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Speciation and Fate of Arsenic in Three Lakes of the Aberjona Watershed

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The speciation of arsenic in the environment is controlled by reduction, methylation, and oxidation processes and is therefore influenced by redox conditions. However, in the lakes studied, speciation was found to be far from thermodynamic equilibrium. A Superfund site is a major source of As to the watershed, with the Aberjona River being the main conduit for As found in the Mystic Lakes. Total As concentrations in the water column decrease downstream, from >100 nM in the Hall's Brook Storage Area (HBSA), where As(III) enters via reducing groundwater, to <20 nM in the Lower Mystic Lake (LML); the sediments of all the lakes are sinks for As. Biologically mediated reduction, at rates of 0.2–0.5% of the total As day^{-1}, and methylation, at rates of 0.4–0.6% of the total As day^{-1}, occur in the mixed layers of these lakes. However, these processes are slow or absent in the hypolimnion, allowing As(V) to accumulate in seasonally anoxic hypolimnetic waters. High micromolar concentrations of As, predominantly As(III), persist in the saline, sulfidic monimolimnion of the LML. The production of As(III) and methylated As species in the water column of these lakes inhibits the removal of As to the sediments, thereby increasing the mobility of As in this watershed.

Introduction

The Aberjona Watershed is an industrialized 65-km^2 watershed located in eastern Massachusetts, north of Boston (Figure 1). Leather and chemical manufacturing industries released large quantities of metals, including arsenic (As) and chromium (Cr), into the watershed during the early to mid-1900s (*1*), and these metals have subsequently migrated extensively. Arsenic because of its abundance, toxicity, and complex geochemistry is of particular concern and interest. Knowledge of As speciation and mobility in the watershed is required to evaluate the effects on human health of these past manufacturing activities and the potential for continued migration and further impact in the future.

This study is a survey of arsenic cycling in three water bodies: Upper Mystic Lake (UML), Lower Mystic Lake (LML), and Hall's Brook Storage Area (Figure 1). Both the Upper and Lower Mystic Lakes are used extensively for recreation. Each lake studied has elevated sedimentary As concentrations, yet each represents a distinct chemical regime that could strongly influence the behavior of As.

Background. In the aquatic environment, inorganic As is known to exist in the +5, +3, 0, and −3 oxidation states (*2*). Both the +3 and the −3 oxidation states [arsenite (As(III), and arsine (AsH_3)] are considered more toxic to humans than the +5 state (*3, 4*). In the pH range of natural waters, inorganic As(III) is present primarily as H_3AsO_3 (pK_{a1} of arsinous acid = 9.2), and inorganic As(V) is present as $H_2AsO_4^-$ or $HAsO_4^{2-}$ (pK_{a1} of arsenic acid = 2.2, pK_{a2} = 6.96). Thermodynamically, As(V) should prevail in oxic waters, while As(III) should dominate under reducing conditions (*2*). However, previous studies suggest that inorganic As speciation is rarely at thermodynamic equilibrium (*2, 5, 6*). Two organic species, monomethylarsonate (MMAs, $CH_3AsO_2OH^-$; pK_a of monomethylarsonic acid = 2.6) and dimethylarsinate (DMAs, $(CH_3)_2AsOO^-$; pK_a of dimethylarsinic acid = 6.19), are also frequently detected in freshwater and marine systems and may at times dominate dissolved As speciation (*6–8*).

It has been shown that both pure and mixed cultures of marine and freshwater phytoplankton can methylate and/or reduce As(V) (*9–11*), and it is thought that As(V), as a phosphate analog, is readily taken up by aquatic organisms. Both reduction and methylation of As(V) may lead to increased mobilization of As because As(III), DMAs, and MMAs are much less particle-reactive than As(V) (*12*); arsenate has been shown to coprecipitate with iron and manganese oxides, leading to the removal of As(V) from the water column to the sediments (*2, 13*).

On the Aberjona, watershed-wide arsenic transport has occurred, and arsenic deposition has been documented both in the Mystic Lakes and at intermediate points along the Aberjona River, typically in areas where fine sediments can be observed. However, virtually no prior work has been done on the chemical speciation of these reservoirs of arsenic or their possibilities for chemical transformation or mobilization.

Study Sites

Hall's Brook Storage Area. The Hall's Brook Storage Area (HBSA), located south of the Industri-Plex Superfund site (Figure 1), is an artificial 9-ha impoundment created in the 1970s for flood control purposes. The northern end of the basin holds an elongated, shallow 1.7-ha pond (average depth of 3 m); to the south lies approximately 6.6 ha of wetlands and small ponds. The northern end of the pond is fed by small springs, which flow up through flocculent orange-red sediments apparently deposited upon oxidation of reduced iron in the inflowing groundwater. Sediments in the northern portion of the basin contain up to 9800 mg/kg As (dry weight). The central portion of the impoundment receives surface inflow from Hall's Brook (Figure 1). A ditch and a culvert may also serve as intermittent sources of surface inflow to this area, but no flow was observed on the three sampling dates. The marshy southern portion of the basin receives no visible surface water inputs, but discharges into the Aberjona River. Sediments in the marshy area contain up to 1330 mg/kg As (dry weight) (*14, 15*; Figure 1). Concentrations in sediment near the outlet to the Aberjona range from 96 to 760 mg/kg (dry weight), and surface sediments in the river south of the HBSA contain up to 960 mg/kg As (*15*). Water was sampled from the springs and ponded area at the northern end of the impoundment (locations A and B, respectively); the Hall's Brook inflow (C); the wetlands area (D); and the outlet (E) (Figure 1).

