlo-Erba HRGC 5160 equipped with a Tekmar LSC 2000). Sulfate, nitrate, chloride, sulfide, methane, and phosphate measurements were carried out within 48 hours of sampling. Arsenite (As-III) was quantified within 24 hours of sample collection by hydride generator atomic absorption spectrometry (PSA Excalibur). For total arsenic, samples were acidified with 5% nitric acid and allowed to stand overnight prior to measurement by graphite furnace atomic absorption spectrometry (Perkin-Elmer 4100ZL). Standard curves were analyzed for all analytes each day that measurements were made.

Results and Discussion

Arsenic chemistry is dominated by the redox status of the system of interest. The primary inorganic arsenic species of environmental significance are arsenate, As(V), and arsenite, As(III). Organic forms of arsenic may be significant under certain conditions, but they were not considered in this study. As(V) readily binds to insoluble iron oxides, thus making As(V) much less soluble than As(III) overall. As(III) itself may precipitate in the presence of sulfides as amorphous forms of orpiment, realgar, and arsenopyrite; however, the kinetics of formation of these solids may be slow in the absence of bacterial catalysis. Evidence also suggests that As(III) is more toxic than As(V). Therefore, the redox conditions of aquatic systems can greatly influence the mobility, as well as the potential toxicity, of arsenic.

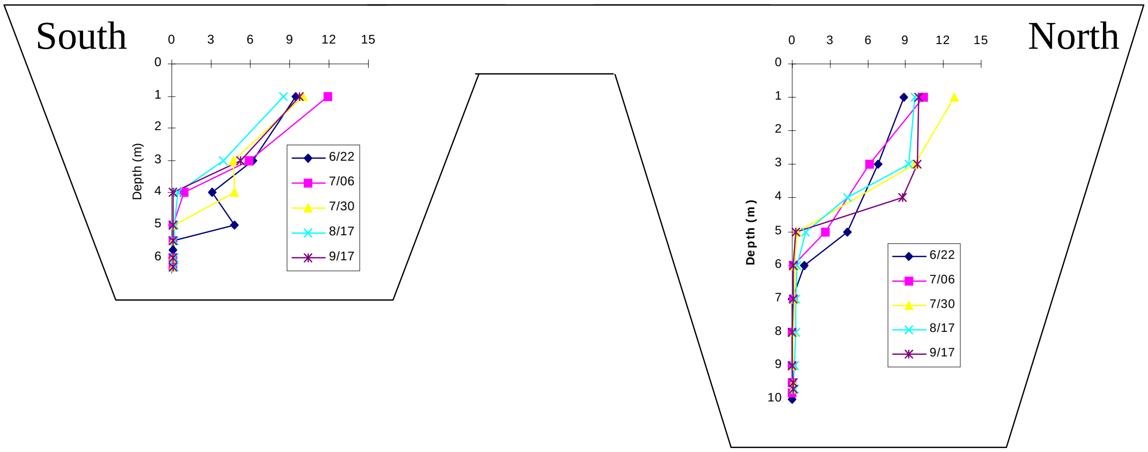

Figure 2: Dissolved oxygen content (mg/L) in Spy Pond during 1998.

Field sampling in 1998 revealed that both the North and the South Basins of Spy Pond show the classic symptoms of a hyper-eutrophic lake. The hypolimnetic waters in both basins were almost completely anoxic by June 22, and this anoxic layer continued to move upwards throughout the summer [Figure 2]. The thermocline was established at a depth of 4-5 m in both basins. Sampling in 1999 has shown that anoxia in the South Basin begins as early as April 5, while in the North Basin it begins by May 19 (Gawel and Senn, unpublished data). Previous reports have shown that nutrients in runoff emptying into the lake promote algal blooms from spring to fall (Environmental Design and Planning Inc. 1982). In addition, macrophyte growth in Spy Pond is thick, dominated recently by the invasive Eurasian watermilfoil (*Myriophyllum spicatum*), which thrives on nutrients buried in the near-shore sediments (Shanahan 1997). The algae and macrophytes in the epilimnion supply a large amount of organic matter to bacteria living in the hypolimnion and the sediments. Then bacteria consume oxygen as the organic matter is respired.

