ARSENIC IN THE ABERJONA WATERSHED

by

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Abstract

Elevated concentrations of arsenic have been found in soils, and riverine and lacustrine sediments in the Aberjona watershed. These data indicate that on the order of 300 metric tons of arsenic are present in contaminated areas of the watershed. Historical records indicate that much of the arsenic resulted from sulfuric acid and arsenical pesticide manufacturing. We used national pesticide and sulfuric acid manufacturing data for the relevant period, as well as historical information on manufacturing techniques and waste generation, to estimate that 200 to 700 metric tons of arsenic may have been released as a result of these activities. A significant fraction, about 10 metric tons, has migrated over 10 km from the site of origin.

A sensitive analytical technique was used to measure inorganic and mono- and dimethylated arsenic compounds in the water column of three lakes. The highest concentrations of arsenic, in the reduced inorganic form (arsenite), were measured at millimolar concentrations in springs near a highly-contaminated site, and in the sulfidic waters of the monimolimnion of the Lower Mystic Lake. Increases of reduced and methylated arsenic in surface waters of both Mystic Lakes were observed to coincide with the growing season. Both reduced and oxidized forms were found under thermodynamically unfavorable conditions.

Thesis Supervisor: Professor Harold F. Hemond, Department of Civil and Environmental Engineering

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CHAPTER ONE - INTRODUCTION

The Aberjona River watershed encompasses an area of 65 square kilometers and contains a multitude of hazardous waste sites, the legacy of over a century of industrial activities. MIT researchers have found that considerable amounts of toxic chemicals are now widely distributed in the watershed (Knox, 1991; Spliethoff and Hemond, 1992, Durant et al., 1991).

One of the most toxic chemicals found in the watershed is arsenic. Compounds containing this element have been used for hundreds of years for medicinal and pesticidal purposes (National Research Council, 1977). Despite this history of medicinal use, arsenic is considered acutely toxic to humans in small amounts (lethal dose of 70-170 mg) (International Agency for Research on Cancer, 1980). Strong epidemiological evidence shows that some forms of arsenic are carcinogenic (International Agency for Research on Cancer, 1980).

Soils at the Industri-Plex site, and river and lake sediments in the watershed have been found to contain extremely high concentrations, up to 30,800 mg/kg (dry weight) of arsenic (United States Environmental Protection Agency, 1986; Knox, 1991). In contrast, arsenic concentrations of 0.4 to 40 mg/kg are considered typical for soils with no geologic or anthropogenic arsenic inputs (National Research Council, 1977).

The geology of the Aberjona watershed does not suggest a significant geological source for elevated levels of arsenic (United States Geological Survey, 1980). Instead, the distribution of arsenic in the watershed, and preliminary historical investigations reveal industrial sources.

The goals of this study were to further our understanding of arsenic occurrence, chemical speciation, and movement within the watershed. Arsenic was the focus because of its toxicity, complex geochemistry and the widespread distribution of arsenic-contaminated soils and sediments in the watershed.

The first part of this study is an investigation into the sources of arsenic in the Aberjona watershed. We estimated total amounts arsenic in watershed areas with elevated arsenic concentrations, and compared these amounts to arsenic releases estimated from historical manufacturing activities.

After the identification of the major source of arsenic in the watershed, and the development of a rough arsenic budget for the watershed based on soil and sediment measurements, we investigated the potential for transfer of arsenic among the known "hot spots" in the watershed.

Arsenic has a complex geochemistry, with four oxidation states which are stable in the range of redox conditions found in natural waters (Cullen and Reimer, 1989). Numerous biologically-mediated transformations, including alkylation, complicate *a priori* attempts to predict arsenic speciation in aquatic systems (Cullen and Reimer, 1989).

Most work on arsenic speciation and cycling has focussed on the marine and estuarine environment. Recent studies of freshwater speciation and cycling have shown that biological transformations may be as important in freshwater as they are in some saltwater systems (Anderson and Bruland, 1991).

A sensitive analytical technique, which can differentiate nanomolar concentrations of reduced and oxidized inorganic arsenic and mono- and dimethylated arsenic species, was used to study arsenic speciation in three lakes in the Aberjona watershed (Andreae, 1977). Each lake had elevated levels of arsenic in bottom sediments. Two of the lakes studied, the Upper and Lower Mystic Lakes, are used extensively for recreation. Arsenic speciation studies in these two lakes are important in evaluating the potential for human exposure to harmful levels of arsenic. The other lake, the Hall's Brook Storage Area, located in an industrially-developed area, is the subject of ongoing studies regarding its role in arsenic migration from an adjacent Superfund site.

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CHAPTER TWO - SOURCES AND DISTRIBUTION OF ARSENIC IN THE ABERJONA WATERSHED

INTRODUCTION

The improper disposal of industrial wastes in the Aberjona watershed, a sixty-five square kilometer, heavily populated watershed in northeastern Massachusetts, has raised concerns that residents may be at risk as a result of exposure to hazardous chemicals (Figure 2.1). Over a century of industrialization has resulted in the release of considerable quantities of chemical wastes to the environment. At present, there are two federally-designated, and over 20 state-identified hazardous waste sites in the Aberjona watershed, some of which contain large quantities of toxic metals, including arsenic, chromium, and lead, and volatile organic compounds (United States Environmental Protection Agency 1989, 1986; Massachusetts Department of Environmental Protection, 1989; Roux Associates, 1991; Nus Corporation, 1986; Ecology and Environment, Inc., 1981). Significant levels of metals and arsenic have been found in lake and river sediments downstream from waste disposal sites (Knox, 1991). These elements may pose a risk to human health in the watershed because both arsenic and chromium may be toxic and carcinogenic to living organisms (International Agency for Research on Cancer, 1980; National Research Council, 1977). Arsenic is of concern because strong epidemiological evidence shows that some inorganic arsenic compounds are human carcinogens (International Agency for Research on Cancer, 1980); and some forms of arsenic are acutely toxic to plants, animals. and humans (National Research Council, 1977).

Durant et al., 1990, investigated the wastes released by tanning and leather finishing activities, once the largest industry in the watershed. Using historical production records, Durant found that thousands of metric tons of waste chromium were generated and released to the environment during 150 years of leather tanning activities in the watershed (Durant et al., 1990).

On the other hand, the presence of high concentrations of arsenic in watershed soils and sediments can be traced primarily to chemical manufacturing activities in north Woburn. In order to better understand the relationship between the sources and distribution of arsenic in the watershed, and hence the risks to human health, we have explored the role of chemical manufacturing in the production of arsenical wastes. The amounts of these wastes historically released to the watershed are estimated using historical records of local and national chemical manufacturing activities. These are then compared to estimates of arsenic found in contaminated soils and sediments in the watershed (Figure 2.2).

ARSENIC DISTRIBUTION IN THE WATERSHED

Arsenic is the 20th most abundant element in the earth's crust, and is usually associated with sulfur-containing ores (National Research Council, 1977). Background arsenic levels in soils range from 0.1 to 40 mg/kg; levels up to 8,000 mg/kg have been reported for soils overlaying sulfide ores (National Research

Council, 1977). The geology of the Aberjona watershed does not suggest a significant geologic source for elevated arsenic levels (United States Geological Survey, 1980), yet arsenic levels of up to 30,800 mg/kg (dry weight) have been found in watershed soils (United States Environmental Protection Agency, 1986). Apparently, human activities have played a leading role in the distribution of arsenic in the watershed.

A Superfund site in north Woburn, the Industri-Plex site, is very heavily contaminated with arsenic; up to 30,800 mg/kg (dry weight), are found in the soils around an old chemical works (Figure 2.3) (Stauffer, 1984). Investigators estimate that a 20-hectare area contains arsenic and/or lead concentrations in excess of 100 mg/kg (Stauffer, 1984). Although there is considerable heterogeneity in the distribution of arsenic within the waste deposits, using an average arsenic concentration of 815 mg/kg (dry weight) from 357 sampling points (Stauffer, 1984), the total amount of arsenic can be estimated. Assuming a soil density of 2 g/mL, we estimate that 270 metric tons of arsenic may be present in the most contaminated soils on the site. The Industri-Plex site contains more arsenic waste than any other site in the watershed (U.S. EPA, 1989; Ecology and Environment, 1981).

Arsenic contamination from chemical manufacturing extends beyond the boundaries of this site. Recent investigations by Knox (1991) and Spliethoff and Hemond (1992) have shown that high levels of arsenic are present in the sediments of the Aberjona River and the Mystic Lakes (Figure 2.2), strongly implying that the river is an important migration route for the arsenic from Industri-Plex to the lakes.

In Halls Brook Storage Area, which receives runoff from the southwestern part of the Industri-Plex site, measurements of arsenic in sediments range from 35 mg/kg (dry weight) to as high as 9,830 mg/kg (dry weight)(Roux Associates, 1991; Knox, 1991). We estimate that four metric tons of arsenic are present in the sediments in Halls Brook Storage Area.

Approximately 3 kilometers south of the Industri-Plex site, a wetland area through which the river flows is also contaminated with arsenic. This 16 hectare wetland is part of the Wells G and H site, another federally-designated hazardous waste or Superfund site (U.S. EPA, 1989). Investigations have revealed dissolved arsenic levels in groundwater of up to 110 ug/L and arsenic levels of up to 3,630 mg/kg in sediments(Cherry, et al., 1989). Assuming a constant sediment density of 0.44 g/mL (the average of five river sediment samples), and a sediment depth of 10 cm, we estimate that approximately 700 kg of arsenic are present in the wetlands sediments at the Wells G and H site.

South of Wells G and H, arsenic concentrations in the river vary considerably, with peaks up to approximately 200 mg/kg (Knox, 1991). Using a weighted average concentration of 130 mg/kg for the entire river, sediment density of 0.44 g/mL, a sediment depth of 10 cm, and river width and length of 6 m and 14 km, respectively, a rough estimate of arsenic present in Aberjona River sediments is 500 kg.

The Aberjona River empties into the Mystic Lakes. Sediment cores taken in the deepest parts of the Upper and Lower Mystic Lakes reveal a depth-dependent arsenic profile (Figure 2.4). Arsenic peaks from several cores range from over 500 to almost 2000 mg/kg (dry weight), and 30 to 450 mg/kg (dry weight) for the Upper and Lower Mystic Lakes, respectively (Knox, 1991, Spliethoff, 1992). If the measured profiles are typical of the entire lakes' area, then the Upper Mystic Lake may contain up to 10 metric tons of arsenic, and the Lower Mystic Lake may contain up to three metric tons.

In summary, soils and sediments with arsenic concentrations far exceeding the published "background" concentrations of 0.1 to 40 mg/kg, may contain on the order of three hundred metric tons of arsenic in the Aberjona watershed.

ARSENIC WASTE GENERATION IN THE WATERSHED

Arsenic was used as a raw material in chemical manufacturing over a forty-year period, from approximately 1888 to 1929 (Haynes, 1939) in the Aberjona watershed. While other anthropogenic sources of arsenic in the watershed are possible, including the use of arsenical pesticides for agriculture and arsenical depilatories (i.e., hair-removing agents) in tanning operations, both historical records and the current distribution of arsenic concentrations in soils and riverine and lacustrine sediments suggest that chemical manufacturing was the most important source. The greatest amounts of arsenical wastes are known to have been produced at the Industri-Plex site in north Woburn (Figure 2.2).

History of Industri-Plex Site

A succession of five chemical manufacturers have occupied the Industri-Plex site since 1853 (Table 2-1). In that year, Robert Eaton, of Woburn, built the Woburn Chemical Works on 43 hectares of farmland and meadows (Darcy, 1982). Woburn Chemical Works manufactured chemicals for use in the growing New England textile industry, and also recycled cattle hooves and other waste material (Middlesex Journal, 1857).

The company grew and merged with a previous competitor in 1863 to form Merrimac Chemical Company. This new company supplied sulfuric acid and related chemicals for the leather tanning, textile and paper-making industries in New England. Historical accounts indicate that arsenic-containing raw materials were first used in sulfuric acid manufacturing processes at the site in 1888 (Haynes, 1939). The manufacture of sulfuric acid probably resulted in the largest quantity of arsenical wastes as explained below.

Merrimac Chemical continuously developed new processes and manufactured new products at the Woburn site. In 1899, Merrimac purchased the William H. Swift Company, manufacturers of arsenical insecticides and other chemicals, thus becoming one of the largest producers of arsenical insecticides in the United States. The manufacture of arsenical insecticides at the Woburn plant constituted a second important source of arsenical wastes. In 1917, Merrimac acquired Cochrane Chemical Company in Everett, Massachusetts, at which point it became the largest chemical manufacturer in New England, with operations divided between the Everett and Woburn plants (Haynes, 1954, Merrimac, 1928). Twelve years later, Monsanto Chemical Company acquired Merrimac, and by 1931, all operations had been consolidated to Everett.

From 1934 until 1968, the Woburn site was occupied by a succession of three glue and gelatin manufacturers which used animal by-products, including chrome-tanned hide trimmings, in their operations (Stauffer Chemical, 1983). The animal glue and gelatin manufacturers which occupied the site after Merrimac Chemical may have contributed some arsenic from traces of arsenical depilatories left on the chrome-tanned hides, but other depilatories were more commonly reported (Durant et al., 1990).

In 1968, the land was purchased by the Mark Phillip Trust, which intended to develop the area into an industrial park, called Industri-Plex 128. However, piles of animal hide wastes from the glue and gelatin-making operations were uncovered when bulldozing began. Large quantities of hydrogen sulfide gas emanated from the partially-decomposed hides, leading to the designation of the site as the cause of the infamous "Woburn Odor" (U.S. EPA, 1986). Complaints about the odor eventually led to litigation, and development of the site was curtailed (Reading Chronicle, 1978). In 1981, the site was placed on the National Priorities List under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, or Superfund) due to the presence of high soil concentrations of arsenic, chromium, lead, and other pollutants (U.S. EPA, 1986).

Arsenic Released from Pesticide Manufacture

In 1892, F.C. Moulton of the Massachusetts Gypsy Moth Commission discovered the effectiveness of lead arsenate against gypsy moths (Haynes, 1954). Lead arsenate quickly grew in popularity. Beginning in 1899, Merrimac Chemical became known for its ".... Arsenate of Lead, which [was] the most successful insecticide ... in use, and which [was] being shipped to all parts of the country" (Woburn Daily Times, 1905). Lead arsenate manufacture at Merrimac Chemical peaked sometime around 1918; however, the company was still manufacturing "Arsenate of Soda", or sodium arsenate, which was a raw material used in the production of lead arsenate, until 1928 (Sanborn, 1915, 1918, 1926; Merrimac, 1928). There is no evidence that other arsenical pesticides used in the United States during this period, including Paris Green (copper acetoarsenite) and calcium arsenate, were manufactured by Merrimac Chemical (Haynes, 1954). Therefore, we estimated arsenic releases at the site based on the assumption that lead arsenate was the only arsenical pesticide manufactured at the site from 1899 through 1928.

Several processes were developed for the manufacture of lead arsenate. The most commonly reported is a reaction between lead oxide, acetic acid, nitric acid and arsenic acid (H_3AsO_4). Briefly, lead oxide reacts with acetic acid to form lead acetate. Following the addition of arsenic acid, lead arsenate precipitates, is separated by filtration, and the acetic and nitric acids are re-used (Figure 2.5). A 95% to 97% percent yield was reported for this reaction (Shreve, 1945). Assuming that the resultant lead arsenate contained 22% arsenic by weight, (other formulas and mixtures have been reported (Haywood and McDonnell, 1910)), approximately 0.7 to 1% of arsenic used in the manufacture may have been lost as a result of incomplete reaction of the raw materials. This waste was, most likely, arsenic acid in the filtrate, because the resulting lead arsenate was known to contain soluble arsenic pentoxide (Haywood and McDonnell, 1910).

Because actual production data for this company are not available, we estimated lead arsenate production and resultant arsenic releases indirectly. Total amounts of lead arsenate produced annually and number of manufacturers in the United States are presented in Table 2-2. Assuming that the company manufactured lead arsenate at the industry average rate (third column of Table 2-2), using the process described above with a 97% yield, 7 kg waste arsenic per metric ton of lead arsenate would have been produced due solely to incomplete reaction of the starting materials. Using these conservative assumptions, an estimated 35 metric tons of waste arsenic were produced at the site from 1899 to 1928 if Merrimac Chemical was producing lead arsenate at the industry average rate.

Two factors support a higher estimate of waste arsenic produced from lead arsenate manufacture, however. Given the company's hegemony in New England chemical manufacturing, and the importance of its arsenical pesticide production from 1899 through 1914 (Merrimac, 1928; Haynes, 1939), it likely produced the pesticide at a rate several times higher than the national average. In addition, other unquantified sources of waste arsenic such as inefficient grinding and packaging processes, breakage of the earthenware reaction vessels, and spillage (Armbruster, 1922), probably led to considerably greater waste of arsenic than that predicted by the above method.

Arsenic Released from Sulfuric Acid Manufacture

Although lead arsenate manufacture may have led to the release of large amounts of arsenic, sulfuric acid production constituted a less obvious, but far larger source of arsenical waste at Merrimac Chemical Company. Between 1880 and 1929, sulfuric acid was one of the mainstays of the company's product line. As noted by the local newspaper, "... the base product was, as it always has been, Sulphuric Acid [sic]."(Woburn Daily Times, 1929) This "most important of all chemicals" and products derived from it, were used by the textile and paper industries of New England (Wells and Fogg, 1920; Woburn Daily Times, 1929)

Sulfuric acid was produced by roasting sulfur-containing ores to produce sulfur dioxide gas. This sulfur dioxide gas was then oxidized in lead chambers, in the presence of water, to produce sulfuric acid (Fairlie, 1936). This process was known as the "chamber process".