Upper and Lower Mystic Lakes. Downstream of the HBSA, the river flows through approximately 6 km of

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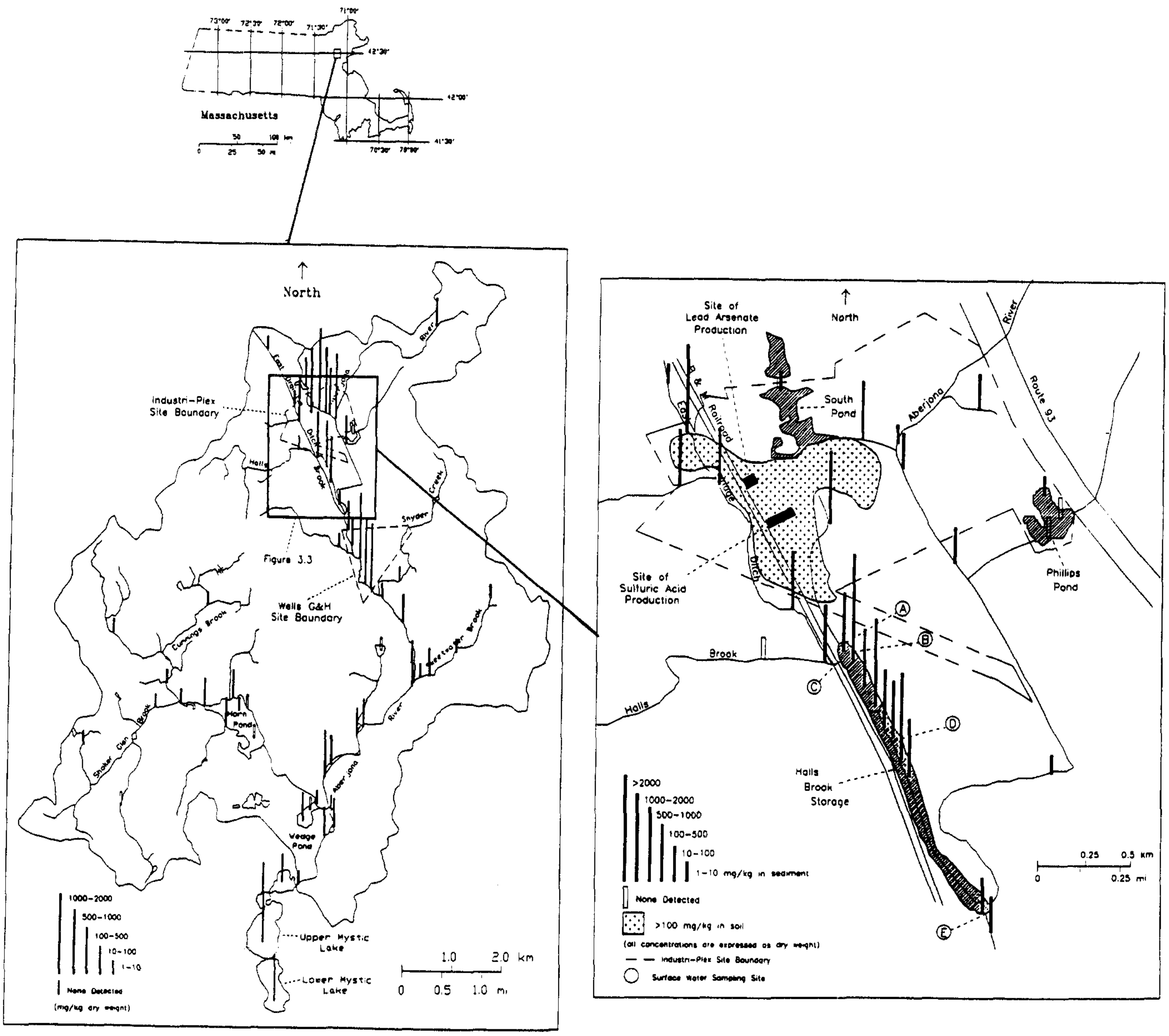

Figure 1. Aberjona Watershed, showing study sites. The insert shows the Industri-Plex Site and Hall's Brook Storage Area. All concentrations reflect surface sediments except Upper and Lower Mystic Lakes, where arsenic maxima in sediment cores are reported.

primarily urban and residential areas to the Upper Mystic Lake (UML), a 51-ha dimictic, eutrophic kettle hole lake (Figure 1). Sediment cores taken from the deepest part of the UML show As levels as high as 2000 mg/kg dry weight at 30 cm below the sediment–water interface. The deeper of the two major As maxima is believed to correspond to the period of arsenical pesticide and sulfuric acid manufacturing from approximately 1890 to 1930. The most recently deposited top 2 cm of sediment contain an average As concentration of 120 mg/kg (dry weight) (*16*).

The Lower Mystic Lake (LML) is separated from the UML by a 2 m high stone dam. The 45-ha LML is meromictic; the monimolimnion is the remnant of salt water intrusion from Boston Harbor, which occurred regularly prior to 1908 (*17*), intermittently after construction of a downstream dam and locks in 1908 (*18*), and finally stopping altogether with the completion of the Amelia Earhart Dam in 1966. The remaining brackish water (salinity 10‰), trapped in the two deepest parts of the lake (*19*) creates a strong picnocline at 16 m depth. Up to 10 mM total sulfide occur in the monimolimnion. Sediment cores taken from the deepest part of the LML show maximum As concentrations of 70 mg/kg (dry weight) 4 cm below the sediment–water interface, while the most recently deposited sediments contain 55 mg/kg (dry weight) As (*15*).

Both the UML and the mixolimnion of the LML stratify in the summer, and oxygen depletion of the deeper waters results. Low oxygen conditions persist into the late fall; overturn typically occurs late in November. In the LML, sulfide was present at 15 m (above the picnocline) in the late fall of 1992, while no sulfide was detected (by odor) in the anoxic hypolimnion of the UML; thus, sulfide in the LML at 15 m may have resulted from diffusion across the chemocline and does not necessarily imply that sulfide-reducing conditions occur in the hypolimnetic water column.

