

The Annual Cycle of Arsenic in a Temperate Estuary

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ABSTRACT: Dissolved concentrations of four forms of arsenic: arsenite, arsenate, monomethylarsenic, and dimethylarsenic, were measured in the Patuxent River Estuary near Benedict, Maryland, over two annual cycles. In each year, total arsenic concentrations peaked in the summer, in late July and August, while minimum concentrations occurred in winter. Except in late winter, arsenate was a predominant form of arsenic present. In late winter and spring, dimethylarsenic was also a predominant form. A period of monomethylarsenic abundance occurred in summer, following the predominance of dimethylarsenic. Arsenite occurred irregularly in spring. Concurrent temperature and salinity measurements indicate that total arsenic concentrations rose before the summer increase in salinity, suggesting an arsenic source other than the end members, the Patuxent River or Chesapeake Bay.

Introduction

Arsenic exists in natural waters in a variety of forms. Two inorganic forms are commonly found in nature. Arsenate (AsO_4^{3-}), the oxidized form, is the most common, while arsenite (AsO_2^-) is found predominantly in reducing conditions such as sediment pore waters or anoxic bottom waters (Andreae 1978, 1979; Peterson and Carpenter 1983; Andreae and Froelich 1984; Aggett and O'Brien 1985; Van der Weijden et al. 1990). In oxalic water or sediment, arsenite oxidizes relatively rapidly, with a half-time on the order of days, depending upon temperature, pH, biological activity, and the presence of iron and manganese hydroxides (Johnson and Pilson 1975; Scudlark and Johnson 1982; De Vitre et al. 1991). However, many algae can convert arsenate to arsenite (Johnson and Burke 1978; Sanders and Windom 1980; Sanders and Riedel 1993). This may be a process to avoid toxicity from arsenate, which can replace phosphate in many physiological pathways with undesirable results (Planas and Healey 1978; Sanders 1979; Nissen and Benson 1982; Wangberg and Blanck 1990).

Two organic forms of arsenic are also frequently present in aquatic systems, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Both are formed by biological processes, but the pathways of their creation and destruction are poorly known. Both methyl species have been found in arsenic-contaminated sediments (Holm et al. 1980; Riedel et al. 1987, 1989), where they may result from the actions of methanogenic or sulfate-reducing bacteria (McBride and Edwards 1977). Methyl arsenic species have also been frequently observed in natural waters (Andreae 1978, 1979; Howard et al. 1988; Sanders 1983, 1985; Riedel et al. 1987; An-

derson and Bruland 1991). Production of DMA (and more rarely MMA) from arsenate has been observed in phytoplankton cultures (Andreae and Klumpp 1979; Sanders and Windom 1980) and natural phytoplankton populations (Sanders and Riedel 1993).

In Chesapeake Bay, all four forms of arsenic have been observed. For example, in a transect down the bay, Sanders (1985) found arsenate predominant near the freshwater end, followed by arsenite, then MMA and DMA predominant in the middle reaches, and arsenate again dominating at the seaward end. This pattern was ascribed to successive biological transformations and eventual dilution with oceanic arsenate as it was transported through the estuary (Sanders 1985; Sanders and Riedel 1993). In this transect, the abundance of MMA correlated with the occurrence of a particular phytoplankton group, the Cryptophyceae, suggesting that individual species or phytoplankton classes might selectively produce MMA rather than the more common DMA.

On some occasions, virtually all the arsenic in the Patuxent River at Benedict, Maryland, can be in the form of DMA (Riedel et al. 1987). These periods coincide with dense winter blooms of the dinoflagellate *Katodinium rotundatum*, leading to the conclusion that this organism is likely responsible for the methylation of inorganic arsenic during this time period.