In the late 1800's, "brimstone", or sulfur from Sicilian sulfur deposits, was burned to produce sulfur dioxide (Wells and Fogg, 1920). As Sicilian producers began raising their prices, American sulfuric acid manufacturers began burning pyrites (FeS_2), commonly known as "fool's gold" (Haynes, 1939). The pyrites were cheaper, but contained many impurities, including zinc, copper, lead, calcium, magnesium, and arsenic (Wells and Fogg, 1920). Pyrites from Spain, the principal source before World War I, typically contained 0.2% to over 1% arsenic; domestic pyrites contained much less (Fairlie, 1936; Lunge, 1903; Wells and Fogg, 1920).

Three types of arsenical wastes resulted from sulfuric acid manufacture using arsenic-containing pyrites. First, although arsenic is fairly volatile, the spent pyrites cinders contained up to 0.25% arsenic (Lunge, 1903). Second, dusts laden with arsenic pentoxide (As_2O_5, as much as 60% by weight) accumulated in gas flues and were removed periodically (Lunge, 1903). Third, acid made from arsenical ores was reported to contain up to half the arsenic originally present in the raw material (Wyld, 1924; Lunge 1903). Acids which were to be used in food-processing and metal finishing were purified using hydrogen sulfide (H_2S) to precipitate the arsenic as As_2S_3 (Lunge, 1903)

Thus, the amount of arsenic released from sulfuric acid manufacturing during the period of interest depends on the arsenic content of the raw materials, and whether the resulting acid was then purified.

In the absence of actual production data, we estimated sulfuric acid manufacturing operations and resultant arsenic releases at Merrimac Chemical's Woburn, Massachusetts plant using national manufacturing data from various sources. First, since Spanish pyrites were the most important source of arsenic, the percent of U.S. sulfuric acid manufactured from Spanish pyrites was estimated. Merrimac Chemical began burning pyrites in 1888 (Haynes, 1954), and regularly imported

Spanish pyrites (Woburn Daily Times Chronicle, 1905). For most years, information on Spanish pyrite imports was used to calculate a percentage of acid produced from pyrites, based on an average sulfur content of 47% by weight (Wells and Fogg, 1920). A national average sulfuric acid production rate was calculated using the number of "chamber process" manufacturers. (Another type of sulfuric acid manufacture, the "contact process", was also in use at Merrimac Chemical, after 1907, but arsenic-rich ores were unsuitable for this process (Fairlie, 1936).) Assuming an average sulfur content of 47% by weight and allowing for some loss in the roasting process, we estimated that one metric ton Spanish pyrite was burned for every 1.4 metric tons of sulfuric acid produced (Wells and Fogg, 1920).

Up to half of the arsenic present in pyrites was retained in the acid (Wyld, 1924; Lunge 1903). Merrimac's customers, the textile, paper, fertilizer manufacturers, and tanneries, were indifferent to arsenic in sulfuric acid and related products, so we assumed that no purification process was used for the resulting acid (Wells and Fogg, 1920). Using an average arsenic content of 0.4% in Spanish pyrites, and the conservative assumption that 50% of the arsenic was retained in the product, we estimate that approximately 1.5 kg of arsenic were released per metric ton of sulfuric acid produced using Spanish pyrites. These wastes may have consisted mainly of arsenic pentoxide-laden flue dusts as well as some arsenical pyrites cinders.

Table 2.3 presents the results of this analysis for the years in which national data are available. Production rates in the years for which no national data were available were interpolated linearly.

Assuming that Merrimac Chemical produced sulfuric acid from Spanish pyrites at national average rates, approximately 170 metric tons of arsenic would have been released during the period from 1888 through 1929. However, limited financial data from 1898 suggest that Merrimac Chemical Company produced sulfuric acid at four or five times the national average rate (The News, 1898; Haynes, 1954; Abbott, 1920). At this rate, the company would have generated on the order of 700 metric tons of arsenic from sulfuric acid production. Another factor which supports a higher estimate is geography. We assumed that every "chamber process" manufacturer in the country used the same proportion of Spanish pyrites. It is more likely that, due to overland transportation costs, coastal producers such as Merrimac Chemical Company used most of the Spanish pyrites imported to this country, while inland producers used domestic sources of sulfur-containing ores (Duecker and West, 1959).

Discharge of Arsenic Waste in the Watershed

A considerable historical record indicates that Merrimac Chemical routinely discharged wastes into wetlands, streams and lagoons on and adjacent to its property (Massachusetts Department of Public Health, 1915, 1916, 1923, 1932, 1933, 1934; Massachusetts Fisheries and Wildlife, 1921). Sanborn (1926), shows a "Sludge Pond", currently known as the "Arsenic Pit", on Merrimac's property. This may have been the recipient of flue dusts and pesticide wastes. In 1915, the Massachusetts Department of Public Health annual report on water quality in the Aberjona watershed attributed "... the discharge of oil in condensing water into the stream and also acid" to Merrimac Chemical (Massachusetts Department of Public Health, 1915). Later reports describe a "...reddish color, due largely to the discharge into the river of certain wastes and drainage from a chemical works in North Woburn..." in all samples of Aberjona River and Mystic Lakes water (Massachusetts Department of Public Health, 1923). After the Merrimac Chemical works were moved to Everett in 1929, the reports attribute the continuing color in the river and lakes to "... deposits of iron pyrites" and ".. deposits of partially-spent chemicals" at the site (Massachusetts Department of Public Health 1932, 1933, 1934).

DISCUSSION

Variability in arsenic concentrations, soil and sediment densities, and geometries of the various compartments are all sources of potential error in the estimation of the actual amount of arsenic present. In addition, reservoirs of arsenic that were not quantified, such as the groundwater plume recently discovered at Industri-Plex, may affect the arsenic budget presented here (Roux Associates, 1991). However, it seems likely that the above estimates fall within an order of magnitude of the actual amount present in the contaminated watershed soils and sediments. Comparison of the estimated amount of arsenic released by Merrimac Chemical, 200 to over 700 metric tons, versus the amount now found in the watershed, 300 metric tons, shows a remarkable similarity. Other potential sources of arsenic released to the watershed include both agricultural and other industrial activities. For example, arsenical depilatories may have been used in leather tanning. Local greenhouses and pig farms may have used arsenical compounds as pesticides and feed additives (Woolson, 1975; Tarr, 1987). Atmospheric inputs from coal burning may also have contributed, as coal fly ash has been found to contain up to several hundred mg/kg arsenic (National Research Council, 1977).

As is indicated by river sediment sampling results, sediment transport is an important mechanism of contaminant distribution. Some portion of the wastes that migrated downstream into the Mystic Lakes could have flowed into the Mystic River, which is fed by the lakes. Until 1908, the Lower Mystic Lake was tidally influenced (MDC, 1980), so there is a strong possibility that arsenic from Merrimac eventually reached Boston Harbor.

Groundwater contamination, the trucking of wastes from the site, and microbially-mediated transformations represent other pathways which were not accounted for in this mass-balance. For example, recent studies confirm the presence of an arsenic plume in the groundwater which extends past the official Industri-Plex site boundaries. Dissolved arsenic levels of up to 23,000 ug/L have been detected within this plume (Roux Associates, 1991). Wastes also may have been physically removed from the site through sales of chemical process by-products (Merrimac, 1928) or salvage operations (Table 2.1). Finally, microbially-mediated transformations, such as production of arsine or organic arsenic gas by fungi and bacteria may have led to volatilization of some of the arsenic wastes (Cullen and Reimer, 1989).

An extremely important question, which still needs to be addressed is that of risk to human health. Although the area with the highest concentration of arsenic, the Industri-plex site, has been fenced, the potential exists for human exposure to arsenic. The watershed is densely populated, and the Upper Mystic Lake is extensively used for swimming, sailing and fishing.

CONCLUSION

Widespread arsenic contamination in an industrialized watershed has been linked to historical manufacture of arsenical pesticides and sulfuric acid. As much as 200 to over 700 metric tons of arsenic are estimated to have been released as a result of pesticide and sulfuric acid manufacturing at one site in the watershed. Present inventories of arsenic contamination in soils and sediments suggest that on the order of 300 metric tons of arsenic -- a significant fraction of the total amount released -- remain in the watershed. The possibility also exists that some arsenic wastes were transported out of the watershed to the Boston Harbor. Even with limited production and waste generation data, a mass-balance approach has proved useful in identifying a major source of anthropogenic pollutants in a watershed. Finally, it is evident that waste chemicals discarded at a single location can become widely distributed in a watershed and may constitute a potential health risk long after waste production has ceased.

Figure 2.1. The Aberjona Watershed, showing study sites.

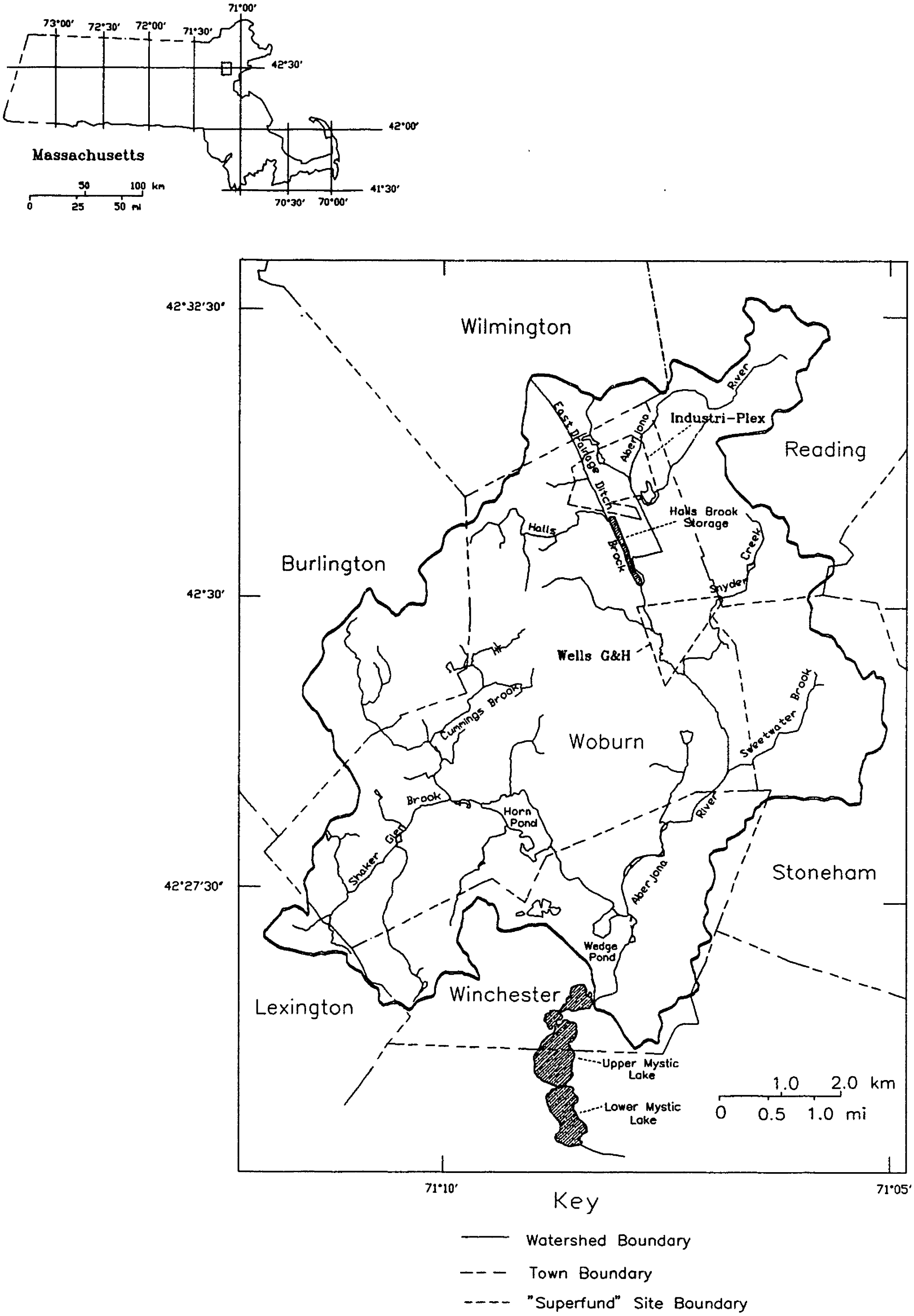

Figure 2.2. Arsenic in Aberjona Watershed Sediments - All samples taken of surface sediments except Upper and Lower Mystic Lakes, which reflect arsenic maxima in sediment cores.