Methods

Dissolved oxygen and temperature were measured using an Orbisphere Model 2607 meter. Very low (less than 1 ppm) oxygen levels were checked using the azide modification of the Winkler titration. pH was measured using an Orion Research Model 407A meter. Water flows at the HBSA were measured using a Marsh-McBirney current meter along transects across the inlet and the outlet.

In the Mystic Lakes, samples for As 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 LML, samples were also taken within the chemocline and the monimolimnion. The river input to the UML was sampled on July 8, 1992. HBSA samples were collected by hand in acid-washed polyethylene bottles and acid-washed silanized glass syringes. All samples were immediately placed on ice and analyzed within 24 h of collection, because significant decreases in As(III) and methylated As concentrations were observed to occur after 2 days of storage time. Wetted glass syringes were used in order to minimize oxygen transfer from the atmosphere into the anoxic samples. No difference was found in the As 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-μm acid-washed Nuclepore polycarbonate filters.

Arsenic speciation was determined by hydride generation, cold-trapping, and chromatographic separation followed by detection using atomic absorption. The method described by Andreae (*20*) was modified to include a water trap which helped prevent column clogging (*21*). Inorganic As and mono- and dimethylated forms, converted into their respective hydrides by the addition of sodium borohydride ($NaBH_4$), were sparged from solution and cryogenically trapped with liquid nitrogen. Upon heating, the As species, separated by their boiling points, were swept into a hydrogen/air flame in a quartz cuvette mounted in a Perkin Elmer Model 372, and later a Model 401, atomic absorption spectrophotometer. Speciation analysis was a two-step process. Inorganic As(III) was first reduced to arsine (AsH_3) by adding a 4% $NaBH_4$ solution to a final concentration of 2.4 g/L, at near-neutral pH. The sample was then acidified to pH <1 with HCl. Addition of a further 2.4 g/L of $NaBH_4$ converted As(V) and the methylated As species to the corresponding arsine derivatives (*2, 22*). Precision of replicate samples was 15% or better (1 standard deviation) for the inorganic forms and DMAs, but as high as 30% for MMAs, which was never found to exceed 2 nM concentration in this study. Detection limits, taken as three times the standard deviation of the blank, for a 25-mL sample were 0.4 and 0.5 nM for As(III) and As(V), respectively, and 0.3 and 0.2 nM for MMAs and DMAs, respectively (blanks are lower for the organic species).

Results and Discussion

Hall's Brook Storage Area. All waters sampled, except Hall's Brook, contained total As concentrations significantly elevated above background levels expected in most uncontaminated waters (<50 nM) (*6*). Water from springs on the northern end of the pond (A) contained much higher total As concentrations (up to 1100 nM) than either Hall's Brook (location C, maximum 35 nM), the wetlands area (D, maximum 188 nM), or the outlet of the impoundment (E, maximum 138 nM) (Figures 1 & 2). As(III) was the dominant form of As in water collected at the springs, representing, on average, 80% of the total As. At the outlet, on the other hand, As(V) prevailed and represented, on average, 85% of the total As (Figure 2). No methylated forms of As were detected on three sampling days although preanalysis dilution necessitated by high concentrations of inorganic As in most samples could have masked concentrations up to a few nanomolar; however, no methylated forms were found in Hall's Brook water where samples were analyzed undiluted.

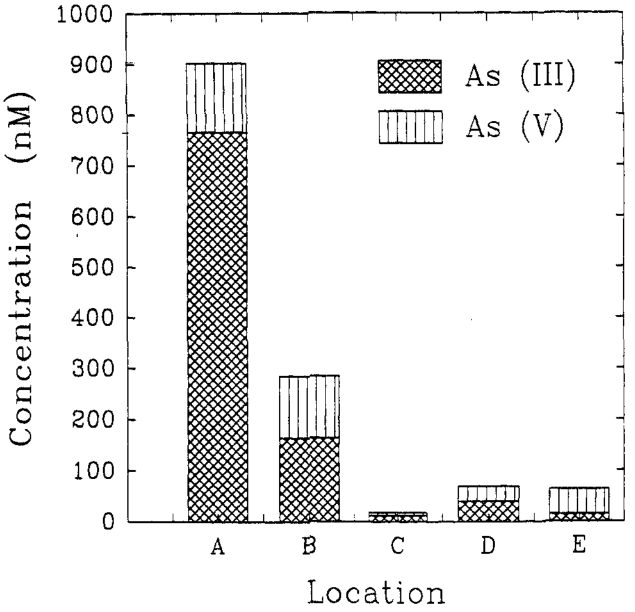

Figure 2. Average arsenic concentrations measured in the Hall's Brook Storage Area.

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

	flow (L/s)	As(III) (g/day)	As(V) (g/day)
Hall's Brook Storage Area outlet (E)	70	9	53
Hall's 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

Because of large contrasts in water flows, As concentration, and speciation, it is possible to infer some general features of the water and As mass balances for the HBSA. On June 26, 1992, inflow from Hall's Brook accounted for 60% of the water flow at the impoundment outlet; assuming approximate hydraulic steady state and neglecting evaporation, the remaining 40% of the inflow was supplied by groundwater. The Hall's Brook As influx (0.11 mol/day) was only 13% of the As flux measured at the storage area outlet (0.83 mol/day; Table 1). Consequently, the major source of As leaving the basin must have been either groundwater or mobilization from sediments, the latter appearing unlikely under the moderate flow conditions prevailing. The large groundwater inflow together with high As concentrations found at the visible springs in the northern end of the basin (A in Figure 1) suggest that groundwater was the principal source of arsenic to the HBSA. The mobilization of As in the groundwaters of the adjoining Industri-Plex site is known to have occurred (*14*).