Stimulated by these results and intrigued by the potential for phytoplankton to control the geochemistry of an element, a study was undertaken to examine the annual cycle of arsenic species, in the Patuxent River near Benedict. The first set of data was collected monthly from June 1988 to May 1989. Based on these results, a second annual cycle

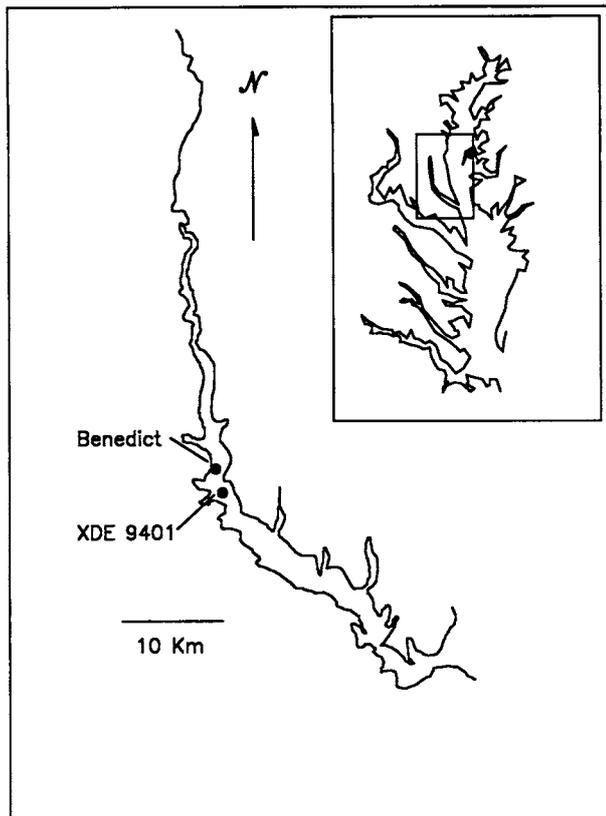


Fig. 1. Map of Patuxent River showing sampling site at Benedict and Maryland Department of the Environment sampling station XDE 9401, with an inset of Chesapeake Bay showing location of Patuxent River.

of data was collected from March 1990 to June 1991, on a weekly schedule. At this site the estuary is relatively shallow and narrow, easily mixed by tides and winds, and rarely shows significant vertical gradients of salinity or temperature. Unlike the more common geographically-oriented sampling designs, this time course sampling emphasizes the relationship of changes in concentration to factors that change seasonally, such as phytoplankton blooms, nutrient cycles, temperature cycles, and changes in river flows, etc. Because samples from other sites were not sampled simultaneously, we do not have data on the concentrations of arsenic species in other areas that could be transported into our study site, contributing to the seasonal cycles observed. Therefore, some possible explanations for the cycles observed will remain speculative until further sampling with greater geographic coverage is undertaken.

Methods

Water samples were collected for arsenic over two periods, June 1988 to May 1989 and from March 1990 to May 1991. In the first sampling