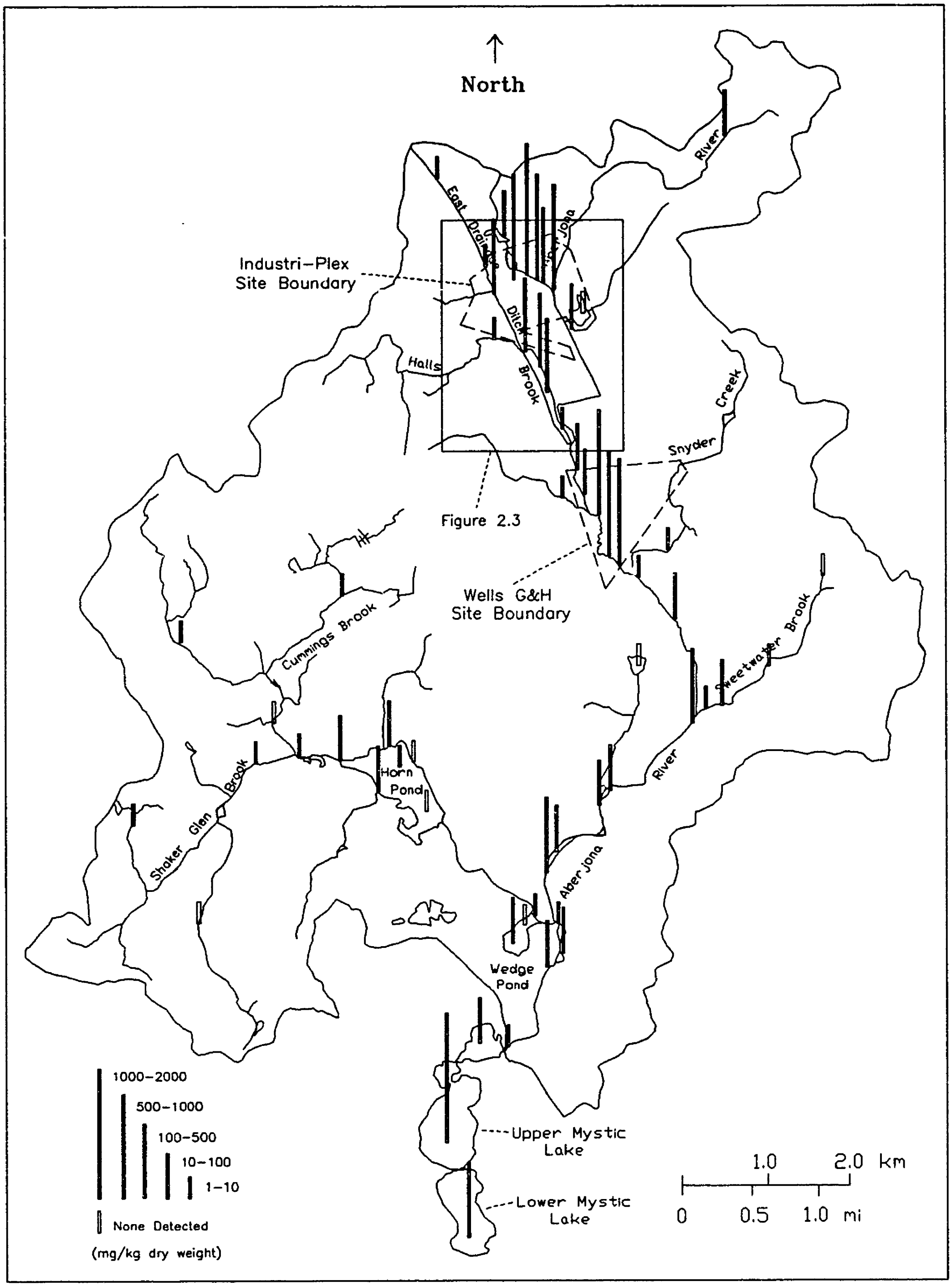

Figure 2.3. Industri-Plex Site and Hall's Brook Storage Area

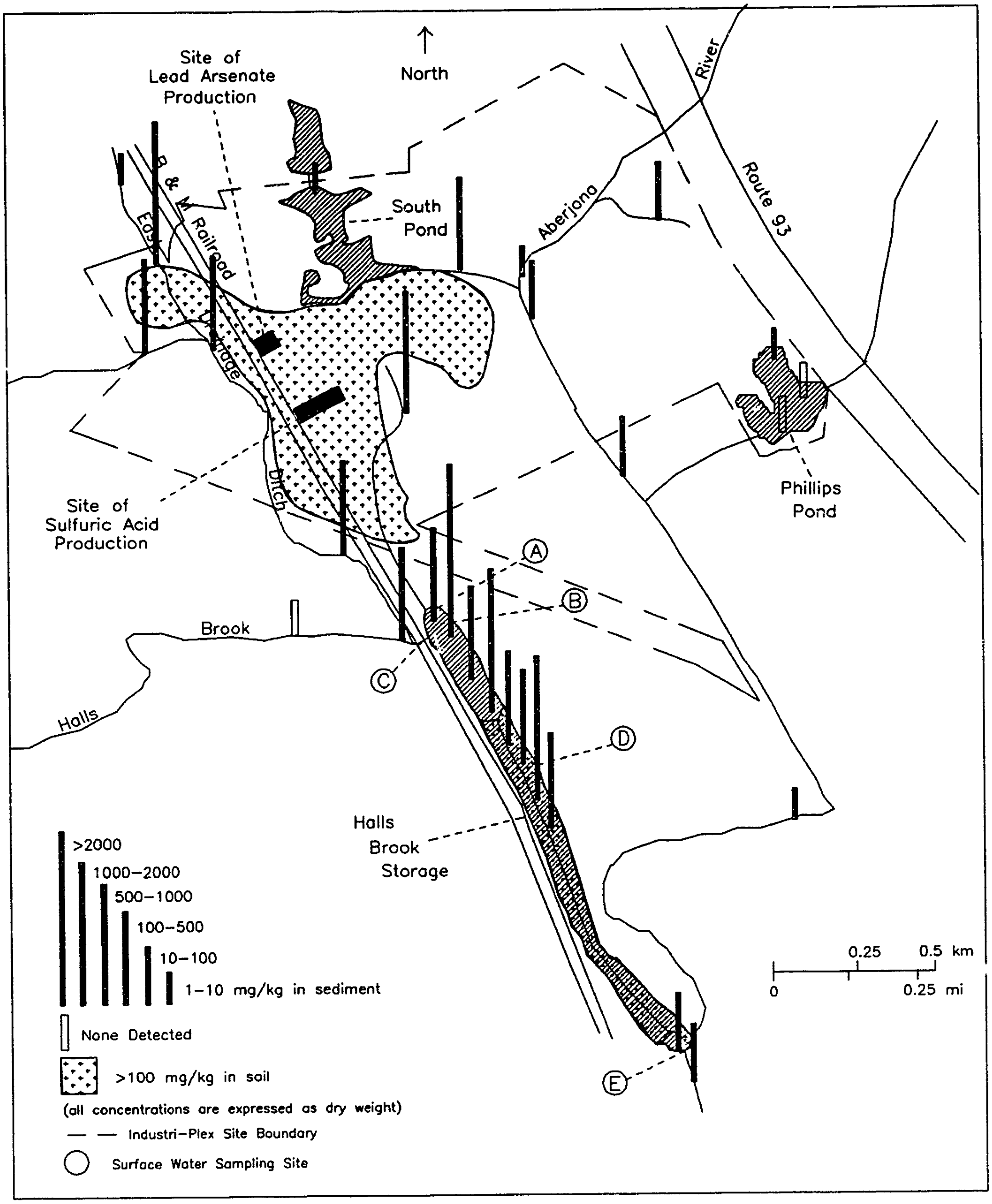

Figure 2.4. Arsenic in Upper Mystic Lake Sediments (Ref.: Knox, 1991).

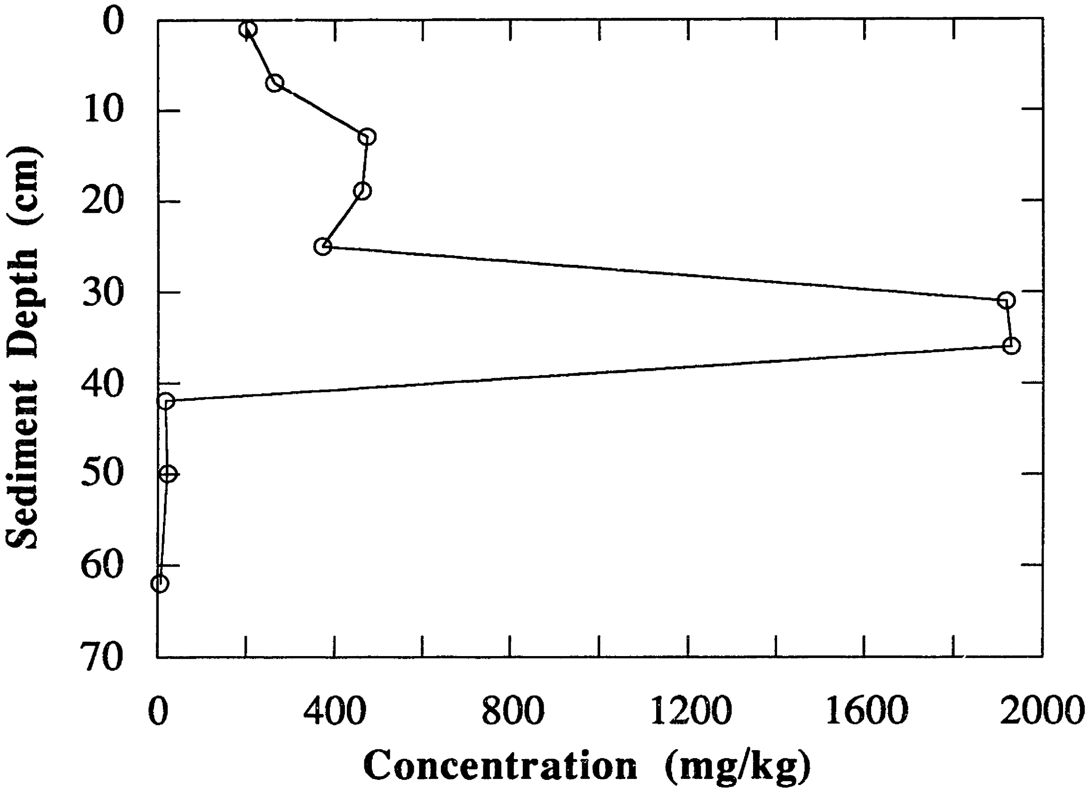

TABLE 2-1. HISTORY OF INDUSTRI-PLEX SITE[1]

DATE	COMPANY	PRINCIPAL PRODUCTS
1853 - 1863	Woburn Chemical Works	Sulfuric Acid, nitrates, glue, gum
1863 - 1929	Merrimac Chemical Company	Sulfuric Acid and other acids, arsenical pesticides, tin chloride, aluminum chloride, alum, various sulfates and sulfites
1929 - 1931	Monsanto Chemical Company	Similar to Merrimac Chemical
1931 - 1934	F & L Land Salvage and Improvement Company	Salvage equipment
1934 - 1936	New England Chemical Industries, Inc.	Animal glues and gelatin
1936 - 1961	Consolidated Chemical Industries	Animal glues and gelatin
1961 - 1968	Stauffer Chemical Company	Animal glues and gelatin

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[1] United States Environmental Protection Agency, 1986

Figure 2.5. Lead Arsenate Manufacturing Process

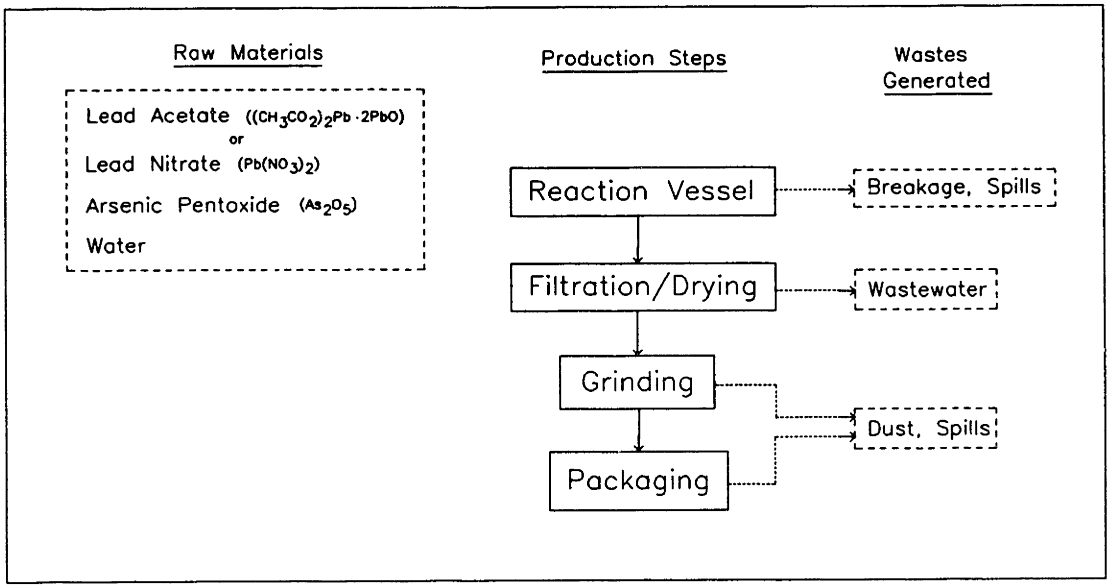

Table 2-2. Waste Arsenic from Lead Arsenate Manufacture

Year	Lead Arsenate[1] Production (metric tons)	Number of[2] Manufacturers	Average Production (metric tons)	Average Waste Arsenic[3] (metric tons)
1899	998	7	143	1
1900	1134	7	162	1.1
1901	1270	8	159	1.1
1902	1406	9	156	1
1903	1542	10	154	1
1904	1678	11	153	1
1905	1814	12	151	1
1906	1950	13	150	1
1907	2086	14	149	1
1908	2268	15	151	1
1909	2268	15	151	1
1910	2268	15	151	1
1911	2268	15	151	1
1912	2268	15	151	1
1913	2268	15	151	1
1914	2268	15	151	1
1915	2268	16	142	0.9
1916	2268	17	133	0.9
1917	2268	18	126	0.8
1918	2358	18	131	0.9
1919	2449	18	136	0.9
1920	2540	19	134	0.9
1921	2630	19	138	0.9
1922	2721	20	136	0.9
1923	2721	20	136	0.9
1924	9525	18	529	3.5
1925	6287	19	331	2.2
1926	7663	19	403	2.7
1927	7663	19	403	2.7

Average total waste arsenic produced per manufacturer: 35.3
(United States 1899 - 1927)

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[1] Production data for 1908 from Haywood and McDonnell, 1910: data for 1913, 1917, and 1923 from Haynes, 1954: data for 1924 from Chemical and Metallurgical Engineering, 1925; data for 1925 and 1926, which represents 70% of production, taken from Heckel, 1927 production data for other years was interpolated, 1899-1907 interpolation assumed zero produciton in 1892.

[2] Number of U.S. manufactureers taken from same sources as production data except for 1913 and 1924 which were interpolated along with the other intervening years.

[3] Based on 6.7 kg arsenic released per ton of lead arsenate produced.

Table 2-3. Waste Arsenic from Sulfuric Acid Manufacture

Year	United States			Merrimac Chemical Company	
	Sulfuric Acid[1] Production (1000s metric tons)	Percent[2] Produced From Span. Pyrites	Chamber Acid[3] Producers	Sulfuric Acid[4] Production (metric tons)	Waste Arsenic[5] Produced (metric tons)
1888	136	4	75	73	0.1
1889	442	5	105	210	0.3
1890	433	14	107	566	0.8
1891	482	20	109	884	1.3
1892	531	20	111	956	1.4
1893	580	20	113	1026	1.5
1894	629	30	115	1640	2.4
1895	678	30	117	1737	2.5
1896	727	30	119	1832	2.7
1897	775	30	121	1923	2.8
1898	824	40	123	2681	3.9
1899	873	40	127	2751	4.0
1900	902	41	133	2782	4.1
1901	941	40	139	2707	4.0
1902	979	40	145	2700	3.9
1903	1017	40	151	2693	3.9
1904	1054	40	157	2685	3.9
1905	1153	45	163	3183	4.6
1906	1252	47	169	3481	5.1
1907	1351	52	175	4013	5.9
1908	1451	51	181	4089	6.0
1909	1550	55	183	4659	6.8
1910	1536	56	189	4552	6.6
1911	1523	74	192	5869	8.6
1912	1663	71	195	6057	8.8
1913	2015	43	198	4377	6.4
1914	2283	50	201	5679	8.3
1915	2288	53	204	5945	8.7
1916	3432	43	207	7129	10.4
1917	3793	23	210	4100	6.0
1918	4201	8	213	1499	2.2
1919	3131	12	216	1739	2.5
1920	2797	14	206	1901	2.8
1921	2464	11	197	1376	2.0
1922	3084	12	191	1937	2.8
1923	3697	9	185	1878	2.7
1924	3824	9	181	1859	2.7
1925	3950	10	177	2142	3.1
1926	4043	12	179	2711	4.0
1927	4137	8	181	1828	2.7
1928	4462	12	175	3060	4.5
1929	4789	13	170	3662	5.3
				Total:	173.1

Table 2.3 (*continued*).

[1] U.S. sulfuric acid production expressed as 100% sulfuric acid; 1889 data from Duecker and West, 1959; 1890, 1899, 1904, 1909, 1914-1919, 1921, 1923, 1925, 1927, and 1929 data from Fairlie , 1936; 1911-1913 data from Wells and Fogg, 1920; intervening years are interpolated; 1888 interpolated from Fairlie, 1936.

[2] Percent acid from spanish pyrites for 1914, 1917, 1918 taken from Wells and Fogg, 1920; 1890-1904 calculated from Wells and Fogg, 1920; remaining years calculated from Fairlie (1936) using 1.37 tons spanish pyrites per ton 100% sulfuric acid produced.

[3] 1888, 1889 data are estimated from Duecker and West, 1959; 1890, 1900 are taken from Haynes, 1933; 1919 data is taken from Wells and Fogg, 1920; 1921, 1923, 1925, 1927, and 1929 are estimated from Fairlie, 1936; intervening years are interpolated.

[4] Estimated by multiplying U.S. production by percent from spanish pyrites, divided by the number of chamber acid producers.

[5] Estimated using 1.5 kg arsenic released per ton of acid produced.

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CHAPTER THREE - FATE OF ARSENIC IN THE ABERJONA WATERSHED: SPECIATION IN THREE LAKES

INTRODUCTION

The Aberjona watershed is a 65-square kilometer watershed located in eastern Massachusetts, just north of Boston (Figure 3.1). During the nineteenth and early part of the twentieth century, the region's leather and chemical manufacturing industries released considerable quantities of heavy metals and other pollutants into the watershed (Durant et al., 1990). While some of the most contaminated former industrial sites have been designated by the state or federal government for detailed study and remediation, extremely high concentrations of metals and arsenic can also be found in some lakes, ponds and river sediments outside these areas (Figure 3.2).

Arsenic is of particular concern and interest because of its toxicity to humans and other living things, and because of its complex geochemistry. In the aquatic environment, arsenic is known to exist in the +5, +3, 0, and -3 oxidation states (Cullen and Reimer, 1989). In the pH range of natural waters, inorganic As(III) is present primarily H_3AsO_3 ($pK_{a1} = 9.2$), and inorganic As(V) as $H_2AsO_4^-$ ($pK_{a1} = 2.2$, $pK_{a2} = 6.96$). Both the +3 and the -3 oxidation states (arsenite, and arsine AsH_3) are considered more toxic than the +5 state, arsenate (National Research Council, 1977; International Agency for Research on Cancer, 1980). However, arsenate, as a phosphate analog, may be more readily taken up by aquatic organisms. Additionally, arsenate has been shown to co-precipitate with iron and manganese oxides, leading to removal of arsenate from the water column to the sediments (Cullen and Reimer, 1989; Carpenter et al., 1978). Thermodynamically, As(V) is predicted as the prevalent form in oxic waters, while As(III) should dominate under more acidic, anoxic conditions (Cullen and Reimer, 1989 and references therein). However, numerous studies of freshwater and marine systems have revealed that inorganic speciation can rarely be predicted by thermodynamic equilibrium considerations alone (Cullen and Reimer, 1989, and references therein; Seyler and Martin, 1989; Anderson and Bruland, 1991). In addition, studies of marine, lacustrine and estuarine systems have shown that monomethylarsonate, (MMAA, $CH_3AsO_2OH^-$; $pK_a = 2.6$) and dimethylarsenate (DMAA, $(CH_3)_2AsOO^-$; $pK_a = 6.19$), are frequently detected and may dominate dissolved arsenic speciation (Andreae and Froelich, 1984; Anderson and Bruland, 1991; Crecelius, 1975). Laboratory experiments using pure and mixed phytoplankton cultures have demonstrated that marine phytoplankton can methylate and/or reduce much of the arsenate added to the culture (Sanders and Windom, 1980; Andreae and Klumpp, 1979). Reduction and methylation of arsenate may lead to increased mobilization of arsenic because arsenite, DMAA, and MMAA are much less particle-reactive than arsenate (Holm et al., 1979).