Approximate groundwater inputs, calculated from the estimated groundwater inflow rate and the concentration of As species over the springs, were 2 mol/day of As(III) and 0.5 mol/day of As(V) (Table 1). These values exceed the outlet flux by about a factor of 3, suggesting that groundwater input is not only capable of supplying the observed output flux but that a significant fraction of the groundwater As input to the HBSA is being removed to the sediments, probably via scavenging by freshly precipitated iron oxides following As oxidation.

It is also interesting that the difference between the estimated groundwater inputs and outputs, approximately 1.7 mol/day, is of similar magnitude to the product of the average As concentration in HBSA sediment (500 mg kg^{-1}), the HBSA basin area (5×10^4 m^2), and a sedimentation rate of 2 kg m^{-2} yr^{-1} (which is not greatly different from rates determined by lead-210 dating in the UML) (*16*). While this may be a coincidence, it could also be a consequence of a relatively steady inflow of As-containing groundwater throughout the year.

It is likely that the As(III) supplied by groundwater input is oxidized within the HBSA. At the time measurements were made, As(III) input exceeded output by about 800 nM, and the hydraulic residence time was approximately 15 days. The implied rate of As(III) oxidation to As(V) is about 50 nM day^{-1} (6% day^{-1}), similar to estimated rates for As(III) oxidation in the Mystic Lakes (below).

Upper Mystic Lake. *Temperature and Oxygen.* Upper Mystic Lake samples were collected over a 12 month period, from the end of summer stratification in 1991 until November 1992 (Figures 3, panels a and b). Oxygen concentration in the bottom waters decreased progressively through the summer, and stratification persisted well into the fall season. However, the odor of H_2S was never detected in the hypolimnetic waters of this lake. In 1991, the thermocline was almost completely eroded by November 10 (Figure 3a). A similar pattern was found in November 1992. The lake was totally or partially ice-covered from early January until late February. By the end of April, the lake had begun to thermally stratify, and by May 21, 1992, the thermocline was well-developed and dissolved oxygen depletion was apparent in the deeper waters (Figure 3b). Summer dissolved oxygen profiles had a local dissolved oxygen minimum at the thermocline, a feature also observed periodically in previous years, as far back as 1949 (*23*).

Temporal and Spatial Trends in Arsenic Speciation. Over the year of sampling, the mixed layer As concentration (<5 m) changed by only a factor of 3, in a fairly consistent pattern. Concentrations of total As were somewhat lower in the colder months (average 12.0 ± 2.1 nM for November to April inclusive) than in the remainder of the year (17.0 ± 6.6 nM). While the total As concentration was highest in the warmer months, the As(V) concentration of the upper waters showed the opposite pattern (Figure 3c). Concentrations of As(V) measured from October through April 1 averaged 6.1 ± 2.3 nM, while values for late May through September were, with one exception, all below 5 nM.

As(III) concentrations were low in winter/early spring, but began to increase in the surface waters in May, and continued this trend through the summer and fall. Highest concentrations occurred in the mixed layer, averaging 3.6 ± 2.9 nM during the colder months and 8.6 ± 3.5 nM between May and October. The highest concentration was in October 1992 (Figure 4). Two distinct peaks in As(III) concentration were noted; one in June/July and the other in October (Figure 3d). In February 1992, while the lake was still partially ice-covered, less than 10% of the As in the surface waters was in the reduced form.

DMAs concentrations were also highest during the summer (Figure 3e). Although DMAs buildup lagged As(III) increases in early spring, the highest DMAs concentrations, about 5 nM, occurred at about the same time as the As(III) peaks; the correlation between the concentration of As(III) and DMAs for the surface waters is significant ($r = 0.73, n = 15, p = 0.001$). The concentration of MMAs was always below 2 nM and was below 1 nM except for the late fall samples. Highest concentrations were generally found in the summer/fall, and lowest concentrations were found in the winter. However, trends for MMAs are less certain than for DMAs because concentrations were at or close to the detection limit in several instances. Because conversion of As(V) to As(III) and methylated As occurs near the surface predominantly during the summer months, these transformations are probably associated with primary productivity maxima, as has been suggested by others (*2, 6*). Oxidation depletes these species when production is low during the winter months.

Samples taken in the late summer/fall, when the hypolimnion was anoxic, showed strong depth dependencies for reduced and methylated As species. As(III) represented 48 ± 7% of the total As at the surface in the summer/fall. In the anoxic hypolimnion, however, As(III) concentrations were lower than in the oxic epilimnion, while As(V) concentrations were comparable or slightly higher and accounted for 78 ± 11% of the total. The concentration of As(V) in the hypolimnion of the UML was highest in October of 1991 and 1992 and November 1991 (Figure 3c).

Arsenic Reduction and Methylation Rates. Arsenic speciation in the UML does not correspond to thermodynamic considerations, which predict that As(V) should dominate in oxygenated waters, whereas As(III) should prevail under anoxic conditions (*2*). There was always measurable As(III) in the oxic surface waters—30 ± 22% of the total As for the colder months, 48 ± 7% for the summer/fall–while As(V) decreased from 62 ± 28% of the total in the winter/early spring to 28 ± 13% in the warmer months. Accordingly, As speciation appeared to be kinetically controlled. The high relative concentrations of As(III) in the epilimnion–up to 60% of the total As in some instances–and the presence of MMAs and DMAs suggest that biota are responsible for As reduction and methylation. Significant increases in DMAs and As(III) occurred in this study as the surface water temperature warmed from 5 to 19 °C. Likewise, Howard et al. (*24*) observed that the appearance of methylated As and As(III) in an English estuary coincided with increasing water temperatures, and Anderson and Bruland (*6*) reported significant production of DMAs in the epilimnion of a California reservoir during the summer and fall.