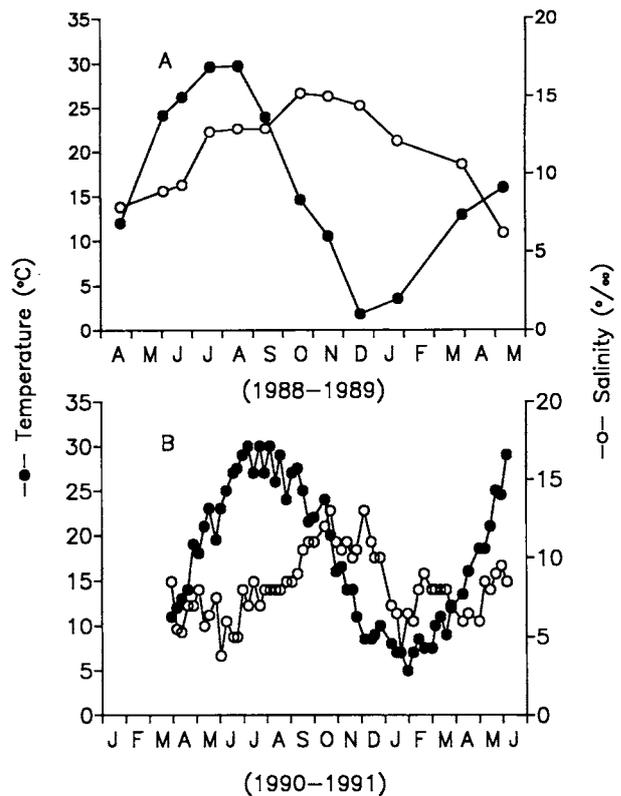


Fig. 2. A) Salinity and temperature in the Patuxent River at Benedict from June 1988 to May 1989. B) Salinity and temperature in the Patuxent River at Benedict from May 1990 to June 1991.

period, samples were collected approximately monthly from a small boat in the middle of the Patuxent River at Holland Point near Benedict, Maryland (Fig. 1). The second series of samples were collected weekly from the Benedict Estuarine Research Laboratory dock. These sampling sites are approximately 500 m apart. Samples were collected in 250 ml or 500 ml polyethylene bottles and returned to the laboratory. Samples were filtered through acid-washed GF/F filters and fast-frozen, using either liquid N_2 or a mixture of dry ice and isopropanol, and kept frozen until analysis. Temperature and salinity were measured at the time of collection. Salinity and temperature conditions during both sampling periods varied in a manner typical of temperate estuaries (Fig. 2). Nutrient and chlorophyll data for a station near the sampling site was obtained from the Maryland Department of the Environment.

Water samples were analyzed for arsenic by modifications of the hydride generation and cryogenic trapping method of Braman et al. (1977), using an apparatus and materials similar to those described by Andreae (1977). Minimum detectable concentrations are approximately 0.1 ng for arsenate and

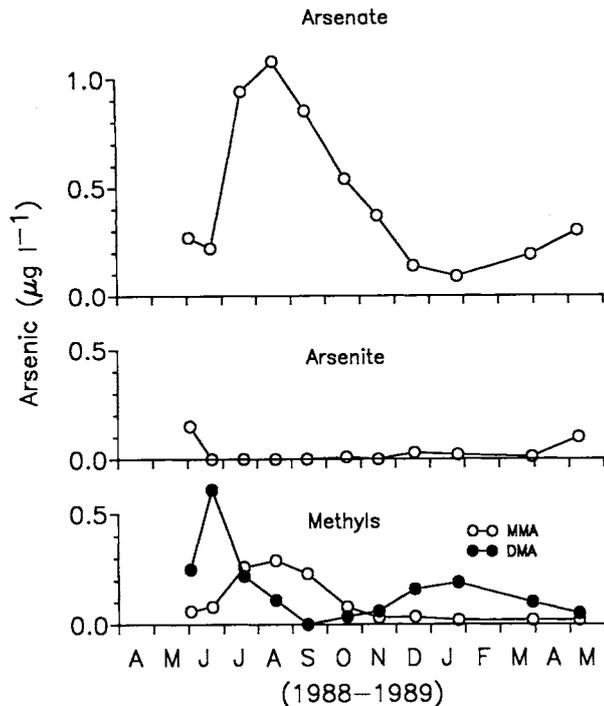


Fig. 3. Arsenic concentrations in the Patuxent River at Benedict from June 1988 to May 1989. MMA = monomethylarsonic acid. DMA = dimethylarsinic acid.

arsenite, and 0.2 ng for the methyl species, and as much as 40 ml may be analyzed. Samples of a standard reference material (CASS-1, National Research Council of Canada) were analyzed with the same method, and values were in good agreement with the certified values ($1.01 \pm 0.05 \mu\text{g l}^{-1}$ vs the certified value of $1.04 \pm 0.07 \mu\text{g l}^{-1}$).