In the Aberjona watershed, questions of arsenic mobility are of particular interest in evaluating the potential threats to human health posed by past manufacturing activities. Historical research has shown that arsenic released from sulfuric acid and arsenical pesticide manufacturing activities at the Industri-Plex site in North Woburn (Figure 3.3) may account for much or all of the arsenic found at the site and in river and lake sediments in the watershed. In order to investigate the potential for continued migration of arsenic, either from the site or from watershed sediments, we studied the speciation of arsenic in the water columns of three lakes in the watershed. Each lake has elevated sedimentary arsenic concentrations, yet each represents a different chemical regime in the watershed.

METHODS

Study Sites

The Hall's Brook Storage Area, an artificial 9 hectare impoundment, was created in the 1970's for flood control purposes. It consists of an elongated, shallow 1.7 hectare pond (average depth of 3 m) followed by approximately 6.6 hectares of wetlands and small ponds. The storage area is located just outside the boundaries of the Industri-Plex Superfund site in an industrially-developed area (Figure 3.3). The northern end of the pond is fed by small springs which can be seen to flow up through flocculent orange-red fine sediments, apparently caused by oxidation of reduced iron as the relatively anoxic groundwater comes into contact with the air. The central portion receives inflow from Halls Brook. A ditch and a culvert may also serve as sources of inflow to this area, but no flow was observed in either during the three sampling dates. The southern portion of the storage area is marshy and receives no obvious surface water inputs. Previous studies have found that the sediments in the northern portion of the storage area contain up to 9,800 mg/kg arsenic (dry weight). (Roux Associates, 1991) Sediments in the marshy area contain up to 1330 mg/kg arsenic (dry weight) (Roux Associates, 1991; Knox, 1991). Sediment concentrations near the outlet of the Halls Brook Storage Area range from 760 to 96 mg/kg (dry weight) (Roux Associates 1991; Knox, 1991) (Figure 3.3).

The Halls Brook Storage Area drains into the Aberjona River. From this confluence, the river flows about 1 km in a southerly direction into wetlands which form part of another Superfund site, the Wells G and H site. The river then flows through approximately 6 km of primarily urban and residential areas until it drains into the Upper Mystic Lake, a 51-hectare dimictic, eutrophic kettle hole lake (Figure 3.1).

Surface sediments from depositional areas in the river south of the Halls Brook Storage area have been found to contain up to 960 mg/kg of arsenic dry weight (Knox, 1991).

Sediment cores taken from the deepest part of the Upper Mystic Lake show arsenic levels as high as 2000 mg/kg dry weight at 30 cm below the sediment- water interface (Spliethoff and Hemond, 1992). Lead-210 dating shows that a major arsenic maximum corresponds roughly to the period of peak industrial activities in the watershed, from approximately 1890 to 1930, particularly arsenical pesticide and sulfuric acid manufacturing at the Industri-Plex site (Spliethoff and Hemond, 1992). The most-recently deposited top two centimeters of sediment contain an average arsenic concentration of 120 mg/kg (dry weight), indicating that recent arsenic inputs are less than historical ones (Spliethoff and Hemond, 1992).

The Upper Mystic Lake is drained by the Lower Mystic Lake, from which it is separated by a 2 m high stone dam. The 45-hectare Lower Mystic Lake is meromictic. This lake has a mixolimnion, which stratifies seasonally to an epilimnion and hypolimnion, and a monimolimnion which does not mix with the overlying waters.

Until 1908, salt water from Boston Harbor regularly flowed into the Lower Mystic Lake (Metropolitan District Commission, 1979). These tidal intrusions occurred intermittently after construction of a downstream dam and locks in 1908 (Aronson, et al., 1979), and finally stopped altogether with the completion of the Amelia Earhart Dam in 1966 (Commonwealth of Massachusetts, 1979). Brackish water (salinity 10 ppt) is now trapped in the two deepest parts of the lake (DiPietro, 1990). This layer of salt water forms a density gradient now located at a depth of 16 m which prevents mixing between it and the overlying freshwater. Bacterial reduction of sulfate has led to extremely high levels of sulfide (up to 10 mM total sulfide) in the monimolimnion (DiPietro. 1990). Above 16 m, the lake becomes thermally stratified in the summer with anoxic conditions developing in the hypolimnion. Sediment cores taken from the deepest part of the Lower Mystic Lake show maximum arsenic concentrations of 70 mg/kg (dry weight) at 4 cm below the sediment/water interface, while the most recently-deposited sediments contain 55 mg/kg (dry weight) (Knox, 1991).

Both the Upper and Lower Mystic Lakes are used extensively for recreation. The Upper Mystic Lake has a public beach and three boat clubs, while the Lower

Mystic Lake is used primarily for motor boating.

Sampling and Field Measurement Methods

Dissolved oxygen and temperature were measured using an Orbisphere 2607 meter. Very low (less than one part per million) oxygen levels were checked using the azide modification of Winkler titration. pH was measured using an Orion Research 407A meter. Flows at the Halls Brook Storage Area were measured using a Marsh-McBirney current meter at transects in the inlet and outlet.

In the Upper and Lower Mystic Lakes, samples for arsenic determination were collected using a peristaltic pump with acid-washed, weighted Tygon tubing. In order to examine the effects of changing chemical conditions during stratification, samples were collected at depths representative of the epilimnion, thermocline and hypolimnion. For the Lower Mystic Lake, samples were also taken at depths representing the chemocline and monimolimnion. Inflow to the Upper Mystic Lake from the Aberjona River was sampled on July 8, 1992.

Halls Brook Storage Area samples were collected by hand. Samples were collected in acid-washed polyethylene bottles and acid-washed silanized glass syringes. The samples were immediately placed on ice and analyzed within 24 hours of collection because significant decreases in arsenite and methylated arsenic concentrations were observed to occur after two days. Syringes were used in order to minimize gas transfer in low oxygen and anoxic samples. No difference was found in arsenic content or speciation between oxygenated samples collected using syringes and bottles. Filtration was done in the field using an in-line 47 mm-diameter Millipore (Teflon) filter holder and 0.45 micron acid-washed Nuclepore polycarbonate filters.

Analytical Methods

Arsenic speciation was determined by hydride generation, cold-trapping and chromatographic separation followed by detection using atomic absorption. This method, described by Andreae (1977) was modified to include a water trap (consisting of a U-tube immersed in an ice-water bath upstream of the column) which helped prevent column clogging (Masschelyn, 1991). Inorganic arsenic and mono- and dimethylated forms are converted into their respective hydrides by addition of sodium borohydride ($NaBH_4$) and trapped on a column filled with silanized chromatographic packing immersed in liquid nitrogen. The trap is slowly warmed and the arsenic species, separated by boiling points, are swept into a hydrogen/air flame in a quartz cuvette mounted in a Perkin Elmer 372 atomic absorption spectrometer. Inorganic As(III) is reduced to arsine (AsH_3) by adding the borohydride reagent at near-neutral pH. The sample is then acidified to $pH < 1$ by adding HCl and the inorganic As(V) is reduced to arsine (AsH_3). Dimethyl- and monomethylarsine evolved during this step are generally believed to correspond to dimethylarsenate and monomethylarsonate in the sample (Cullen and Reimer, 1989;

Andreae, 1981), although Howard et al., (1982) have suggested that mono- and dimethylarsines may be evolved from other methylated arsenic compounds. Precision of replicate samples was 15% or less for the inorganic forms and DMAA, but as high as 30% for MMAA, which was always found at less than 1 nM concentration. Detection limits for a 25 mL sample were 0.4 nM and 0.5 nM (three times the standard deviation of the blank) for As(III) and As(V), and 0.3 nM amd 0.2nm for MMAA and DMAA, respectively (three times std. deviation of the lowest sample).

RESULTS AND DISCUSSION

Halls Brook Storage Area - Results

In order to investigate the potential role of Halls Brook Storage Area in arsenic transport from the Industri-plex site, we sampled the springs and ponded area at the northern end of the impoundment (A and B, respectively); the known surface water inflow, Halls Brook (C); the wetlands area (D); and the outlet (E) (Figure 3.3). No methylated forms were detected in measurements from three sampling trips, however dilution necessitated by high inorganic concentrations may have masked their presence (Figure 3.4). Springs on the northern end of the pond (A) contain much more arsenic, up to 1100 nM, than either Halls Brook (C) which contains a maximum total arsenic concentration of 35 nM, the wetlands area (D) which contains a maximum total arsenic concentration of 188 nM, or the outlet of the impoundment

(E) which contains a maximum total arsenic concentration of 138 nM (Figure 3.4). As(III) is the dominant form of arsenic in the springs, representing, on average, 80% of total arsenic. At the outlet, on the other hand, As(V) prevails, and represents, on average, 85% of total arsenic. Overall, arsenic concentrations in the water decrease in the downstream direction, as do sediment concentrations (Figures 3.3 and 3.4).

Halls Brook Storage Area - Mass Balance

Flow measurements made on June 26, 1992 indicate that on that date, Halls Brook accounted for approximately 60% of the inflow of water into the impoundment. The remaining 40% was, by implication, supplied by groundwater. Mass balance modelling using arsenic concentrations and flows measured on June 26, 1992 shows that, on that date, the arsenic inputs from the known surface water source, Halls Brook, can account for less than 10% of the arsenate measured at the storage area outlet (Table 3-1). Assuming that arsenic content of the estimated groundwater input can be described by measurements made at the springs, arsenite supplied by groundwater is much greater than the flux of total arsenic estimated at the outlet. The arsenic gradient observed in the Halls Brook Storage Area cannot be explained by dilution from the surface water input. Instead, these differences in mass fluxes suggest that much of the arsenite, on the order of 1.3 moles of arsenic per day, originating from the groundwater is somehow removed from the water column before the outlet, presumable oxidation to As(V) and scavenging by freshly precipitated iron oxides. This flux to the sediments agrees with estimates of arsenic deposition based on estimated sediment deposition rates and sediment arsenic concentrations. Overall, these estimates suggest that most of the arsenic originating from the groundwater may be removed within the storage area, presumably by scavenging by freshly-precipitated metal oxides and deposition to the sediments within the storage area. The rest, on the order of 0.6 moles of arsenic per day, flows into the Aberjona River.

Upper Mystic Lake - Results

Upper Mystic Lake samples were collected over an eight month period, from the end of summer stratification in 1991, until July, 1992 (Figures 3.5 and 3.6). During the fall of 1991, the lake retained the vestiges of summer stratification. The thermocline was almost completely eroded by the time of the November 1991 sampling date, yet bottom waters were still anoxic. The odor of H_2S was never detected in hypolimnetic waters. This suggests that the lake had not yet "turned over" although the mixed layer was deepening. The lake was totally or partially ice-covered until late February. A grab sample taken at the outlet in mid-February showed that the surface water temperature was 2.6 C, so inverse stratification, reported for other winters in this lake, may have occurred in 1991 (Chesebrough et al., 1975). Fully mixed, oxygen-saturated conditions were evident on the April 1, 1992 sample date. By the end of the month, the lake had begun to thermally stratify, and by May 21, 1992, the thermocline was well developed and dissolved oxygen levels exhibited a negative heterograde profile. This type of profile, with a dissolved oxygen minimum just at the thermocline, implies the operation of a localized oxygen-depleting process, possibly the oxidation of sinking detritus, trapped by the density gradient at the thermocline. Later profiles show a local dissolved oxygen minimum at the thermocline. This hypolimnetic "bulge" suggests that the net rate of oxygen depletion is lower just below the thermocline than above it (Wetzel, 1983). A similar negative heterograde dissolved oxygen profile was observed in 1991, and periodically in previous years, to as far back as 1949 (Commonwealth of Massachusetts, 1975).

Only inorganic forms of arsenic are reported for the 1991 sampling dates (Figure 3.7 (a) and (b)) because the analytical system was not operating satisfactorily for methylated arsenic detection at that time. Samples taken in October, 1991, when the lake had been stratified for at least four months, and the hypolimnion had been anoxic for at least two months, show a depth-dependent profile for arsenic in the water column. Arsenite represents forty percent of the total arsenic at the surface, but in the anoxic hypolimnion, arsenate accounted for more than ninety percent of the total. At 16 nM, the concentration of arsenate observed in the hypolimnion on October 26, 1992 (Figure 3.7 (a)) represented the highest concentration of any one arsenic species measured in the water column of the Upper Mystic Lake during this study period. One month later, when the thermocline had almost completely disappeared, arsenite represented just 13% of the inorganic form at the surface, and less than 5% of the total in the still-anoxic bottom waters (Figure 3.7 (b)). A grab sample of surface water taken in February, 1992, after winter overturn while the lake was still partially ice-covered, showed that less than 10% of the arsenic in the surface was in the reduced form (Figure 7 (c)). Monomethylarsonate was detected only in the unfiltered sample; dimethylarsenate was not detected. Filtered arsenate was significantly (36%) lower than unfiltered arsenate for this date. Samples taken in early April, show a fairly uniform distribution of arsenic species (Figure 3.7 (d)). Filtered samples from the surface and at a depth of ten meters contained about half (41%) of the arsenate found in the unfiltered samples. Arsenite accounted for 30% of total arsenic throughout the water column. Monomethylarsonate was detected at less than 1 nM concentration in all samples, as it was for the rest of the sampling dates.

With the onset of summer stratification, the surface speciation had changed dramatically (Figure 3.7 (e)). At the surface, arsenite concentrations were higher than arsenate concentrations and represented 55% of total arsenic. Dimethylarsenate represented more than 10% of total arsenic. Samples taken in mid-June revealed increasing epilimnetic arsenite and DMAA concentrations (although As(III) and DMAA represented 50% and 10%, respectively, of the total on this date), while hypolimnetic concentrations of inorganic forms continued to decrease (Figure 3.7 (f)). At the beginning of July, surface DMAA represented 25% of the total arsenic, and, at a concentration of 5 nM, was higher than arsenate (Figure 3.7 (g)). Arsenite still accounted for 50% of total arsenic on this date. By July 21, 1992, DMAA represented 30% of surface arsenic, and arsenite concentrations (again representing 50% of the total), were more than three times greater than arsenate, but absolute concentrations of all species had decreased (Figure 3.7 (h)).

Upper Mystic Lake - Discussion

Arsenic speciation in the Upper Mystic Lake does not correspond to predictions based on purely thermodynamic considerations which predict that arsenate should dominate arsenite in oxygenated waters, whereas arsenite should prevail under anoxic conditions (Cullen and Reimer, 1989, and references therein). In the epilimnion, the high relative concentrations of arsenite -- representing up to 60% of total arsenic on June 16, 1992 -- and the presence of monomethylarsonate and dimethylarsenate indicate that biologically-mediated reduction and methylation are important here (Anderson and Bruland, 1991; Cullen and Reimer, 1989, and references therein). Howard et al., 1982, observed that the appearance of methylated arsenic in an English estuary coincided with water temperatures greater than 9 C, and that arsenite was found more frequently above this temperature, as well. We detected arsenite and monomethylarsonate at water temperatures as low as 2.6 C, but observed that significant increases in DMAA and arsenite concentrations occurred when the surface water temperature warmed from 5 C to 19 C. Anderson et al., 1991, reported significant production of DMAA in the epilimnion of a California reservoir during the summer and fall.

The maximum increases in arsenite concentration were observed in the surface waters between April 1, 1992 and May 21, 1992. This increase corresponds to an arsenate reduction rate of 8 ng day^{-1} L^{-1} or 0.5% of total arsenic reduced per day. Sanders et al, 1980, in experiments involving pure cultures of a marine phytoplankton *Skeletonema costatum* found a peak arsenate reduction rate of 11.4% of total arsenic reduced per day during the log phase of growth, and much lower rates during stationary and lag phases. The observed net reduction rate in the Upper Mystic Lakes is probably lower than the actual rate of arsenate reduction to arsenite, since competing chemical and perhaps photochemical oxidation processes were probably occurring during the same time period (Cullen and Reimer, 1989).

Maximum DMAA concentrations occur one month after maximum arsenite increases. The increase in DMAA concentrations corresponds to a rate of 10.5 ng day^{-1} L^{-1} (0.6% of total arsenic methylated per day) from June 16 to July 8, 1992. In the same experiment described above, Sanders et al., 1980, reported a rate of 1.5% of total arsenic methylated per day during the log phase of growth for *S. costatum* concurrently with peak arsenite reduction.

Maximum decreases in arsenite concentrations were observed between October 26, 1991 and November 10, 1991, corresponding to an oxidation rate of 23 ng day^{-1} L^{-1} (2% of total arsenic oxidized per day). This is quite similar to a reported rate of 1.4% of total arsenic oxidized per day in pure O_2- saturated distilled water (Cherry et al., 1979), and 1.6% of total arsenic oxidized per day for filtered seawater, with antibiotics added, from Saanich Inlet, British Columbia (Peterson and Carpenter, 1983). A much higher rate of 24 ng day^{-1} L^{-1} (14% of total arsenic oxidized per day) was obtained for filtered Saanich Inlet seawater to which no antibiotics had been added (Petersen and Carpenter, 1983). This may mean that oxidation of arsenite observed in Upper Mystic Lake is not biologically-mediated, but results from chemical oxidation during fall mixing.

The predominance of arsenate over arsenite in the hypolimnion of the Upper Mystic Lake, even after prolonged periods of anoxia, suggests that arsenate reduction under hypolimnetic conditions is kinetically slow (Cherry et al., 1979; Cullen and Reimer, 1989). Hypolimnetic arsenite concentrations did not increase during this period. In addition, hypolimnetic arsenate concentrations were highest after long periods of anoxia, which indicates that bottom sediments release arsenate during prolonged anoxic periods. This is consistent with observations in other intermittently anoxic water bodies (Carpenter, et al., 1978; Belzile and Tessier, 1990). Under reducing conditions, such as those which developed in the hypolimnion of the Upper Mystic Lake, both iron and manganese oxides will dissolve, releasing adsorbed arsenate into the hypolimnion (Carpenter and Peterson, 1978; Aggett and O'Brien, 1985; Belzile and Tessier, 1990; Brannon and Patrick, 1987).