The role of phytoplankton in the reduction and methylation can be assessed from historical data. The phytoplankton community in the UML was dominated by diatoms in spring of 1974 (*23*), with a maximum concentration occurring in May. In July, there were few diatoms remaining and the overall phytoplankton population was at a minimum. Cyanobacteria were present in August and September. Green algae dominated in September, but were present throughout the summer. Comparison of the distribution of As(III) and DMAs with the phytoplankton distribution (assuming the same seasonal succession in the UML in 1991/1992) indicates that diatoms and green algae are probably responsible for the reduction and methylation in the UML. Furthermore, the bimodal distribution of As(III) (Figure 4) and DMAs (Figure 3e) reflects the likely phytoplankton distribution. Diatoms have been shown to reduce and methylate As in culture studies (*9*).

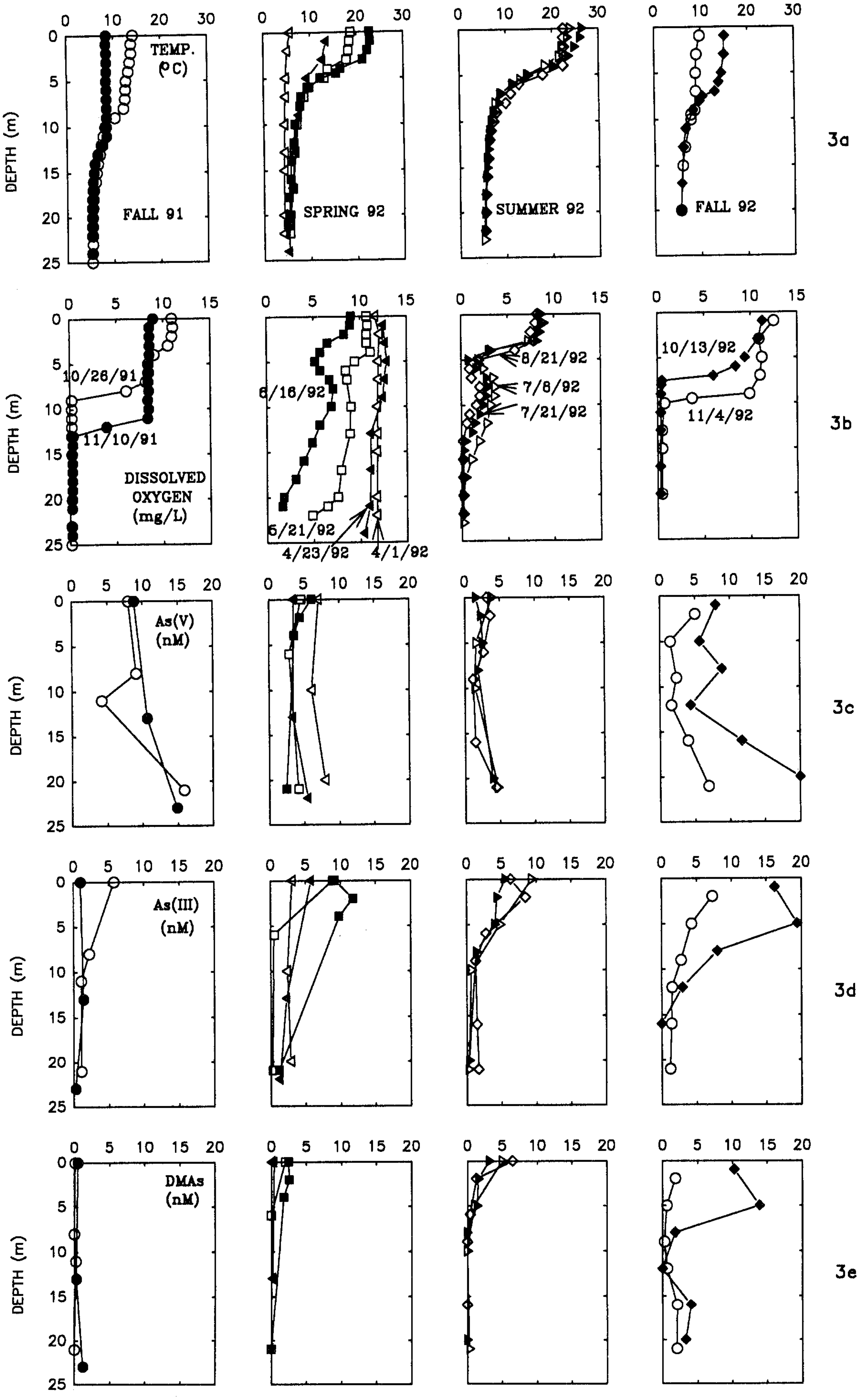

Figure 3. Temperature, dissolved oxygen, and arsenic profiles for the Upper Mystic Lake. Plots reflect the season of collection (fall, spring, or summer). Samples were collected on 10/26/91 (○); 11/10/91 (●); 4/1/92 (△); 4/23/92 (▲); 5/21/92 (□); 6/16/92 (■); 7/8/92 (▽); 7/21/92 (▼); 8/21/92 (◇); 10/13/92 (♦); and 11/4/92 (○). (a) Temperature, (b) dissolved oyxgen, (c) As(V), (d) As(III), (e) DMAs.

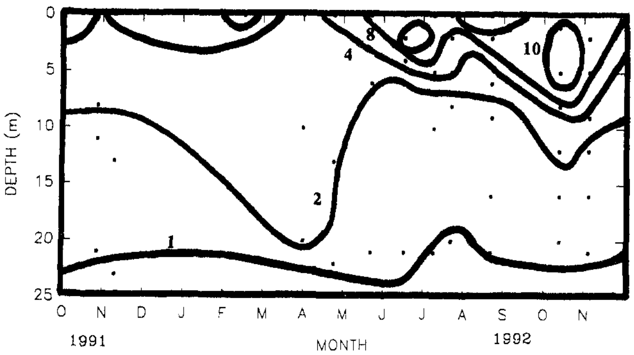

Figure 4. Contour plot covering the entire sampling season for As(III) in the Upper Mystic Lake. Points indicate sample depth and time. Concentrations in nmol/L and contours reflect 2 nM intervals.