Results and Discussion

ARSENATE

Over the first sampling period, arsenate was the predominant form of arsenic present from July to December and again from March to May, with maximum concentrations of $1.1 \mu\text{g l}^{-1}$ in August, and minimum concentrations of $0.1 \mu\text{g l}^{-1}$ in January 1989 (Fig. 3). In the second sampling, the pattern for arsenate was very similar to the first year, with maximum concentrations of slightly below $1.0 \mu\text{g l}^{-1}$ in August 1990 and with a minimum around $0.2 \mu\text{g l}^{-1}$ from January to April 1991 (Fig. 4).

Clearly, there is a large-scale temporal cycle with arsenate. Several possible causes exist. First, there could be a large input of arsenate via fresh water from the Patuxent River or via Chesapeake Bay during summer. Second, there might be local sources, from land or from some of the many creeks that drain into the Patuxent River Estuary. Finally,

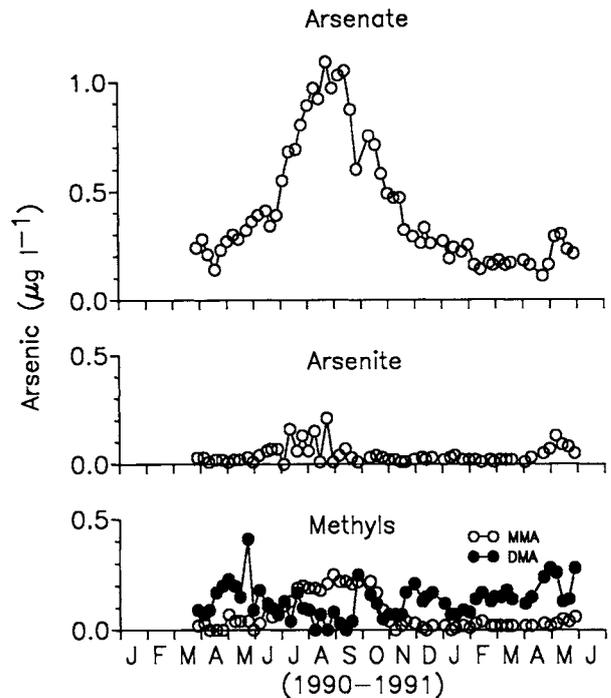


Fig. 4. Arsenic concentrations in the Patuxent River at Benedict from May 1990 to June 1991. MMA = monomethylarsonic acid. DMA = dimethylarsinic acid.

arsenic bound in sediments could be released into the water in summer, to produce the broad summer maximum.

At present, we do not have seasonal data on arsenic concentrations in the fresh water of the Patuxent River to rule out the possibility of summer increases in Patuxent River arsenic concentrations. Similarly, we cannot rule out the possibility that the summer arsenate peak results from higher concentrations in Chesapeake Bay. However, we can address both potential sources indirectly by examining the relationship between salinity and arsenate. If arsenate input into the freshwater Patuxent River is uniform with time, as has been demonstrated for other estuaries (Waslenchuk 1978; Andreae and Andreae 1989), the concentration in the fresh water will vary inversely with river flow, which in turn, determines the salinity at a polyhaline site such as Benedict. If the arsenate concentration in the fresh water is varying and the seawater component is fixed (seawater concentrations of arsenic in the North Atlantic are fairly constant at about $1.5 \mu\text{g l}^{-1}$; Waslenchuk 1978; Burton et al. 1983), then the arsenate maximum would coincide with the salinity maximum at Benedict. Similarly, if Chesapeake Bay water were the source (and Patuxent River freshwater concentrations were constant), we would also expect the peak to coincide with the salinity maximum.