Upper Mystic Lake - Total Arsenic Mass Balance

In order to evaluate the potential sources and sinks for arsenic in the Upper Mystic Lake, we have estimated a mass balance for arsenic in the lake (Figure 3.8). Total moles of arsenic were calculated using a digitized map of depth contours and planimetry to calculate a volume for the epilimnion and hypolimnion for each sample date. These volumes were multiplied by the average concentrations of samples taken within those compartments (Figure 3.8).

Total moles of arsenic vary seasonally, with the highest amounts present in late fall through early spring. Concentrations then slowly decrease throughout the summer. On July 8, 1992, arsenic concentrations in the Aberjona River, at the inlet to the lake, were 5 nM and 23 nM for arsenite and arsenate, respectively, while both methylated forms were found at less than 1 nM. Thus total arsenic measured at the inlet to the lake were approximately twice as high as those measured in the epilimnion on that date. There appears to be a correlation between total arsenic in the lake and Aberjona River flow.

Arsenic loadings to the lake were estimated using Aberjona River concentrations measured on July 8,1992 and the average of annual flows from 1980 through 1990 (United States Geological Survey, 1990).

The Aberjona River is the main surface water input to the lake, accounting for 90% of the inflow (Commonwealth of Massachusetts, 1982). Flow measurements at a United States Geological Survey gage, located just upstream from the lake inlet, show that Aberjona River flow peaks in the spring (February through April) and in the fall (September through November) (United States Geological Survey, 1990). Since 1979, the average annual flow of the Aberjona River at this gage has been 54,000 L/min (Solo, 1992). The estimated annual arsenic load of river, 850 moles, is much higher than what is present in the lake during any one month. Using a water budget which assumes a constant lake volume, and a 3% evaporation rate, the average outflow to the Lower Mystic Lake is 58,000 L/min (Commonwealth of

Massachusetts, 1982). Using the average epilimnetic arsenic concentration of 14 nM, the overflow to the Lower Mystic Lake removes 430 moles of arsenic per year from the Upper Mystic Lake. This means that 420 moles of arsenic are added to the lake each year.

Freshly-deposited sediments from the deepest part of Upper Mystic Lake, analyzed using ICP-AES after digestion with HCl/HNO_3, contain an average arsenic concentration of 120 mg/kg (dry weight)(Spliethoff and Hemond, 1992). Using a wet sediment density of 0.06 g/mL, and a lead-210 estimated sediment deposition rate of 1 cm/yr (Spliethoff and Hemond, 1992), and assuming a uniform deposition over the entire lake area, the annual flux of arsenic to the Upper Mystic Lake sediments is estimated to be 500 moles. This means that the estimated flux from the Aberjona River is of the right order of magnitude to account for the majority of the arsenic flux to the sediments.

Lower Mystic Lake - Results

The Lower Mystic Lake was sampled over a three-month period in the late spring and early summer of 1992. Due to a similar morphology and chemical nature, the mixolimnion of the Lower Mystic Lake is similar to the Upper Mystic Lake. The existence of a monimolimnion in the lower lake, however, leads to crucial differences between the two lakes (Figures 3.9 and 3.10)). Dissolved oxygen has been completely depleted from the layer of trapped salt water below 16 m, and total sulfide levels as high as 10 mM have been measured in this layer (Commonwealth of Massachusetts, 1990). With the onset of summer stratification, dissolved oxygen depletion above the chemocline resulted in concentrations of less than 1 mg/L below 5 m on June 30, 1992.

In late May and June the Lower Mystic Lake exhibited a negative heterograde dissolved oxygen profile, indicating that some of the same oxygen-depleting mechanisms are at work in the epilimnion of both lakes (Figure 3.10).

Thermal stratification was similar to Upper Mystic Lake, except that the temperature of the monimolimnion in the Lower Mystic Lake was between 6.3 and 6.8, while the hypolimnion of the Upper Mystic Lake was almost a degree cooler (Figures 3.5 and 3.9).

Above the chemocline, proportions of the different arsenic species were similar to those observed in the upper lake, but concentrations of all species were about half those observed in the Upper Mystic Lake (Figure 3.11). MMAA concentrations remained relatively constant throughout the sampling period, similar to what was observed in the Upper Mystic Lake. As(III) concentrations were constant from the end of April (Figure 3.11(a)) to mid-May (Figure 3.11(b)), but rose considerably by the last sample date, June 30, 1992. Near the surface, arsenite concentrations increase in the spring in both lakes, although maximum concentrations occurred later in the Lower Mystic Lake. DMAA was not detectable on the first sampling date, when the surface water temperature was 13 C, but was detected on the next date, when the surface water had warmed to 19 C (Fig 3.11(a) and (b)). By the end of June, As(III), at a concentration of 4 nM, represented 40% of total arsenic while DMAA, at a concentration of 2.4 nM, accounted for 20%. This is similar to percentages of these species (50% of total for As(III) and 10% of total for DMAA) observed in Upper Mystic Lake two weeks earlier and two weeks later (50% and 25% of total for As(III) and DMAA, respectively) (Fig 3.11 (c)).

Lower Mystic Lake - Discussion

The maximum increases in concentration of arsenite and DMAA, measured between May 21, 1992 and June 30, 1992, were 3.3 and 3.5 ng day^{-1} L^{-1} (0.2% and 0.4% conversion of total arsenic), respectively. These rates are somewhat lower than the maximum conversion rates (0.5% and 0.6% conversion of total arsenic per day) observed in the surface waters of the Upper Mystic Lake. This difference may simply reflect the lower sampling frequency for the lower lake, or it may mean that arsenate reduction and DMAA production mechanisms are less effective in this lake.

Hypolimnetic arsenic speciation in the Lower Mystic Lake is dominated by arsenate (2.6 nM As(III) and 9.6 nM As(V) on April 30, 1992). Arsenic concentrations and speciation just above the chemocline, at 15 m, did not change when dissolved oxygen decreased from 6 mg/L (on April 30, 1992) to less than 1 mg/L (on June 30, 1992). As shown by the persistence of hypolimnetic arsenate in the upper lake, reduction of arsenate may be kinetically slow (Cherry et al., 1979), and further sampling is needed to determine whether late-summer and fall conditions lead to a release of arsenate from the chemocline similar to the release of arsenate from the sediments of the Upper Mystic Lake.

Below the chemocline, arsenic speciation and concentrations in the Lower Mystic Lake reflect the effects of radically different chemical conditions in the monimolimnion (Figure 3.10). A chemical boundary is evident visually and by odor, as well as chemically. Water from above the chemocline was relatively clear and odor-free. At a depth of 16 m, a layer of very dark water was encountered, associated with a strong H_2S odor, which appeared green after removal of black particulate material by filtration. A similar layer has been observed at the redox interface in Lake Pavin, a meromictic lake in France, and may consist of an accumulation of iron and manganese oxides, bacteria colonies, and organic detritus trapped by the density gradient (Seyler and Martin, 1989). Water from 17 m and below was clear and yellow-colored, but still odorous, indicating that this dark layer is less than two meters thick.

The reducing conditions in the monimolimnion create a steep gradient of both concentration and oxidation state for arsenic (Figure 3.11, note the log scale for concentration). Total arsenic concentrations at 16 m ranged from 1210 nM to 2600 nM from April 30, 1992 to June 30, 1992. This reflects a total arsenic increase by a factor of 500 to 1000 across the chemocline. In a sharp reversal of species dominance, arsenate dominates above the chemocline, while arsenite is by far more abundant at 16 m. Arsenite exhibits the most dramatic change, increasing an average of 600-fold across the chemocline, while arsenate concentrations increase an average of 20-fold. Methylated forms were not detected in the monimolimnion, however, detection limits were 125 times higher, because of sample dilution.

Thermodynamic equilibrium considerations predict that at conditions present in the lower lake's monimolimnion (pH 6.3, total sulfide concentration of 3 mM (DiPietro, 1990), As(V) should be non-detectable. As(V) actually increased with depth, which is intriguing because of the intensely reducing conditions in the monimolimnion. The increase in arsenate concentrations across the chemocline indicate that this system is not at thermodynamic equilibrium.

Seyler and Martin (1989) found that arsenate increases across the chemocline in Lake Pavin were strongly correlated to increases in dissolved iron concentrations, however neither the absolute arsenic concentrations nor the relative increase across the chemocline was as high as those measured here.

Lower Mystic Lake - Mass Balance

Assuming that arsenic in the monimolimnion is not released to the overlying waters in appreciable amounts, the net source of arsenic is 430 moles from Upper Mystic Lake. Assuming 3% evaporation and a constant lake volume, 210 moles per year flow to the Mystic River. The remaining 220 moles, represent the net arsenic flux to the Lower Mystic Lake.

Freshly deposited sediments from the Lower Mystic Lake, analyzed using ICP-AES after digestion with HNO_3/HCl, contain 55 mg/kg (dry weight) arsenic (Spliethoff and Hemond, 1992). Lead-210 dating has been less conclusive for lower lake sediments than for the upper lake, hence only a tentative sediment deposition rate of 0.8 cm/yr is available at this time. (Spliethoff and Hemond, 1992). Using this tentative deposition rate, a sediment density of 0.06 g/cc, and assuming uniform deposition over the lake area, the estimated flux to the sediments is 160 moles/year.

CONCLUSION

Arsenic speciation in three lakes in the Aberjona watershed appears to be controlled by a number of mechanisms, including biological reduction and methylation, and adsorption and desorption onto particles.

Arsenite originating from groundwater is a major input of arsenic to the Halls Brook Storage Area. Much of this influx appears to be removed, perhaps by oxidation to arsenate followed by adsorption to freshly precipitated iron oxides and settling to the sediments. Scavenging of arsenic in the Halls Brook Storage Area does not remove 100% of the groundwater input, however. Based on limited data, the estimated surface water export of arsenic from the storage area appears to exceed the estimated surface water inflow.

The Industri-Plex area, together with Halls Brook Storage, is a major source of arsenic to the whole watershed (Spliethoff and Hemond, 1992). The river is a conduit for this arsenic. At the time of several measurements, concentrations of total arsenic decreased from the outlet of the Halls Brook Storage Area to the inlet of the Upper Mystic Lake; however, mass fluxes of the same order of magnitude were observed at both locations. This observation does not, however, rule out the existence of other arsenic sources and sinks along the Aberjona River.

Total arsenic concentrations, measured using borohydride reduction, in the surface waters of the Upper Mystic Lake are approximately half of those measured at the inlet in the Aberjona River, implying that Upper Mystic Lake is a sink. Similarly, surface arsenic concentrations in the Lower Mystic Lake are approximately half of those measured in the Upper Mystic Lake. Net annual deposition of arsenic into both the Upper and Lower Mystic Lakes sediments, calculated from annual average flows and total arsenic concentrations, is of the same magnitude as net sediment deposition of arsenic calculated using lead-210 - based sediment deposition rates.

Arsenic speciation in the surface waters of both the Upper and Lower Mystic Lakes is dominated by reduced inorganic and methylated arsenic compounds during the growing season. These measurements show the importance of biologically-mediated reduction and methylation in the surface waters. These conversions may inhibit removal of arsenic from the surface waters, since they are less particle-reactive than arsenate.

Interestingly, less arsenate reduction was observed in the hypolimnion than the epilimnion of both lakes despite the presumably favorable conditions for As(III) formation created by anoxia. This suggests slow reduction is absent of photosynthetic organisms. Hypolimnetic concentrations of arsenate actually increased with time under anoxic conditions in the Upper Mystic Lake. It is suggested that sediment releases of arsenate under anoxic conditions may support hypolimnetic arsenate concentration in the lakes.

The Lower Mystic Lake is unique in that extremely reducing conditions are found in a permanently stratified bottom layer. Very high concentrations (millimolar) of arsenite were observed in this layer which were similar to arsenite levels observed in low oxygen groundwater near the highly contaminated Industri-Plex site. The Lower Mystic lake monimolimnion also showed the apparent persistence of arsenate, even under extremely reducing, sulfidic conditions.

This study shows that arsenic speciation in three lakes which have received significant anthropogenic arsenic inputs reflects diverse chemical, physical and biological controls on the mobility of arsenic. These mechanisms must be taken into account when various remediation plans are designed.

Figure 3.1. The Aberjona Watershed, showing study sites.

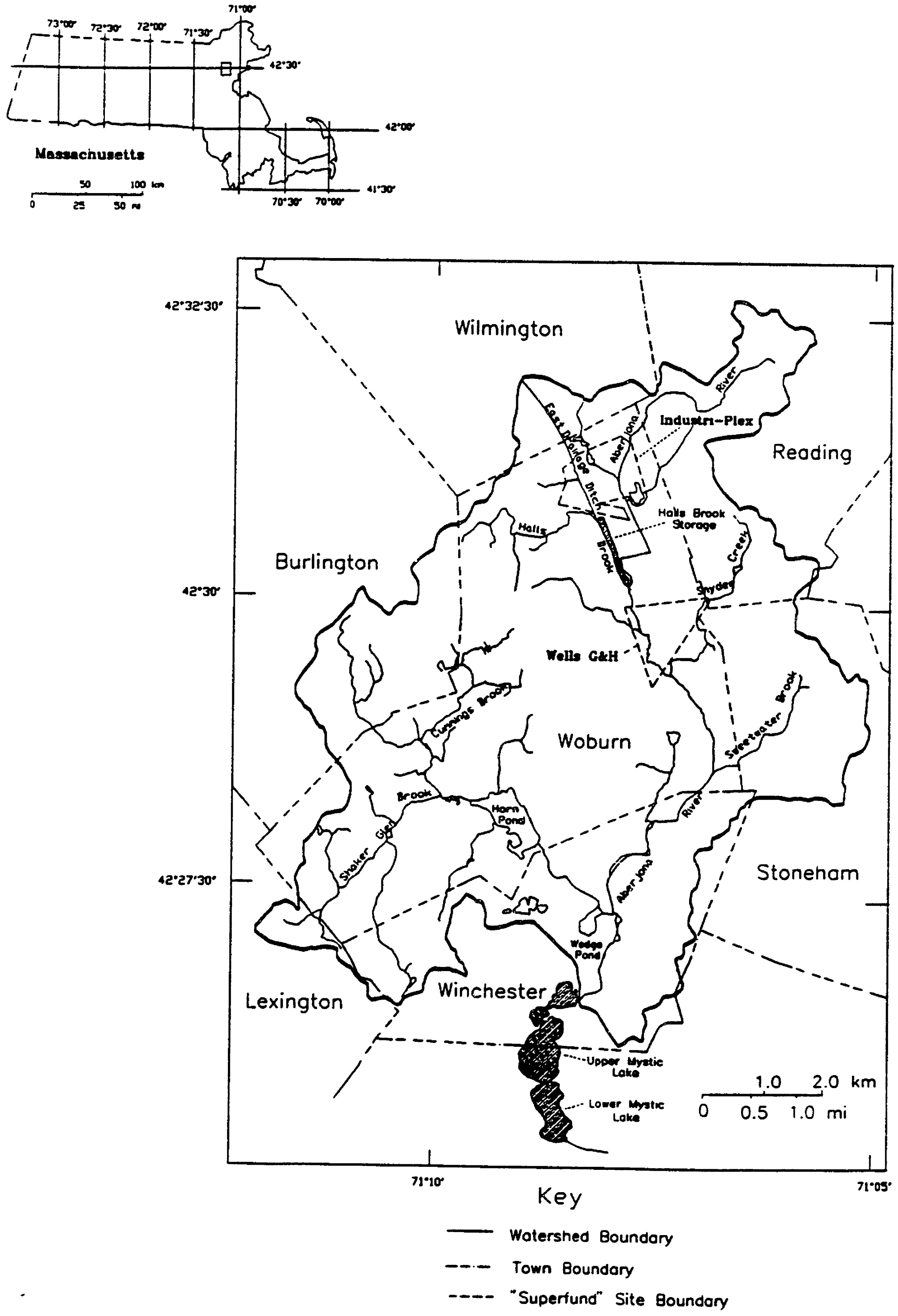


Figure 3.2. Arsenic in Aberjona Watershed Sediments - All samples taken of surface sediments except Upper and Lower Mystic Lakes, which reflect arsenic maxima in sediment cores.