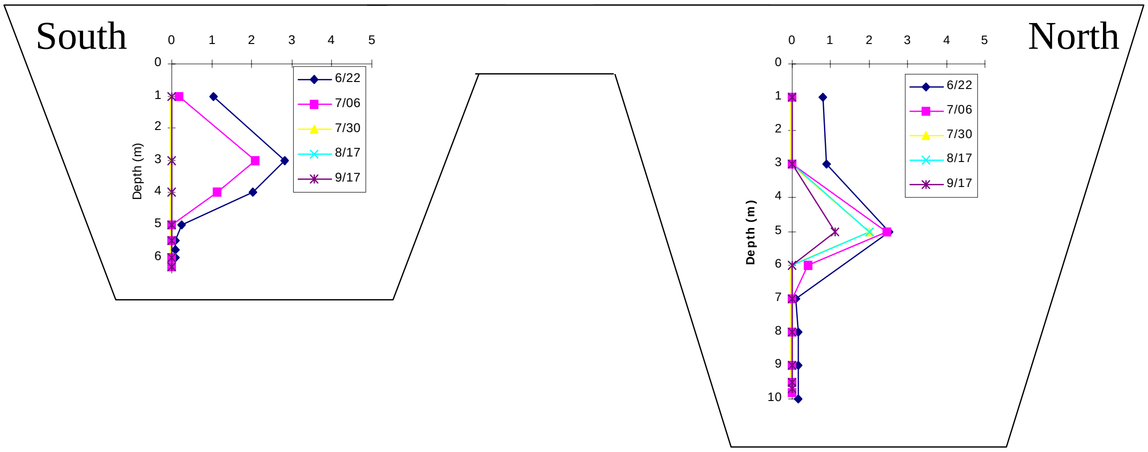

Figure 3: Nitrate concentrations (ppm) in Spy Pond during 1998.

Alone, the respiration of all the dissolved oxygen in the hypolimnion does not lower the redox potential of the system to the point where it would be thermodynamically favorable to reduce As(V) to As(III). Several environmentally relevant oxidants (NO_3^-, NO_2^-, Mn(IV), and Fe(III))

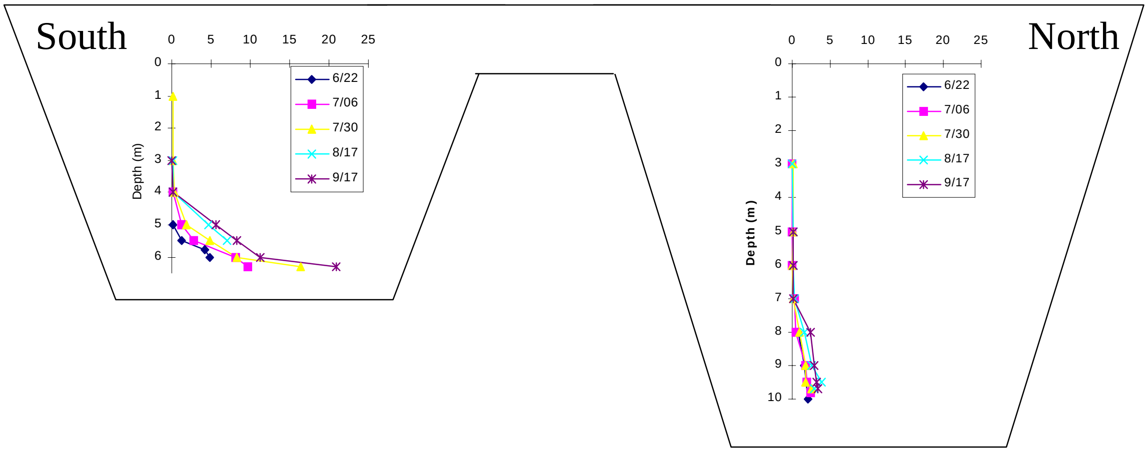

Figure 4: Ferrous iron concentrations (ppm) in Spy Pond water during 1998.