Rates of interconversion of As species can be estimated from observed rates of change in concentration, with due consideration to the maximum probable influence of riverine input. On July 8, 1992, As concentrations in the Aberjona River, at the inlet to the lake, were 23 and 5 nM for As(V) and As(III), respectively, while both methylated forms were found at less than 1 nM. Thus, although the contribution of the river to the arsenic budget of the UML is very significant, most of the input appears to be as As(V); thus, the appearance of relatively high levels of reduced and methylated arsenic in the lake could be attributed mostly to internal transformation. As(III) increased from 3 to 9 nM in the surface waters between April 1, 1992, and May 21, 1992. This increase corresponds to an As(V) reduction rate of 0.12 ± 0.04 nM day^{-1}, assuming a 15% analytical precision (or 0.5% of total As reduced per day). The maximum rate of increase of DMAs concentration occurred from June 16 to July 8, 1992, a month later. The increase in DMAs concentration corresponds to a rate of conversion of 0.14 ± 0.02 nM day^{-1} (0.6% of total As methylated per day). Thus, As(III) and DMAs are being formed at similar rates.

Sanders and Windom (*9*), using pure cultures of a marine diatom *Skeletonema costatum*, measured a peak As(V) reduction rate of 11.4% of total As reduced per day during the log phase of growth and much lower rates during stationary and lag phases. Furthermore, they reported a methylation rate of 1.5% of total As per day, concurrent with As(III) reduction, during the log phase of growth for *S. costatum*. The observed maximum As reduction rate in the UML is probably lower than the actual rate of As(V) reduction to As(III), since competing oxidation processes were probably operating (*2*), and a net hydrologic export may have also occurred during the same time period.

Rates of Arsenic Oxidation. Maximum rates of decrease in As(III) concentration, observed between the October and November samplings in 1991 and 1992, correspond to oxidation rates of 0.25–0.3 nM day^{-1} (about 2% of total As oxidized per day). This is quite similar to a reported rate of 1.4% of total As oxidized per day in pure O_2 saturated distilled water (*25*). Petersen and Carpenter (*26*) found that 1.6% of total added As was oxidized per day (0.04 nM day^{-1}) for filtered seawater from Saanich Inlet, British Columbia, when antibiotics were added. In the absence of antibiotics, the rate was 0.32 nM day^{-1} (or 14% of total As oxidized per day). While percent conversion rates are lower in the UML compared to those found by Petersen and Carpenter (*26*), the absolute rates of conversion are similar.

In contrast, Kuhn and Sigg (*27*), corroborating the observations of Oscarson et al. (*28*), show that As(III) oxidation by manganese oxides is the principal oxidation route in eutrophic Lake Greifen, Switzerland. Iron oxides are not important oxidizing agents for As(III) in this lake; however, iron oxides were the principal scavengers of inorganic As (*27*). In the UML hypolimnion, As(V) concentrations were highest after long periods of anoxia, suggesting that the release of As(V) from bottom sediments and/or settling particulate matter occurs after prolonged anoxia. These results are consistent with observations in other intermittently anoxic water bodies (*13*, *29*) and suggest that iron and manganese oxides, which dissolve under low oxygen conditions, are releasing adsorbed As(V) into the hypolimnion (*13*, *30*, *31*). Thus, iron and manganese oxide scavenging and dissolution control the vertical distribution of inorganic As in the Mystic Lakes while only manganese oxides are potential oxidizing agents for As(III).

The predominance of As(V) over As(III) in the hypolimnion of the UML, even after prolonged periods of anoxia, suggests that As(V) reduction under hypolimnetic conditions by dissimilatory reduction by heterotrophic bacteria or by chemical reduction is kinetically slow. This is consistent with the data of others (*2*, *25*). Hypolimnetic As(III) concentrations in the UML did not increase during the anoxic period. Kuhn and Sigg (*27*) suggest that abiotic reduction of As(V) by sulfide occurs in Lake Greifen. The absence of As(III) under the conditions found in the hypolimnion of the UML (anoxic but no sulfide, little reduced iron) (*23*) in contrast to the the predominance of As(III) in the sulfidic waters of the monimolimnion of the LML is consistent with the conclusions. Furthermore, as discussed below, the increase in As(III) above the chemocline (15 m) in the late summer/fall in the LML coincides with the appearance of sulfide at this depth (Figure 5), possibly a result of chemical reduction although upward mixing of As(III)-rich sulfidic waters cannot be ruled out. These results suggest that the As speciation in the hypolimnion is delicately poised and that season-to-season variability in hypolimnetic redox status (e.g., as found in Bickford Reservior) (*32*) may result in aperiodic reduction of As(III).

Mass Balance. The total arsenic content of the water column in the UML varies seasonally, with the highest amounts present in late fall through early spring. Total As concentration at the inlet to the lake on July 8, 1992, was approximately twice as high as the concentration measured in the epilimnion on that date. Since 1979, the average annual flow of the Aberjona River at the USGS gage has been 54 000 L/min (*33*). The estimated annual As load of the river is therefore in the vicinity of 850 mol, much higher than what is present in the lake at any instant. Average outflow to the LML is 58 000 L/min (*34*), which with an average As concentration of 14 nM corresponds to 430 mol of As per year. The difference, approximately 400 mol of As, thus appears to be added to the UML each year. The sediments are the most likely sink for this additional As. Freshly deposited sediments from the deepest part of the UML contain an average As concentration of 120 mg/kg (dry weight) and the annual flux of As to the UML sediments is estimated to be 500 mol (*16*); a value that is consistent with the above estimate of the net hydrologic input of arsenic.