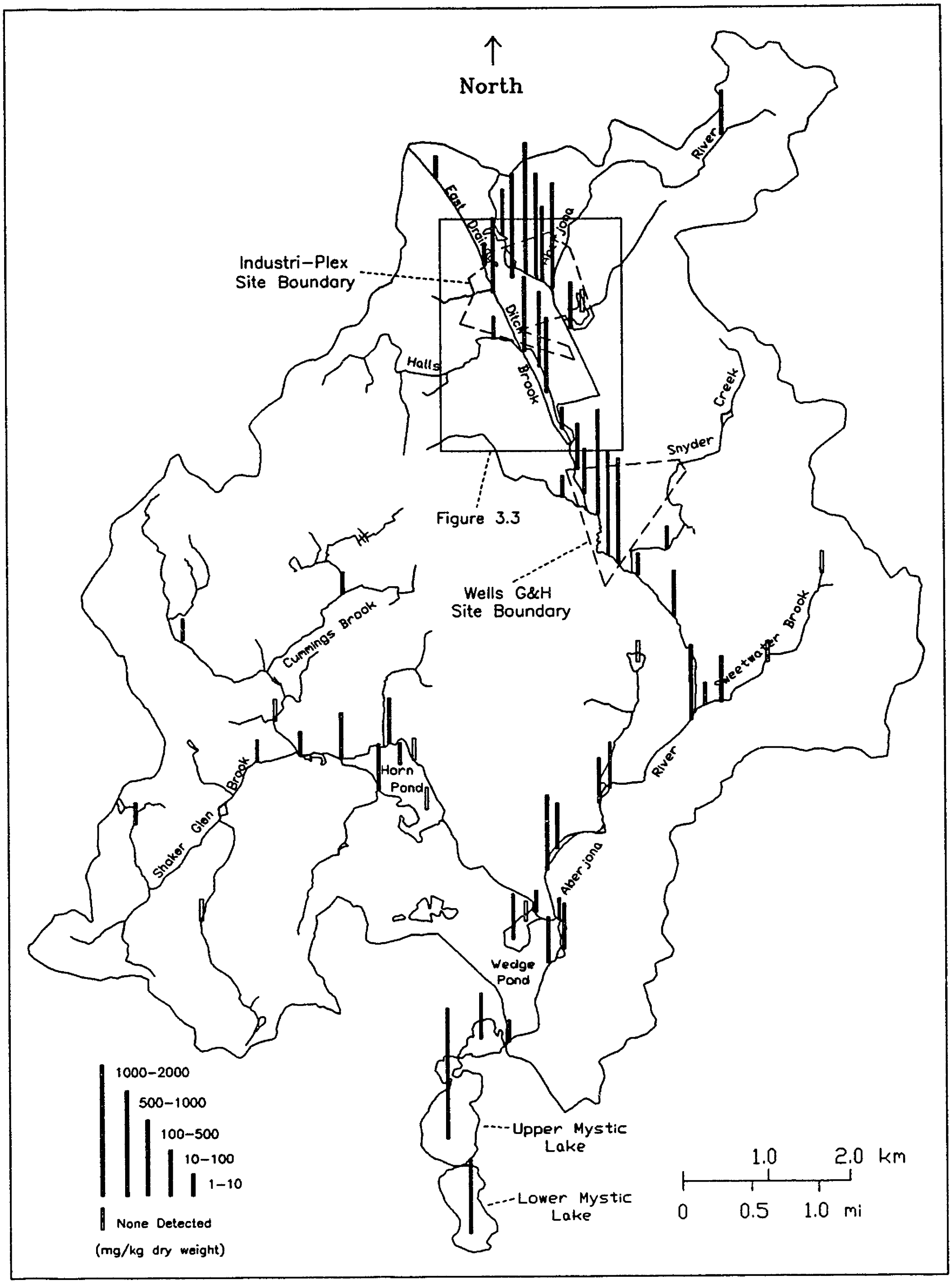


Figure 3.3. Industri-Plex Site and Hall's Brook Storage Area

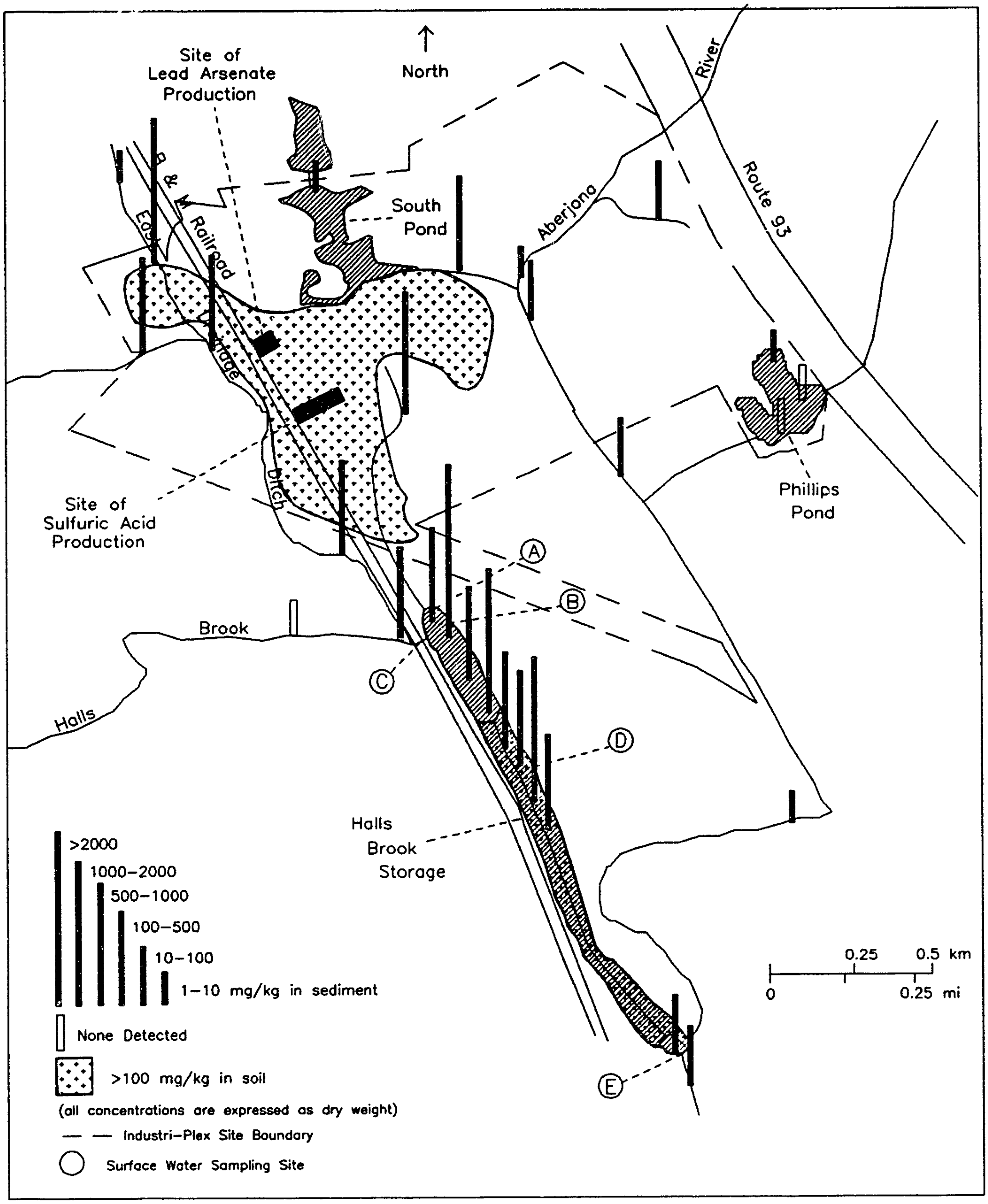
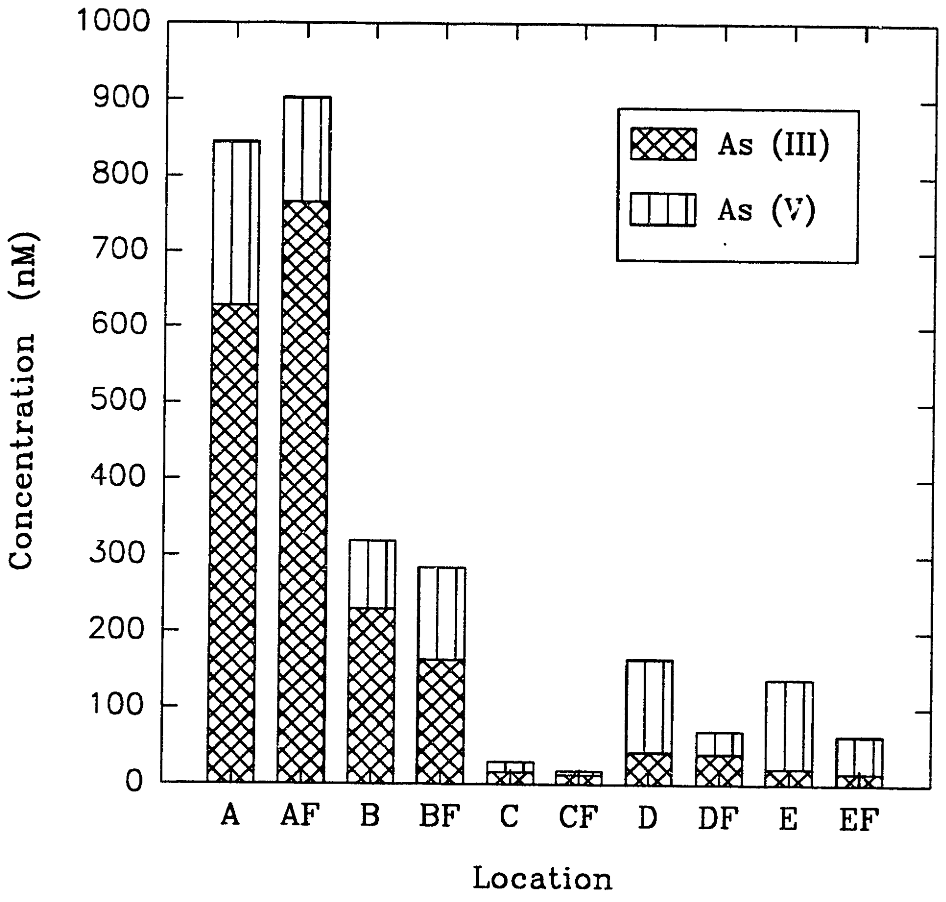


Figure 3.4. Average Arsenic Concentrations measured in the Hall's Brook Storage Area.



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Direction of Flow

Table 3-1. Hall's Brook Storage Area - Mass Balance for June 26, 1992

	Flow L/s	As(III) g/day	As(V) g/day
Halls Brook Storage Area Outlet (E)	70	9	53
Halls Brook Inlet (C)	40	3	5
Net Increase ((E)-(C))	30	6	48
Estimated Groundwater Inflow (A)	30	146	38
Arsenic Removal ((A)-Net Increase)		140	-11

Figure 3.5. Temperature Measurements - Upper Mystic Lake

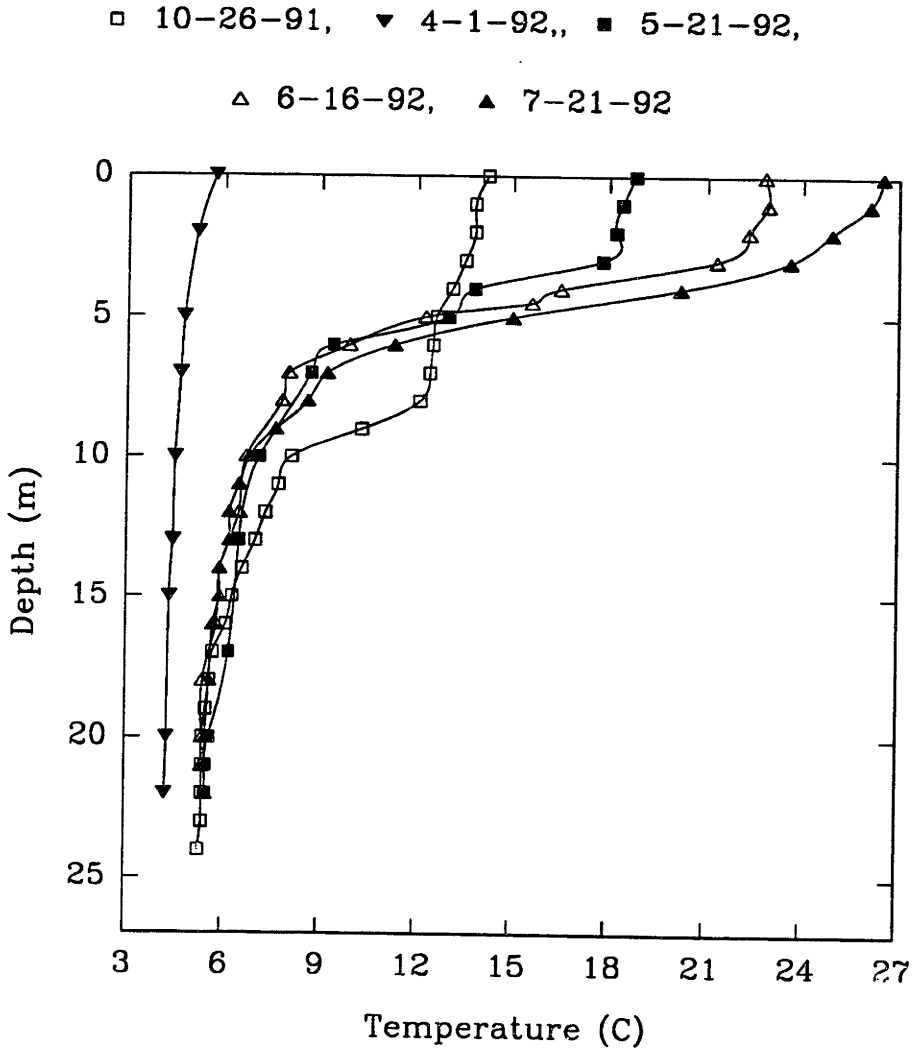


Figure 3.6. Upper Mystic Lake - Dissolved Oxygen.

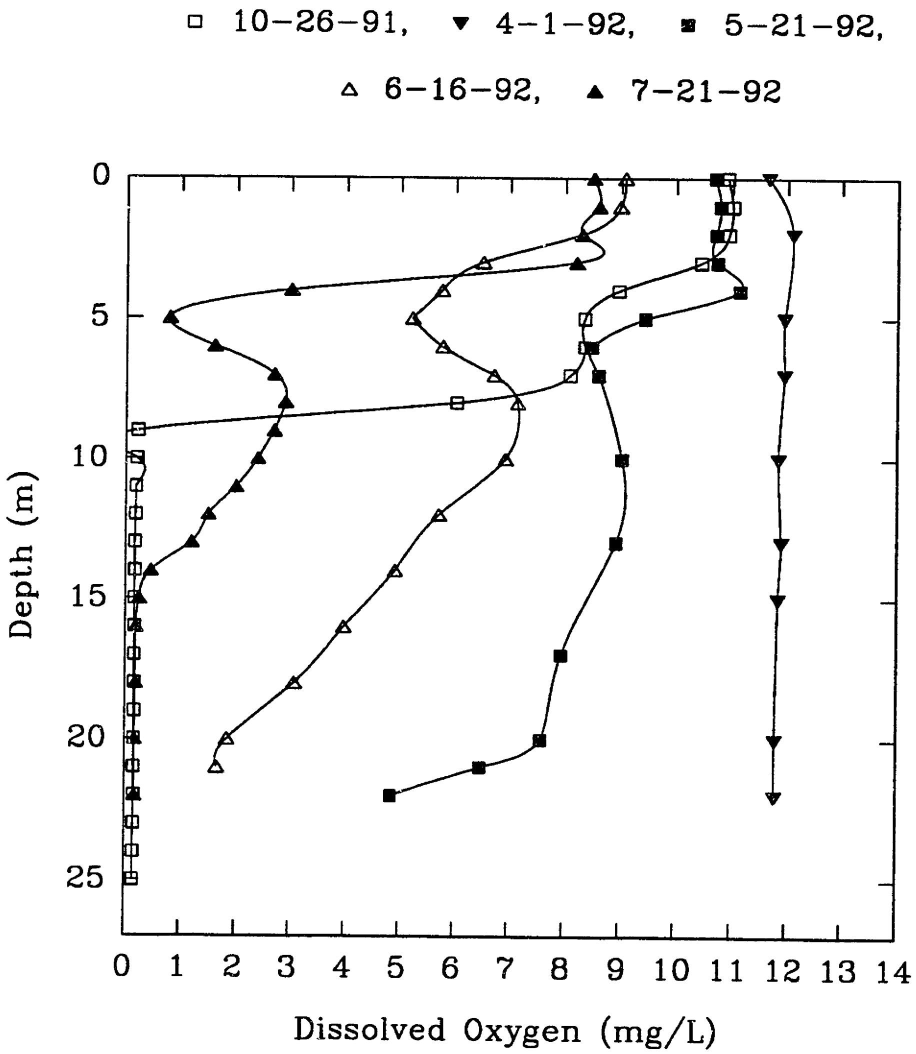


Figure 3.7. Arsenic Speciation.