have a higher oxidation potential than As(V). Therefore, the presence of significant quantities of these oxidants would indicate a redox potential that would favor As(V) over As(III). Concentrations of NO_3^- were undetectable throughout the hypolimnion of both basins by July 6 [Figure 3]. Periodic measurements of NO_2^- also showed undetectable levels (data not shown). The spike in NO_3^- concentrations at the thermocline most likely indicates the presence of nitrifying bacteria near the oxic/anoxic interface. Fe(II) concentrations were measurable in the hypolimnion of both basins by June 22 [Figure 4]. Preliminary total iron measurements (by ICP-AES) carried out for the July 30, 1998, sampling date indicate that all iron in the hypolimnetic waters is in the reduced form (data not shown). Thus, all chemical constituents with greater oxidative potential than As(V) were already depleted by early summer in Spy Pond.

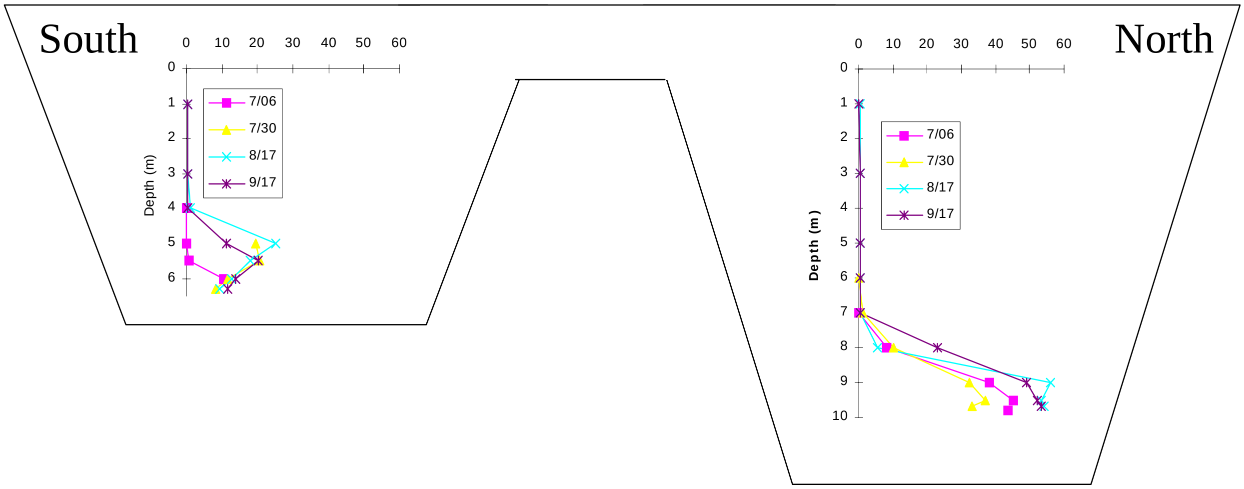

Figure 5: Sulfide concentrations (µM) in Spy Pond waters during 1998.

Other oxidants of environmental significance with lower oxidation potentials than As(V) include sulfate and carbon dioxide. Sulfide concentrations were detected in the bottom waters of both basins throughout the summer, accompanied by the loss of sulfate from the hypolimnion by August [Figures 5 and 6]. Methane was also detectable in the hypolimnion of both basins by mid-summer, indicating the reduction of CO_2 [Figure 7].