Lower Mystic Lake. The LML was sampled from March to November 1992. The mixolimnion has a similar morphology to the UML, and physical conditions were generally comparable between the two lakes. Thermal

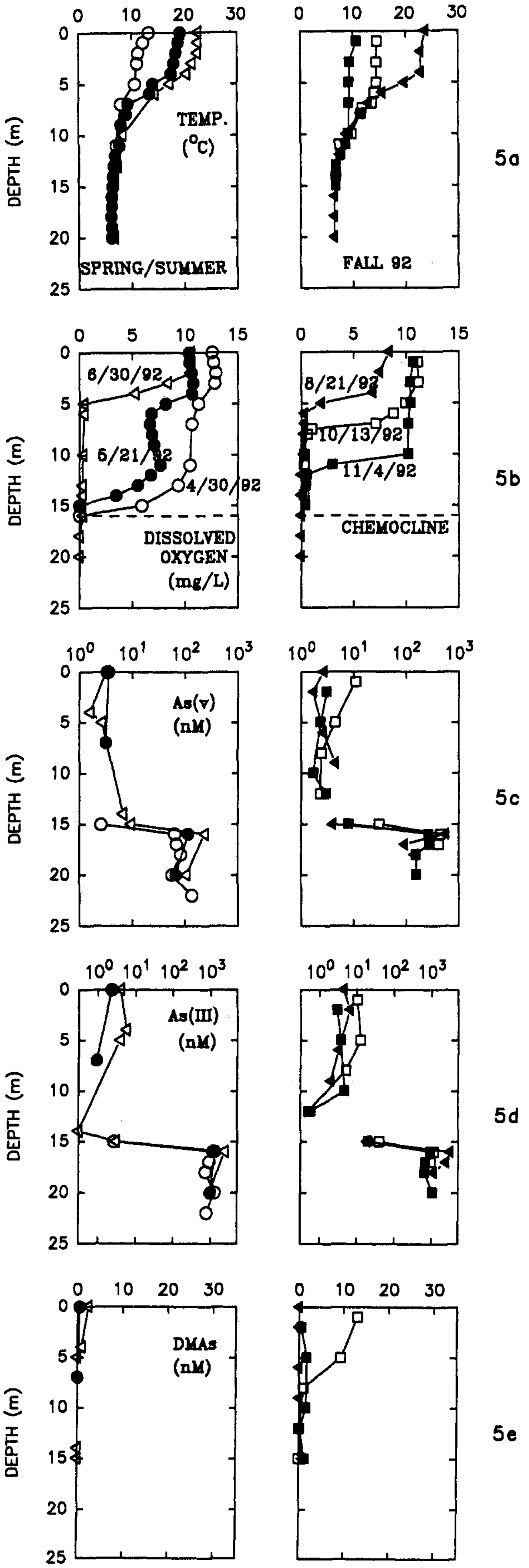

Figure 5. Temperature, dissolved oxygen, and arsenic profiles for the Lower Mystic Lake. Plots reflect the season of collection (spring or summer/fall). Samples were collected on 4/30/92 (○); 5/21/92 (●); 6/30/92 (△); 8/21/92 (▲); 10/13/92 (□); and 11/4/92 (■). (a) Temperature, (b) dissolved oyxgen, (c) As(V), (d) As(III), (e) DMAs.

stratification was similar to the UML, although the hypolimnion of the UML was almost a degree cooler (Figure 5a). Generally, the dissolved oxygen profiles were similar to those found in the UML, suggesting similar lake metabolism (Figure 5b). The existence of a monimolimnion in the LML, however, leads to certain differences between the two lakes (Figures 3 and 5). Dissolved oxygen is 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 (*18*). Sulfide was present in the 15-m sample in the late fall of 1992, probably resulting from diffusion of sulfide from the monimolimnion across the chemocline (no odor of sulfide was detected in the anoxic hypolimnion of the UML).

Arsenic Speciation in the Mixolimnion. Above the chemocline in the LML, proportions of the different As species were similar to those observed in the UML, but absolute concentrations were about half (Figure 5; note the log scale). MMAs concentrations remained relatively constant throughout the sampling period, similar to what was observed in the UML. As(III) concentrations rose considerably in June and remained elevated through October, although maximum concentrations occurred somewhat later in the LML relative to the UML (Figures 3d and 5d). The concentration of As(III) in November 1992 was lower than the concentration in October, mirroring the decrease in As(III) over the same period in the UML. DMAs was not detected in April but was found on the other sampling dates. Highest DMAs concentrations were measured in October 1992 (Figure 5e). The maximum rates of increase in concentration of As(III) and DMAs, occurring between May 21 and June 30, 1992, were 0.04 and 0.07 nM day^{-1} (0.2% and 0.4% conversion of total As), respectively. These rates are similar to the rates observed in the surface waters of the UML.

The As speciation in the hypolimnetic waters of the LML (10–15 m) was dominated by As(V) in the spring [2.6 nM As(III) and 9.6 nM As(V) on April 30, 1992; Figure 5]. Arsenic concentrations and speciation just above the chemocline, at 15 m, did not change appreciably as dissolved oxygen decreased from 6 mg/L (April 30, 1992) to less than 1 mg/L (June 30, 1992), but later in the summer both As(V) and As(III) concentrations increased at this depth (Figure 5, panels c and d). From August to November, As(III) concentrations exceeded 10 nM at 15 m, whereas on all other sampling dates As(III) concentrations were <5 nM at this depth.

This substantial increase in As(III) concentration at the bottom of the hypolimnion of the LML was not observed in the UML and may therefore be more a result of diffusion of As(III) across the chemocline than the result of *in situ* reduction. An increase in As(V) at the same depth also occurs over the same period at a rate similar to that of As(III) even though the driving gradient for diffusion is much greater in the case of As(III). The additional source of As(V), especially in October when the waters at 15 m contained dissolved sulfide, may be the release of As(V) from settling particulate matter at 15 m.