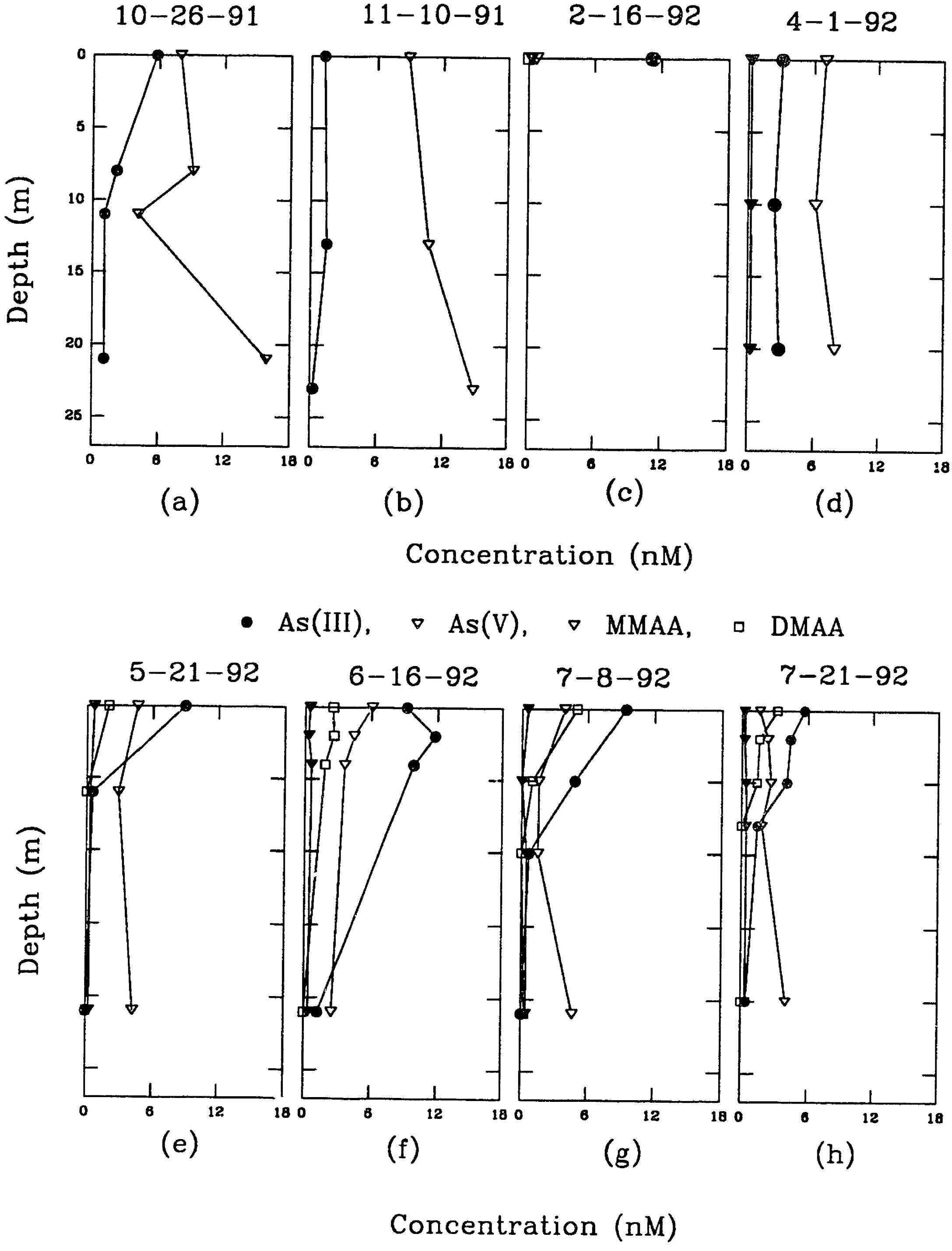


Figure 3.8. Upper Mystic Lake - Mass Balance.

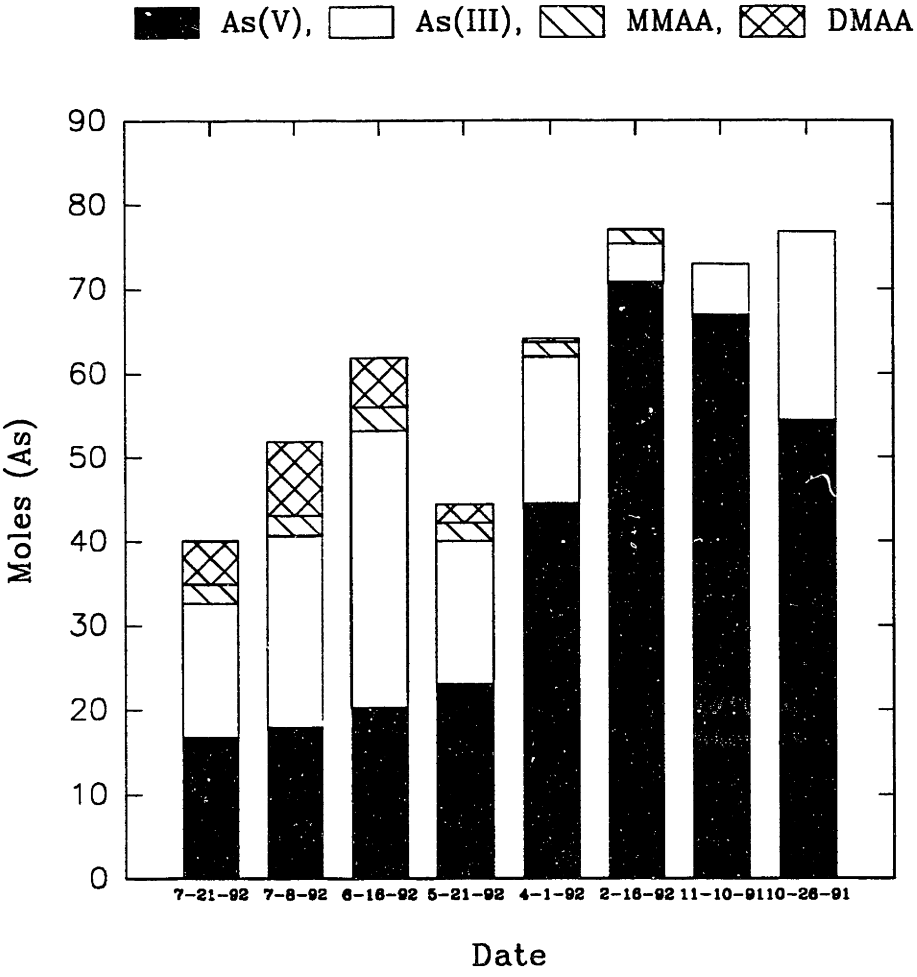


Figure 3.9. Lower Mystic Lake - Temperature.

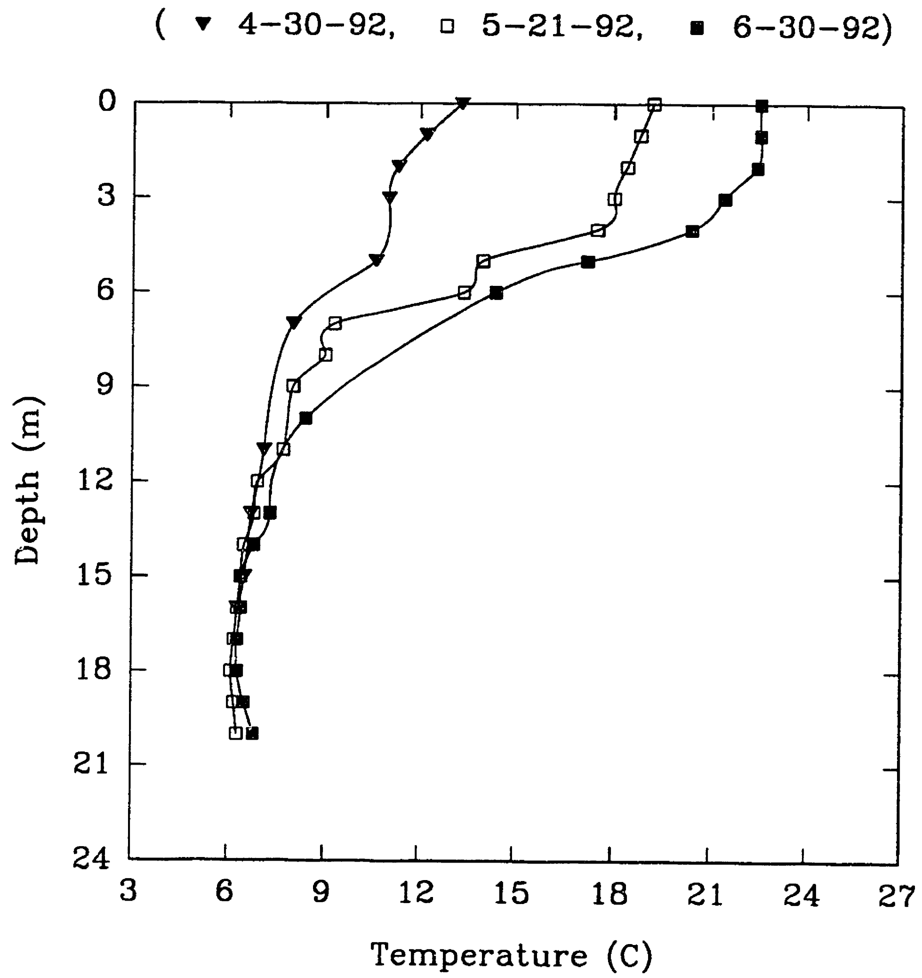


Figure 3.10. Lower Mystic Lake - Dissolved Oxygen.

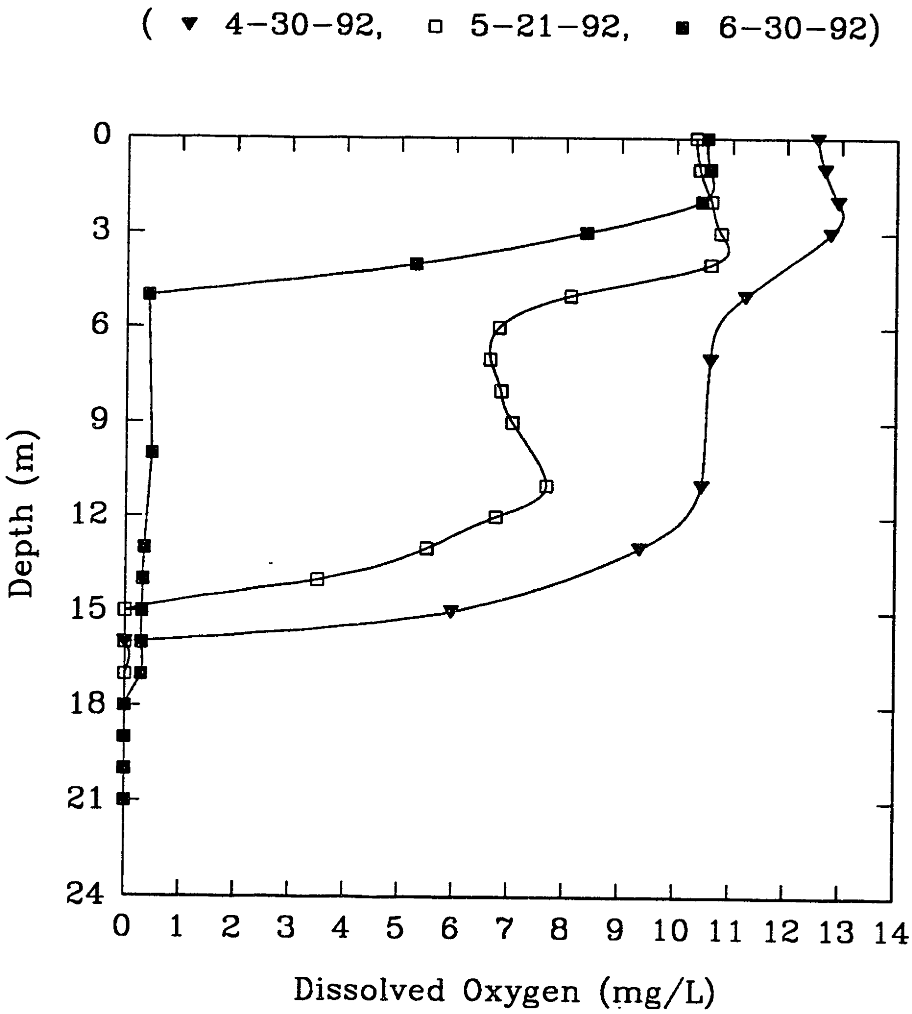
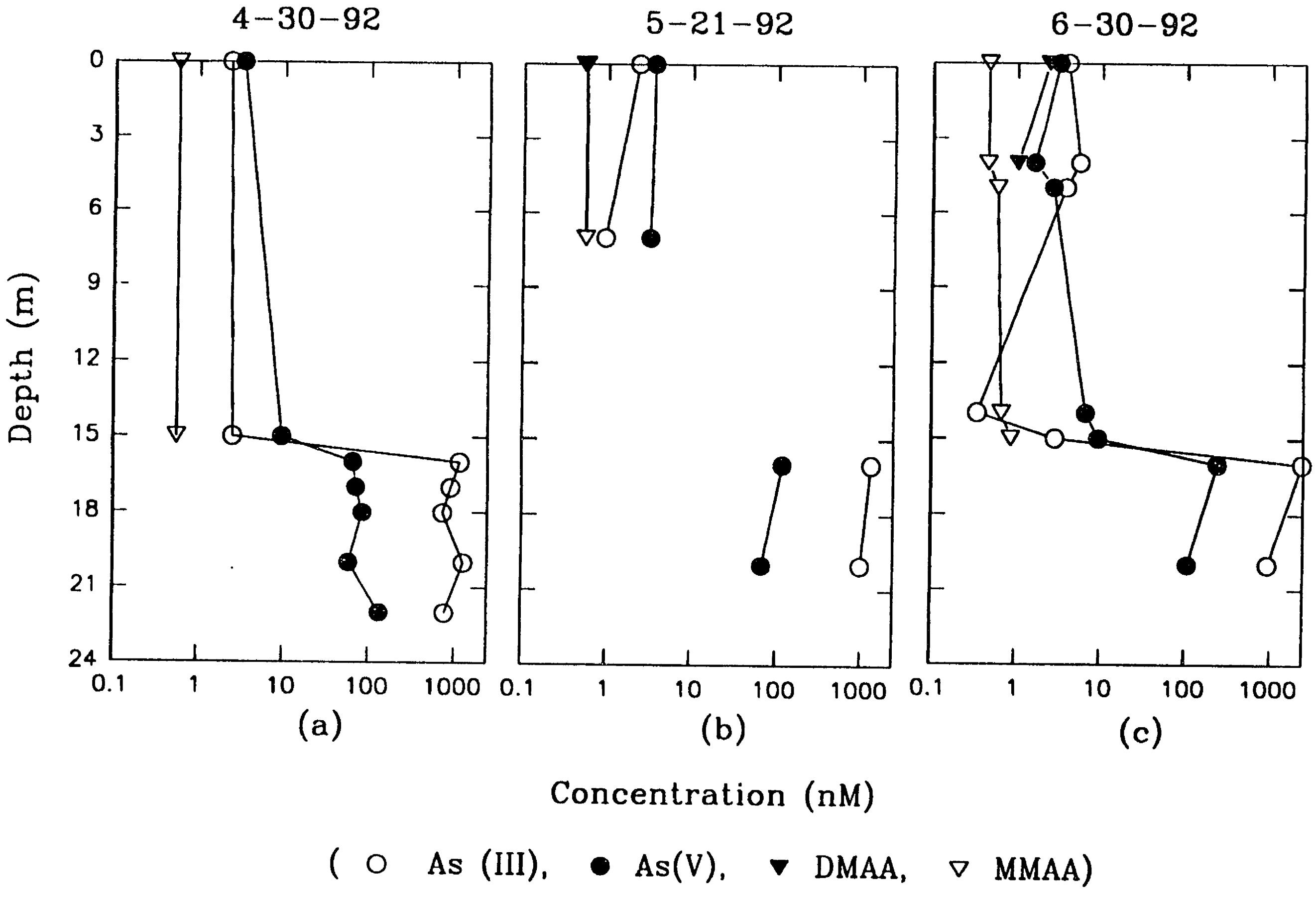


Figure 3.11. Arsenic Speciation in Lower Mystic Lake
(Note log scale for concentration axis)



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APPENDIX 1: Limnological Data

SUMMARY OF LIMNOLOGICAL DATA
Upper Mystic Lake

Date: 10-26-91

Depth (m)	Temp (C)	DO (mg/L)	pH
0	14.2	10.92	8.2
1	13.8	11.01	
2	13.8	10.94	
3	13.5	10.45	
4	13.1	8.96	
5	12.6	8.35	
6	12.5	8.36	
7	12.4	8.1	
8	12.1	6.03	
9	10.3	0.22	
10	8.1	0.207	
11	7.7	0.19	
12	7.3	0.184	
13	7	0.174	
14	6.6	0.176	
15	6.3	0.168	
16	6.1	0.172	
17	5.7	0.167	
18	5.6	0.17	
19	5.5	0.174	
20	5.4	0.168	
21	5.4	0.165	
22	5.4	0.17	
23	5.4	0.164	
24	5.3	0.159	
25	5.3	0.152	

Upper Mystic Lake

Date: 11-10-91

Depth (m)	Temp (C)	DO (mg/L)
0	8.4	8.9
1	8.3	8.5
2	8.4	8.5
3	8.4	8.46
4	8.4	8.5
5	8.3	8.41
6	8.4	8.48
7	8.4	8.38
8	8.4	8.43
9	8.4	8.3
10	8.4	8.43
11	8.4	8.32
12	7.6	3.93
13	6.5	0.35
14	5.9	0.29
15	5.7	0.25
16	5.5	0.26
17	5.4	0.25
18	5.3	0.235
19	5.2	0.23
20	5.2	0.228
21	5.2	0.218
22	5.2	0.238
23	5.2	0.22
24	5.2	0.215