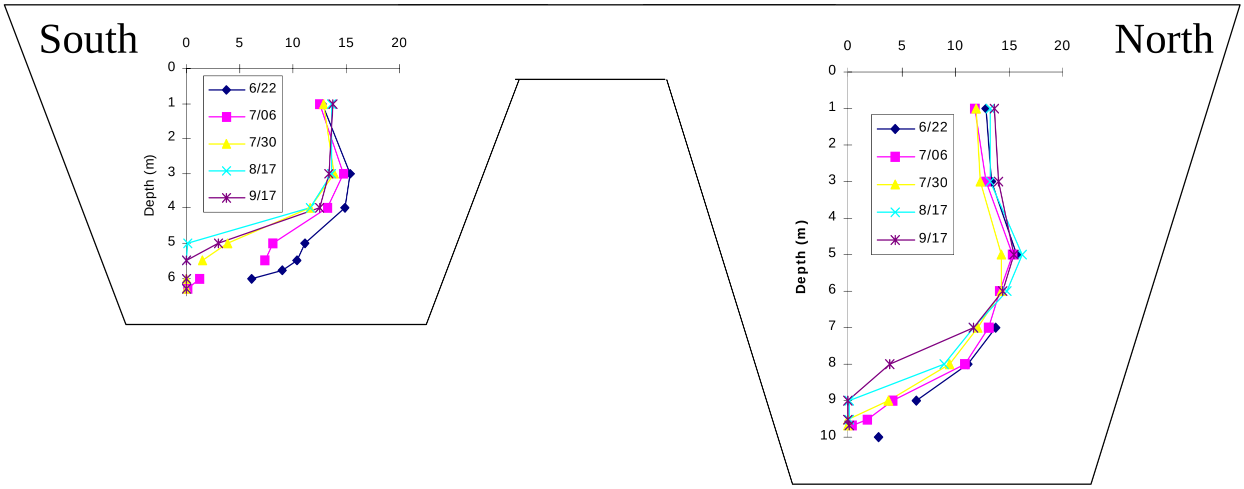

Figure 6: Sulfate concentrations (ppm) in Spy Pond waters during 1998.

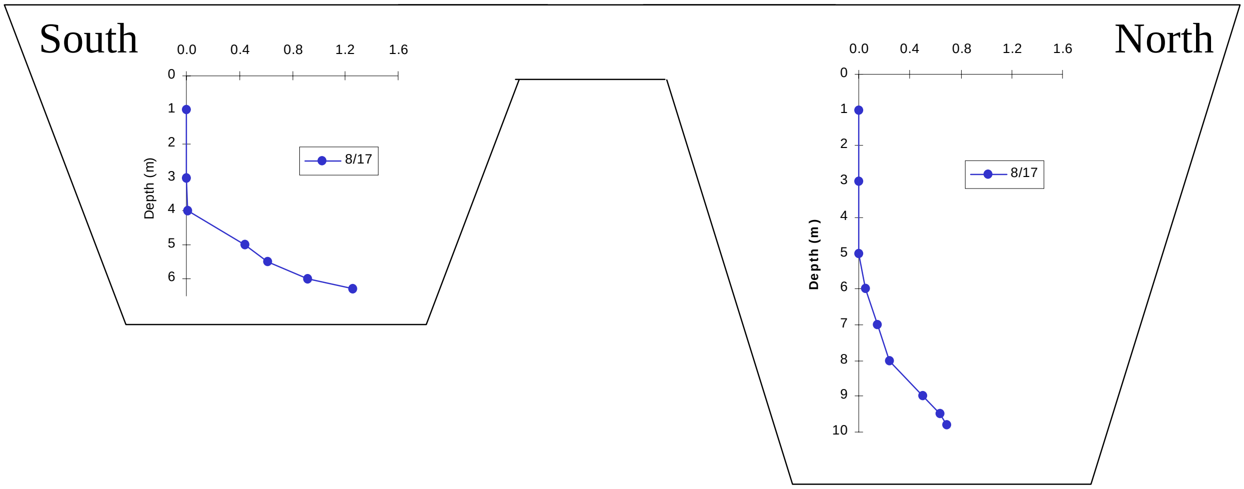

Figure 7: Methane concentrations (ppm) in Spy Pond waters during 1998.