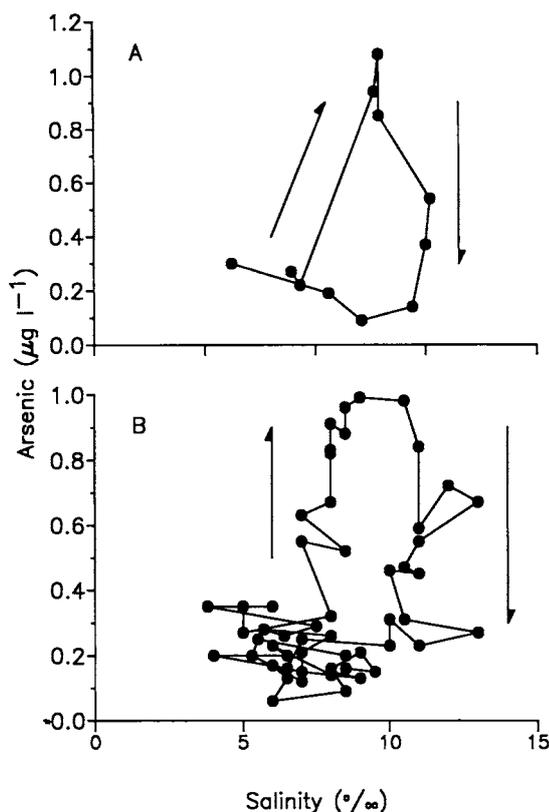


Fig. 5. Arsenic versus salinity for A) June 1988 to May 1989 and B) May 1990 to June 1991. Arrows indicate the progression of time.

Figure 5 shows the concentration of arsenate over the two sampling periods plotted versus salinity. This illustration depicts graphically the temporal relationship between the two variables. In both cases we see that arsenate rises to maximum values before salinity reaches a maximum, and falls off during the period of highest salinities. This behavior argues against the bay as the source for the arsenate, and suggests that if the source is in the fresh water, its timing is not related to fresh-water volume.

Another possible source for the arsenate peak is from sediment recycling. Arsenate is strongly adsorbed to iron hydroxides in oxidized sediment, whereas in anaerobic sediment it is largely free arsenate or reduced to arsenite, which is much less strongly bound to particles (Masscheleyn et al. 1991). Thus, arsenate tends to migrate into oxidized surface sediments from the water column, while arsenite fluxes out of sediments when the surface sediment and bottom water become reducing (Aggett and O'Brien 1985; Riedel et al. 1987, 1989, unpublished data), and accumulates in anoxic bottom water. When that water is mixed with surface oxidized water, it will rapidly be ox-

idized to arsenate, which will persist in the dissolved form. Arsenic enrichment has been observed in anoxic bottom waters in several basins, including Saanich Inlet, Puget Sound (Peterson and Carpenter 1983), the Baltic Sea (Andreae and Froelich 1984), and the eastern Mediterranean (Van der Weijden et al. 1990).

Seasonally, large areas of the deeper waters of Chesapeake Bay and its estuarine tributaries (including the Patuxent River) become anoxic (Officer et al. 1984) through stratification and microbial and benthic oxygen demand. Generally, anoxia sets up in the late spring, and persists through summer into early fall, until storms mix the bay and restore the oxygen to deep water. If sufficient arsenic is present in the anoxic waters due to sediment fluxes, mixing of the subsurface, arsenic-rich water into the surface waters could produce the mid-summer maximum of arsenate in the Patuxent. However, more direct evidence of this hypothesis must await measurements of arsenic in surface waters and subsurface waters in the Patuxent and nearby Chesapeake Bay over an annual cycle.

In addition, anoxia may not be required for significant arsenic flux from sediment. Byrd (1988) has suggested regeneration of arsenic from South Atlantic Bight continental shelf sediments could explain the fall increase in total arsenic in continental shelf waters, in the form of arsenate.