Date: 4-1-92

Depth (m)	Temp (C)	DO (mg/L)	pH
0	5.7	11.65	8.1
2	5.15	12.1	
5	4.75	11.95	
7	4.65	11.95	
10	4.5	11.85	7.3
13	4.45	11.9	
15	4.35	11.85	
20	4.3	11.8	7.3
22	4.25	11.8	

Upper Mystic Lake

Date: 4-23-92

Depth (m)	Temp (C)	DO (mg/L)
0		
1	13.5	12.5
3	12.6	12.65
5	9.3	12.86
7	8.3	12.62
9	7.5	12.45
13	6.9	11.14
17	6.2	11.14
21	5.4	11.01
24	5.3	10.43

Date: 5-21-92

Depth (m)	Temp (C)	DO (mg/L)	pH
0	18.8	10.69	8.3
1	18.4	10.79	
2	18.2	10.72	
3	17.8	10.74	
4	13.8	11.14	
5	13	9.44	
6	9.4	8.48	6.8
7	8.7	8.6	
10	7.1	9.03	
13	6.5	8.93	
17	6.2	7.96	
20	5.6	7.6	
21	5.5	6.48	6.6
22	5.5	4.85	

Upper Mystic Lake

Date: 6-9-92

Depth (m)	Temp (C)	DO (mg/L)
0		
1	20.7	8.9
2	20.7	8.7
3	17.2	7.3
4	16	6.4
6	10.7	6.4
8	8.1	7.6
10	6.8	7.4
12	6.5	6.5
14	5.8	5.8
16	5.7	5.4
18	5.5	4.7
20	5.4	3.6
22	5.4	3.4

Date: 6-16-92

Depth (m)	Temp (C)	DO (mg/L)
0	22.8	9.07
1	22.9	8.98
2	22.3	8.3
3	21.3	6.5
4	16.5	5.75
4.5	15.6	
5	12.25	5.21
6	9.9	5.77
7	8	6.71
8	7.8	7.15
10	6.7	6.93
12	6.5	5.71
14	5.9	4.91
16	5.8	3.97
18	5.4	3.08
20	5.4	1.85
21	5.4	1.67

Upper Mystic Lake

Date: 7-8-92

Depth (m)	Temp (C)	DO (mg/L)
0	24	8.63
1	23.3	8.9
2	22.1	8.43
3	21.5	7.2
4	18.5	3.2
5	14.6	1.78
5	13.1	1.84
5		1.87
6	11.7	2.4
6	11.5	2.3
7	8.8	3.45
8	7.7	3.65
9	7.2	3.57
10	6.8	3.18
12	6.3	2.8
14	6	1.96
16	5.7	1.12
18	5.5	0.48
20	5.4	0.201
22	5.3	0.17
23	5.3	0.17

Upper Mystic Lake

Date: 7-21-92

Depth (m)	Temp (C)	DO (mg/L)
0	26.5	8.5
1	26.1	8.6
2	24.9	8.3
3	23.6	8.2
4	20.2	3
5	15	0.79
6	11.3	1.6
7	9.2	2.7
8	8.6	2.9
9	7.6	2.7
10	6.8	2.4
11	6.5	2
12	6.2	1.5
13	6.2	1.2
14	5.9	0.46
15	5.9	0.25
16	5.7	0.19
18	5.6	0.19
20	5.5	0.18
22	5.5	0.18

SUMMARY OF LIMNOLOGICAL DATA
Lower Mystic Lake

Date: 4-30-92

Depth (m)	Temp (C)	DO (mg/L)	pH
0	13.3	12.55	8.3
1	12.2	12.69	
2	11.3	12.93	
3	11	12.8	
5	10.6	11.25	
7	8	10.63	
11	7.1	10.48	
13	6.7	9.37	
15	6.5	5.96	
16	6.3	0	7
17			6.7
18			6.6
20			6.7
22			6.6

Date: 5-21-92

Depth (m)	Temp (C)	DO (mg/L)	pH
0	19.2	10.35	7.3
1	18.8	10.42	
2	18.4	10.63	
3	18	10.8	
4	17.5	10.63	
5	14	8.1	
6	13.4	6.8	
7	9.3	6.64	6.9
8	9	6.84	
9	8	7.05	
11	7.7	7.68	
12	6.9	6.76	
13	6.8	5.5	
14	6.5	3.5	
15	6.4	0	
16	6.3	0	6.5
17	6.2	0	
18	6.1	0	
19	6.2	0	
20	6.3	0	

Lower Mystic Lake

Date: 6-30-92

Depth (m)	Temp (C)	DO (mg/L)	pH
0	22.5	10.55	8.4
1	22.5	10.6	
2	22.4	10.46	
3	21.4	8.38	
4	20.4	5.27	7.2
5	17.2	0.398	7
6	14.4		
10	8.4	0.468	
13	7.3	0.34	
14	6.8	0.32	
15	6.4	0.31	6.9
16	6.4	0.3	6.4
17	6.3	0.295	
18	6.3	0	
19	6.5	0	
20	6.8	0	6.2
21		0	

APPENDIX 2: Arsenic Speciation Data

SUMMARY OF ARSENIC SPECIATION DATA

Hall's Brook Storage Area

4-12-92 through 6-26-92

(Key: A = Springs, B = ponded area. C = Hall's Brook Inlet, D = Wetlands, E = Hall's Brook Storage Area Outlet. AR = Aberjona River prior to confulence with storage area outlet, F = Filtered)

See Figure 3.3 for sample locations

Date	Location	As(III) (nM)	As(V) (nM)	MMAA (nM)	Total As (nM)
4-12-92	DF	59.4	34.7	0.0	94.1
4-12-92	D	54.2	91.2		145.4
4-12-92	C	16.8	5.4		22.3
4-12-92	CF	16.9	3.1		20.0
4-12-92	BF	163.2	121.1		284.4
4-12-92	B	230.2	89.3		319.4
4-12-92	AR	66.5	82.5		149.0
4-12-92	AR	62.3	104.4		166.7
4-12-92	A	340.1	342.7		682.9
4-12-92	AF	1142.0	140.1		1282.1
4-12-92	AF	986.2	93.5		1079.7
5-21-92	DF	19.5	25.3		44.8
5-21-92	D	29.8	153.0		182.8
5-21-92	C	18.4	16.2		34.6
5-21-92	CF	12.8	0.9		13.8
5-21-92	AF	496.1	28.7		524.8
5-21-92	A	792.4	112.2		904.7
6-26-92	E	22.9	100.9		123.8
6-26-92	EF	14.7	48.9		63.6
6-26-92	E	18.7	133.6		152.3
6-26-92	C	13.9	21.4		35.3
6-26-92	CF	10.3	9.7	0.0	20.1
6-26-92	C	9.9	15.9		25.8
6-26-92	CF	7.1	9.4	0.2	16.7
6-26-92	CF	4.3	16.6	0.3	21.2
6-26-92	AR	58.7	298.6	0.9	358.2
6-26-92	ARF	35.7	16.8		52.5
6-26-92	ARF	45.0	51.4		96.4
6-26-92	AR	44.6	236.6	2.9	284.2
6-26-92	AR	40.9	37.5		78.4
6-26-92	A	769.8	192.8		962.6
6-26-92	AF	366.9	277.5		644.4
6-26-92	A	751.3	193.6		944.9
6-26-92	A	732.8	194.3		927.1
6-26-92	AF	507.9	293.6		801.6

Date	Location	As(III) (nM)	As(V) (nM)	MMAA (nM)	Total As (nM)
Average Values for 6-26-92					
6-26-92	EF	14.7	48.9		63.6
6-26-92	E	20.8	117.2		138.0
6-26-92	CF	7.2	11.9	0.2	19.3
6-26-92	C	11.9	18.7		30.5
6-26-92	ARF	40.3	34.1		74.4
6-26-92	AR	51.7	267.6	1.9	321.2
6-26-92	AF	437.4	285.6		723.0
6-26-92	A	751.3	193.6		944.9

SUMMARY OF ARSENIC SPECIATION DATA
Upper Mystic Lake
10-26-91 through 7-21-92

(Key: "F"= Filtered. "avg." = average, "std. dev." = standard deviation,
"prec." = standard deviation/average)

Date	Depth (m)	As(III) (nM)	As(V) (nM)	MMAA (nM)	DMAA (nM)	Total As (nM)
10-26-91	21.00	1.13	15.89	0.38	0.00	17.39
10-26-91	11.00	1.29	3.79	0.25	0.00	5.33
10-26-91	11.00	0.93	4.46	0.00	0.16	5.39
10-26-91	11F	1.20	4.06	0.38	0.00	5.64
10-26-91	8.00	2.16	9.14	0.00	0.00	11.30
10-26-91	0.00	5.77	7.95	0.63	0.08	14.35
10-26-91	11 avg.	1.11	4.13	0.13	0.08	5.36
10-26-91	std. dev.	0.18	0.33	0.13	0.08	0.41
10-26-91	prec.	0.16	0.08	1.00	1.00	0.08
11-10-91	23.00	0.27	14.89	0.00	1.20	16.35
11-10-91	13.00	1.44	10.69	0.72	0.33	13.17
11-10-91	0.00	1.18	8.85	1.44	0.47	11.93
2-16-92	0.00	0.67	7.16	0.00	0.00	7.83
2-16-92	0.00	0.71	11.25	0.27	0.00	12.22
4-1-92	20.00	2.87	7.96	0.30		11.13
4-1-92	10.00	2.40	6.15	0.27		8.82
4-1-92	0.00	1.96	7.39	0.18	0.00	9.53
4-1-92	0.00	4.14	6.75	0.34	0.14	11.36
4-1-92	0 avg.	3.05	7.07	0.26	0.07	10.44
4-1-92	Std. dev.	1.09	0.32	0.08	0.07	1.14
4-1-92	Prec.	0.36	0.05	0.31	1.00	0.11
4-1-92	20F	2.88	7.37	0.26		10.51
4-1-92	10F	2.52	2.69	0.32		5.53
4-1-92	0F	3.62	2.24	0.27	0.00	6.13
4-1-92	0F	2.79	3.57	0.24	0.15	6.75
4-1-92	0 avg.	3.20	2.91	0.26	0.07	6.44
4-1-92	Std. dev.	0.42	0.67	0.02	0.07	0.79
4-1-92	Prec.	0.13	0.23	0.07	1.00	0.12
4-23-92	22.00	1.32	5.52	0.34		7.18
4-23-92	13.00	2.26	3.40	0.60	0.23	6.48
4-23-92	0.00	5.85	3.49	0.35	0.39	10.07
5-21-92	21.00	0.33	4.25	0.29	0.00	4.87
5-21-92	6.00	0.55	2.88	0.36	0.00	3.79
5-21-92	0.00	8.94	4.58	0.67	1.98	16.16
5-21-92	21F	0.41	2.14	0.28	0.00	2.83
5-21-92	6F	0.90	2.33	0.45	0.00	3.68
5-21-92	0f	10.07	4.76	0.71	1.95	17.49

Date	Depth (m)	As(III) (nM)	As(V) (nM)	MMAA (nM)	DMAA (nM)	Total As (nM)
6-16-92	21.00	1.22	2.51	0.40	0.00	4.12
6-16-92	4.00	9.84	3.55	0.60	1.82	15.82
6-16-92	2.00	11.76	4.39	0.33	2.57	19.06
6-16-92	0.00	9.05	7.17	0.51	2.61	19.33
6-16-92	0.00	9.37	4.97	0.38	2.40	17.12
6-16-92	0 avg.	9.21	6.07	0.44	2.50	18.22
6-16-92	Std. dev.	0.16	1.10	0.06	0.10	1.12
6-16-92	Prec.	0.02	0.18	0.15	0.04	0.06
6-16-92	21F	0.85	1.97	0.28	0.00	3.10
6-16-92	4F	10.59	2.70	0.35	1.91	15.56
6-16-92	2F	10.84	5.69	0.37	2.19	19.09
6-16-92	0F	6.85	4.67	0.23	2.05	13.80
6-16-92	0F	9.10	4.52	0.53	1.54	15.69
6-16-92	0 avg.	7.98	4.60	0.38	1.80	14.75
6-16-92	Std. dev.	1.12	0.07	0.15	0.25	1.16
6-16-92	Prec.	0.14	0.02	0.39	0.14	0.08
7-8-92	21.00	0.31	4.73	0.47	0.31	5.81
7-8-92	10.00	0.71	1.55	0.47	0.00	2.72
7-8-92	5.00	4.85	1.59	0.14	0.99	7.56
7-8-92	0.00	8.75	4.36	0.43	4.70	18.25
7-8-92	0.00	10.81	4.80	0.34	6.03	21.99
7-8-92	0.00	8.71	2.64	0.87	4.36	16.58
7-8-92	0 avg.	9.42	3.94	0.55	5.03	18.94
7-8-92	Std. dev.	1.03	0.22	0.04	0.67	1.24
7-8-92	Prec.	0.11	0.06	0.08	0.13	0.07
7-8-92	21F	0.49	2.70	0.43	0.00	3.62
7-8-92	10F	0.59	1.85	0.47	0.00	2.91
7-8-92	5F	4.77	1.28	0.30	0.55	6.91
7-8-92	0F	5.63	2.67	0.00	3.93	12.23
7-8-92	0F	6.80	2.36	0.00	3.93	13.09
7-8-92	0 avg.	6.22	2.52	0.00	3.93	12.66
7-8-92	Std. dev.	0.59	0.15	0.00	0.00	0.61
7-8-92	Prec.	0.09	0.06	0.00	0.00	0.05
7-8-92	UML inlet	5.08	23.82	0.60	0.25	29.75
7-8-92	UML inletF	5.02	19.75	0.00	0.92	25.69
7-21-92	20	0.43	4.01	0.37	0.00	4.82
7-21-92	8	1.42	1.86	0.42	0.00	3.70
7-21-92	5	4.06	2.63	0.38	1.38	8.45
7-21-92	2	4.35	2.35	0.23	1.58	8.51
7-21-92	0	5.73	1.36	0.16	2.82	10.07
7-21-92	0	5.56	1.86	0.30	3.53	11.24
7-21-92	0 avg.	5.64	1.61	0.23	3.18	10.66
7-21-92	Std. dev.	0.08	0.25	0.07	0.35	0.44
7-21-92	Prec.	0.01	0.15	0.30	0.11	0.04

SUMMARY OF ARSENIC SPECIATION DATA

Lower Mystic Lake
4-30-92 through 6-30-92

(Key: "F"=Filtered, "avg"=average)

Date	Depth (m)	As(III) (nM)	As(V) (nM)	MMAA (nM)	DMAA (nM)	Total As (nM)
4-30-92	22	773.2	134.0	0.0	0.0	907.2
4-30-92	20	1267.1	57.6	0.0	0.0	1324.7
4-30-92	18	724.9	83.6	0.0	0.0	808.5
4-30-92	17	895.4	69.9	0.0	0.0	965.3
4-30-92	16	1142.4	64.6	0.0	0.0	1207.0
4-30-92	15	2.6	9.6	0.6	0.0	12.7
4-30-92	0	2.3	3.3	0.6	0.0	6.2
4-30-92	22F	595.7		0.0		595.7
4-30-92	20F	669.3	118.6	0.0		787.9
4-30-92	18F	1095.0	86.4	0.0	0.0	1181.4
4-30-92	17F	528.8	77.9	0.0	0.0	606.6
4-30-92	16F	1470.1	76.4	0.0	0.0	1546.5
4-30-92	15F	3.0	7.8	0.5	0.0	11.2
5-21-92	20	977.8	67.6	0.0	0.0	1045.4
5-21-92	16	1299.7	117.0	0.0	0.0	1416.8
5-21-92	7	0.9	3.2	0.6	0.0	5.2
5-21-92	0	1.7	3.1	0.6	0.6	6.5
5-21-92	0	2.6	3.7	0.5	0.5	7.8
5-21-92	0	2.6	3.9	0.5	0.5	7.6
5-21-92	0 avg.	2.3	3.6	0.6	0.5	7.5
5-21-92	20F	863.3	37.3	0.0	0.0	900.6
5-21-92	16F	807.0	48.8	0.0	0.0	855.8
5-21-92	7F	1.0	2.5	0.4	0.0	4.4
5-21-92	0F	2.8	3.0	0.4	0.5	6.8
6-30-92	20	925.0	107.0	0.0	0.0	1032.0
6-30-92	16	2328.8	235.8	0.0	0.0	2564.6
6-30-92	15	2.9	9.5	0.9	0.0	13.2
6-30-92	14	0.3	6.7	0.7	0.0	7.7
6-30-92	5	3.8	2.7	0.6	0.0	8.0
6-30-92	4	5.5	1.6	0.4	1.0	10.9
6-30-92	0	4.0	3.2	0.5	2.4	10.0
6-30-92	20F	1045.1	82.5	0.0	0.0	1127.6
6-30-92	16F	1501.5	98.2	0.0	0.0	1599.7
6-30-92	15F	1.9	8.7	0.7	0.0	11.4
6-30-92	14F	0.1	4.0	0.9	0.0	5.4
6-30-92	5F	3.8	1.7	0.5	0.3	8.4
6-30-92	4F	7.2	1.5	0.8	2.0	12.3
6-30-92	0F	3.1	2.1	0.3	0.9	6.4