These measurements are evidence of a redox potential well below that for the As(V)/As(III) couple in both basins of Spy Pond. Measurements of arsenite and arsenate – by difference between total As and As(III) – suggest that at least 50% of total As in the hypolimnion is in the form of As(III) [Figure 8]. This is a conservative estimate, as the overnight delay between sampling and speciation measurements allows the oxidation of a portion of the As(III) to As(V). Two pieces of evidence suggest that the percentage of total As in the As(III) form is much higher (data not shown). First, filtered samples had higher As(III) concentrations than unfiltered samples, suggesting that the removal of bacteria from the bottles helped to preserve As(III).

Second, a preliminary experiment was carried out in which hypolimnetic water samples collected in the field were immediately frozen in liquid nitrogen in an on-board dewar. As(III) in these frozen samples was nearly 100% of the total As, suggesting that the As(V) concentrations measured in samples stored on ice may be an artifact of inadequate sample preservation techniques.

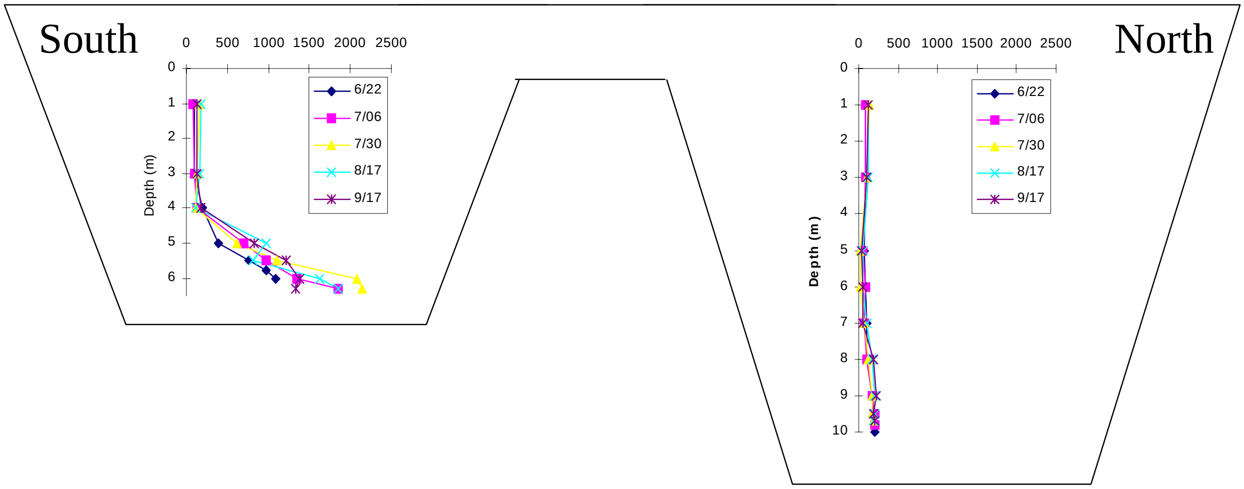

Figure 8: Total arsenic concentrations (nM) in Spy Pond waters during 1998.