ARSENITE

Small concentrations of arsenite, about $0.15 \mu\text{g l}^{-1}$ and $0.1 \mu\text{g l}^{-1}$, occurred in spring (June of 1988 and May 1989); lesser concentrations were also observed from December 1988 to March 1989 (Fig. 3). In the second sampling, arsenite had two small periods of maximum concentration, a somewhat erratic concentration from June to August 1990, and a second maximum in May 1991. The highest values were approximately $0.2 \mu\text{g l}^{-1}$ (Fig. 4). In a seasonal study of arsenic in three English estuaries, Howard et al. (1982) found that arsenite was detected most often when temperatures were intermediate, $12\text{--}18^\circ\text{C}$, and never above 18°C . This is in general agreement with our findings.

Culture experiments have demonstrated that many algae can reduce arsenate to arsenite; however, given the relatively quick oxidation of arsenite in oxygenated water, large amounts do not accumulate in the water. Algal uptake and transformations of arsenate are mediated by phosphate and temperature (Sanders and Riedel 1993), with more rapid uptake and transformation at lower phosphate concentrations and higher temperatures. Thus, in May, the frequent appearance of arsenite in the Patuxent River may be caused by the spring bloom, brought on by increased light

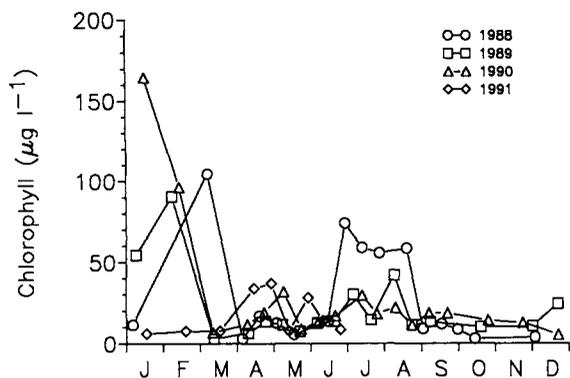


Fig. 6. Chlorophyll concentrations at Maryland Department of the Environment Patuxent River sampling station XDE 4901 from January 1988 to June 1991.

and temperature. This results in phosphate depletion and transformation of some arsenate to arsenite.

As evidence of the potential influence of biology over the occurrence of arsenite, Fig. 6 shows chlorophyll concentrations in the Patuxent River Estuary near Benedict from 1988 to 1991. In all four springs, a peak is seen in the April–May period. Phosphate concentrations exhibit minima, and N:P ratios maxima during the same period, suggesting that phosphate limitation is possible during the spring bloom in this region of the estuary (Fig. 7). In a 10-yr study of the phytoplankton community at Benedict, the peak in abundance that occurs in the April to May period has been one of the most prominent features of the annual cycle of the phytoplankton (Sanders personal communication).

DIMETHYLARSENIC

In the 1988–1989 data, DMA had two maxima, a relatively sharp peak of about $0.6 \mu\text{g l}^{-1}$ in June 1988 and a broader maxima from November 1988 to May 1989, reaching a maximum concentration of only about $0.2 \mu\text{g l}^{-1}$. At the time of both maxima, DMA was the most abundant form of arsenic. In the 1990–1991 data, DMA exhibited several maxima, one from April to June 1990, another in October 1990, another from November 1990 to January 1991, and a last maxima from February to May 1991. Unlike the previous year, DMA was the most abundant form only during one anomalous sample in May 1990; however, it was approximately equal to arsenate for a protracted period during the winter and spring of 1991. Our results for DMA, with a relatively large production in winter and early spring contrast sharply with those of Howard et al. (1982). In this study, dimethyl arsenic was found almost exclusively in warmer water, $12\text{--}21^\circ\text{C}$.