Arsenic in the Monimolimnion. Below the chemocline, As speciation and concentration in the LML reflect the effects of radically different chemical conditions (Figure 5). Whereas water from above the chemocline was relatively clear and odor-free, a layer of very dark water was found at a depth of 16 m, and the odor of H_2S was evident; filtration of this water removed the black precipitate. A similar layer, consisting of an accumulation of iron and manganese oxides, bacterial colonies, and organic detritus trapped by the density gradient, has been observed at the redox interface in Lake Pavin, a meromictic lake in France (*5*). In the LML, water from 17 m and below was clear but yellow-colored and odorous, indicating that the dark layer is less than 2 m thick.

A steep gradient of both concentration and oxidation state for As was found to exist across the chemocline (Figure 5). Total As concentrations at 16 m ranged from 910 to 3090 nM, with an average of 1650 ± 87 nM. This reflects a total As increase by a factor of >500 across the chemocline in the spring and summer, with a diminishing gradient as As builds up at the bottom of the mixolimnion later in the summer/fall. In sharp contrast to findings elsewhere in the Mystic Lakes, As(III) is by far the dominant As species in the monimolimnion of LML. Methylated forms were not detected in the monimolimnion; however, detection limits were approximately 25 times higher (i.e., 10–20 nM) because of necessary sample dilution. Nevertheless, as the concentrations of methylated As decrease with depth in both lakes and little methylated As is found below thermocline, even in summer, it seems unlikely that a significant fraction of the As occurs as methylated As compounds in the monimolimnion of the LML.

The dominance of As(III) is predicted by thermodynamic considerations for the monimolimnion (pH 6.3, total sulfide concentration of 3 mM) (*19*). Although data from elsewhere in the waters of the Aberjona Watershed have suggested that the kinetics of As reduction are slow, this is an intensely reducing environment with a very long hydraulic residence time; the saline water in the monimolimnion predates 1966, when the downstream Amelia Earhart Dam was put into service. Thus, the dominance of As(III) here is not inconsistent with the dominance of As(V) in the anoxic hypolimnion. However, the presence of high levels of As(V) in such a situation poses additional questions; unless the reduction rate of As(V) is *extremely* low, some continuing input of oxidized arsenic must be occurring. The input of settling particulate arsenic may be such a source. The As(V) profiles in the monimolimnion suggest that particulate As sinking from above is solubilized at the chemocline, some of the As(V) released diffuses into the deeper sulfidic waters, and much of this is reduced to As(III) probably due to reaction with sulfide. Seyler and Martin (*5*) found that As(V) increases across the chemocline in Lake Pavin were strongly correlated to increases in dissolved iron concentrations, although neither the absolute As concentrations nor the relative increase across the chemocline was as high as measured here. The decrease in As(III) toward the sediment in the monimolimnion suggests that As(III) is supplied from above and has a continuous sink in the sediments.

Mass Balance. The net annual source of As from the UML to the LML is in the vicinity of 400 mol (input 58 m^3 min^{-1}; hydraulic residence time 75 days), while an estimated 200 mol of As per year are exported to the Mystic River. The balance, of approximately 200 mol, must represent the net As flux to the sediments of the LML. Typical LML surface sediments contain 55 mg/kg (dry weight) As (*16*), about half the concentration in corresponding UML sediments, while the estimated 200 mol yr^{-1} flux of As to LML sediments is also about half of the estimated flux to UML sediments. Since the two lakes are of similar area, the required sediment deposition rates are also comparable.

Conclusion

Arsenic speciation in three lakes of the Aberjona Watershed appears to be controlled by reduction, methylation, and oxidation processes and by adsorption to and desorption from particles. Arsenite transported by groundwater is a principal input of As to the HBSA; much of this influx appears to be removed by adsorption to freshly precipitating iron oxides and subsequent settling to the sediments. Scavenging of As in the HBSA does not remove 100% of the groundwater input, however, and a significant amount is carried into the Aberjona River. Mass fluxes from the outlet of the HBSA are similar to those at the inlet of the UML. This observation does not, however, rule out the existence of other As sources and sinks along the Aberjona River.

Total dissolved As concentrations in the surface waters of the UML are less than those measured at the inlet in the Aberjona River, implying that UML is an As sink. Similarly, surface As concentrations in the LML are approximately half of those measured in the UML. Mass balance calculations indicate that both the UML and the LML are still sinks for As, even though water column concentrations of As are typically less than 20 nM. There is consistency between estimates of deposition of As to the lake sediments based on mass balance considerations and estimates based on sediment concentrations and deposition rates.

Arsenic speciation in the surface waters of both the UML and the LML is dominated by reduced inorganic and methylated As compounds during the warmer months, implying that biologically mediated As reduction and methylation of As is important in the surface waters of the lakes. These interconversions inhibit scavenging of As from the surface waters, since As(III) and organic As forms are less particle-reactive than As(V). Paradoxically, less As(V) reduction was observed in the anoxic hypolimnion than the oxic epilimnion, despite the thermodynamically favorable hypolimnetic conditions for As(III) formation, indicative of slow reduction by heterotrophic bacteria and/or chemical reduction. Hypolimnetic concentrations of As(V) actually increased with time under anoxic conditions in the UML due to sediment and/or particulate release of As(V).

The high micromolar concentrations of As(III) observed in the extremely reducing, permanently stratified bottom layer of the LML were similar to As(III) levels observed in low oxygen groundwater near the highly contaminated Industri-Plex site. At the same time, As(V) persisted even under extremely reducing, sulfidic conditions, perhaps due to a continuous input of particulate As(V) from above.

The speciation found in all the lakes does not reflect thermodynamic equilibrium, probably because of the reduction by autotrophs in the upper water and the slow kinetics of reduction of As(V) under anoxic conditions. Future investigations should focus on these processes, since speciation controls both the mobility and the toxicity of As in this watershed.

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