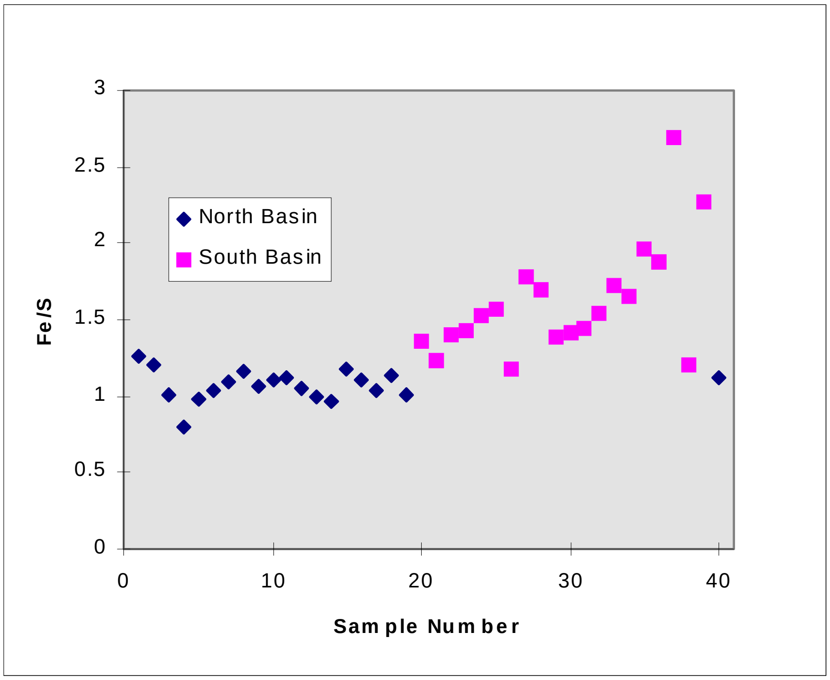

Figure 9: Total iron to sulfur molar ratios in surface sediment samples collected by Ekmann dredge from Spy Pond during 1998-99 (taken from MacLaughlin 1999). Sample numbers are for reference purposes only.

If the redox potentials of the North and South Basins of Spy Pond were the only controlling factors for arsenic mobility, it would be expected that the concentrations of As would be roughly the same in the two basins. Instead, As concentrations in the South Basin are approximately ten times higher than the levels in the North Basin [Figure 8]. It is likely that this difference is due to differences in the Fe(II)/S(-II) ratio in the two basins. Figures 4 and 5 show that the Fe(II)/S(-II) molar ratio in the hypolimnion of the South Basin was 18, but in the bottom waters of the North Basin it was less than 2. This dichotomy is also evident in the Fe/S ratio in the surface sediments of the two basins [Figure 9]. This difference appears to be due to higher overall concentrations of sulfur in the North Basin sediments (iron concentrations were nearly identical in sediment samples collected from both basins). Sulfide readily precipitates with both Fe(II) and As(III), but iron-sulfides are more thermodynamically stable. Therefore, in the presence of excess Fe(II) in relation to S(-II), as in the hypolimnion of the South Basin, the sulfide is largely scavenged from the bottom waters, leaving little in solution to precipitate the As(III) and leading to higher concentrations of As(III) in the water. In the North Basin, more sulfide is available to depress the release of arsenic from the sediments [see Figure 10].

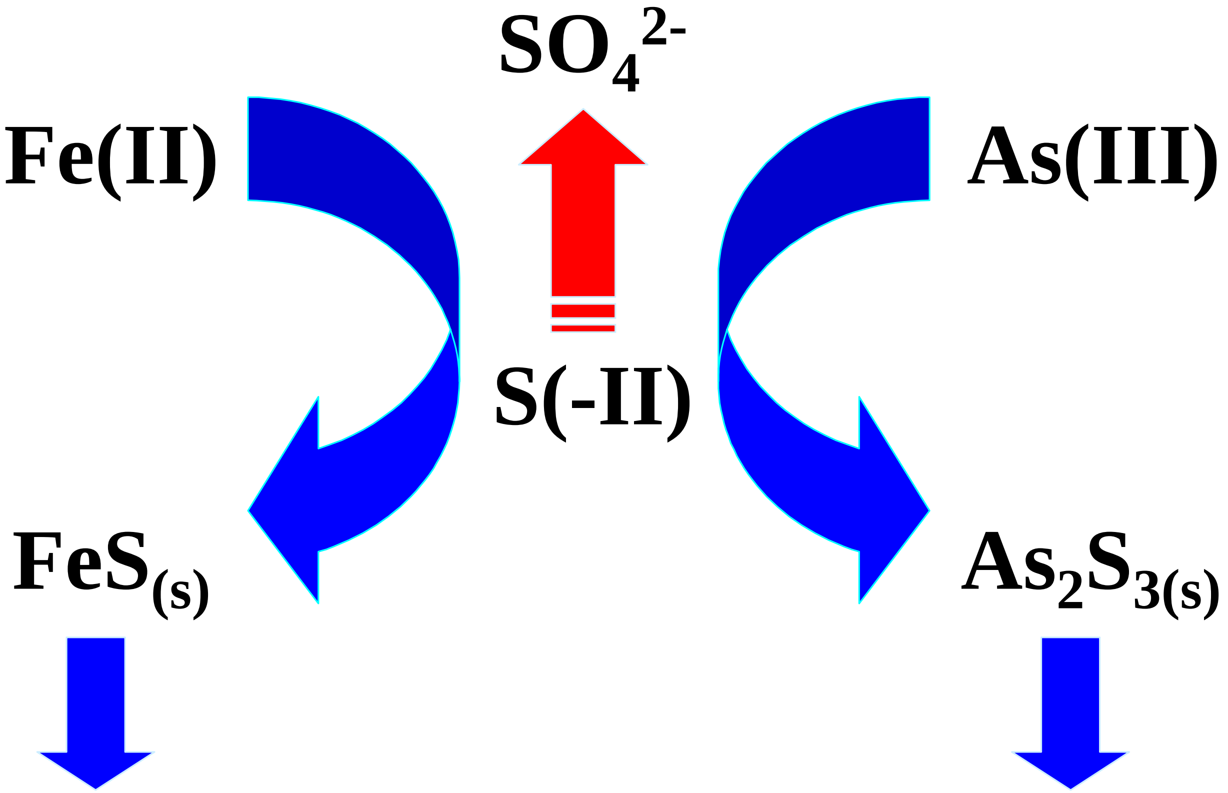

Figure 10: Conceptual model of the competition between As and Fe for sulfide in Spy Pond.

Chloride concentrations in the bottom waters of the South Basin are also much higher than in the North Basin [Figure 11]. This is most likely due to direct inputs of salt-laden winter runoff from the eight-lane highway that drains into the South Basin. Some portion of this salty runoff is effectively trapped in the hypolimnion throughout the summer, which depresses mixing and leads to an earlier onset of stratification in the spring in the South Basin. Moreover, the higher salt content in the South Basin has chemical impacts in addition to the physical effects. First, ion solubility is increased at higher ionic strengths in general. Second, Fe(II) also forms soluble $FeCl_x$ complexes that become significant at higher chloride concentrations. Taking into account these two chemical effects, equilibrium model calculations predict that the trapped salty water results in greater levels of dissolved As(III) and Fe(II) in the South Basin due to the increased solubility of $As_2S_{3(s)}$ and $FeS_{(s)}$. The effects of road salt in the South Basin account for nearly a 10% increase in As(III) concentrations.

In addition to increasing the solubility of As(III), this salty layer may have a more subtle impact. Our field work during the winter season of 1998-99 has shown that dense, salty runoff (introduced into the hypolimnion of the South Basin during road salt applications on the highway) causes the episodic depletion of oxygen in the bottom waters of the South Basin throughout the winter. These periods of anoxia are relatively short-lived because the absence of a thermocline gives rise to rapid mixing with oxygenated surface waters. We hypothesize that this cycle of oxygen enrichment followed by oxygen depletion may result in increased mobilization of arsenic from the sediments during the winter. Additional work is needed to identify the possible mechanisms responsible for the difference in arsenic levels in the two basins.

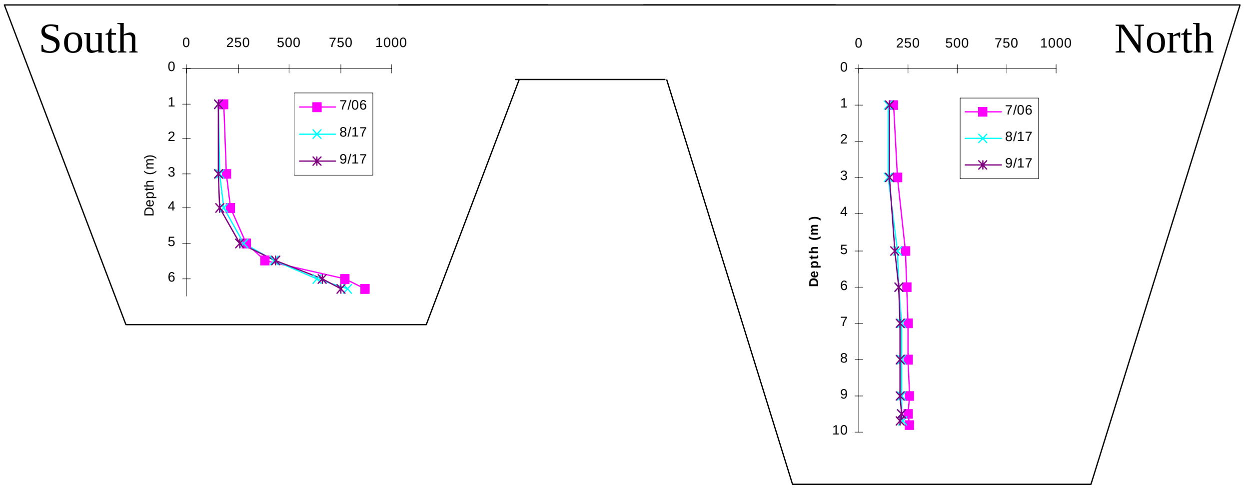

Figure 11: Chloride ion concentrations (ppm) in Spy Pond waters during 1998.

Conclusions

Overall, it is evident that nutrients and organic matter in stormwater runoff increase the solubility of arsenic in urban lakes by lowering the redox status of the bottom waters. This may be especially problematic in ponds with long turnover times (i.e. greater than 1 year). In addition, road salt may exacerbate the problem through depressed mixing and increased solid dissolution. This is not limited to arsenic, however, as the solubility of many toxic metals are sensitive to redox conditions and changes in salinity. Therefore, the control of eutrophication in urban lakes may help to limit potential human exposure to metals, and in the absence of continuing source input may actually remediate the problem in the long term.

Acknowledgements

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Bibliography

Aurilio, A. C., Durant, J. L., Hemond, H. F., and Knox, M. L. (1995). "Sources and distribution of arsenic in the Aberjona watershed, eastern Massachusetts." *Water, Air, and Soil Pollution*, 81, 265-282.

Environmental Design and Planning Inc. (1982). "Feasibility study for the restoration of Spy Pond." Allston, MA.

Ivushkina, T. (1999). "Toxic Elements in the Sediments of the Alewife Brook and Mill Brook Watersheds: Spatial Distribution and Depositional History," M.S., Tufts University, Medford, MA.

Jason M. Cortell and Associates. (1973). "Report of the conditions in Spy Pond, Arlington, Massachusetts; a historical synopsis." Wellesley Hills, MA.

MacLaughlin, K. J. (1999). "An Investigation of Arsenic in Spy Pond," M.Eng., Massachusetts Institute of Technology, Cambridge, MA.

Shanahan, P. (1997). "Review of the recommendations for the restoration of Spy Pond, Arlington, Massachusetts." HydroAnalysis Inc., Acton, MA.