Elevated concentrations (and predominance) of

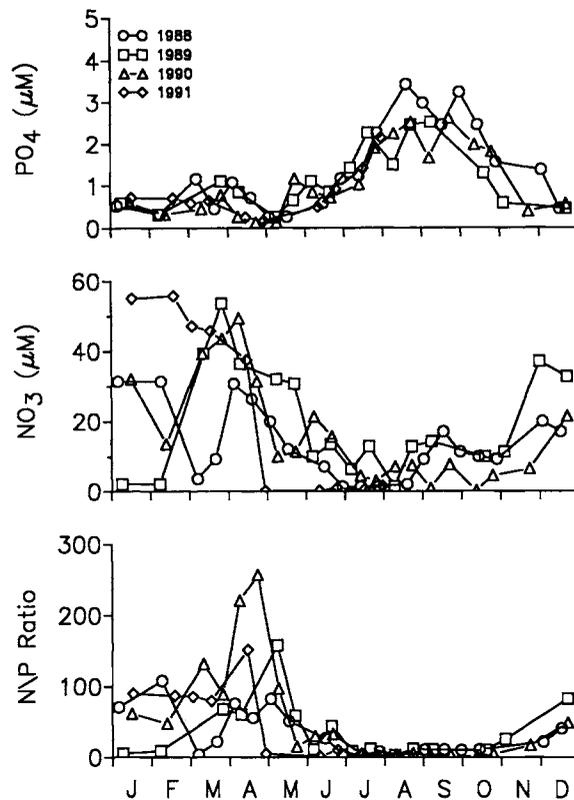


Fig. 7. Nutrient concentrations at Maryland Department of the Environment Patuxent River sampling station XDE 4901 from January 1988 to June 1991.

DMA has been noted on several occasions in the Patuxent River. In the seasonal data presented here, the two years have some features in common and some differences. Both data sets show relatively high concentrations in spring to early summer (June 1988, April and May 1990 and 1991). It seems likely that the spring-summer DMA peak, as with arsenite, is caused by the phytoplankton reduction and methylation during the phosphate-limited spring bloom. In microcosm experiments with Patuxent River phytoplankton, arsenite appears before DMA, but is replaced in a few days by DMA, which persists for several weeks (Sanders and Riedel 1993). Because DMA is more stable than arsenite, the DMA concentrations persist over longer periods before they degrade or are diluted away. Generally low concentrations of DMA are observed during the period when the total arsenic is high (August and September), a period of relatively high phosphorus concentrations and low N:P ratios.

In the first seasonal cycle, a long rise and fall occurred from November 1988 to March 1989. In the second annual cycle, we see several small cycles of shorter duration, with rapid rises of DMA followed by slower declines (e.g., September 1990,

November 1990, and February 1991), and simultaneous losses of similar concentrations of arsenate. In the 1989 data, the occurrence of DMA in winter clearly coincided with the large persistent populations of the red-tide forming dinoflagellate *Katodinium rotundatum* present that year (Sellner et al. 1991). In culture or in experiments with natural samples from blooms, this alga can rapidly transform arsenate into both arsenite and DMA, but ultimately into DMA (Sanders and Riedel 1993) once phosphate in its growth media is depleted. However, in the winter of 1990–1991, the *Katodinium* blooms, which are often present in the Patuxent during winter, were virtually absent. The usual winter chlorophyll maximum was not seen at station XDE 9401 during the winter of 1991 (Fig. 6); however, the nutrient data continued to show low phosphate and high N:P ratios during this period, suggesting that there was at least the potential for arsenic methylation.

This suggests that the 1990–1991 winter pattern was caused by several lesser blooms of other algae which depleted phosphorus, and then transformed arsenate to DMA. However, these algae were unable to maintain populations dense enough to support DMA production over the entire period. Since 1988, phosphate concentrations in the Patuxent River near Benedict have generally been low in January and February (Fig. 7), when biomass is high, corresponding to the time of the *Katodinium* blooms (Fig. 6), and again low in April–May, during the spring (predominantly diatom) blooms. Microcosm experiments have shown that while nitrogen is the main limiting nutrient in the Patuxent River during summer, phosphorus is often the only possible limiting nutrient in winter (D'Elia et al. 1986; Sanders et al. 1987). The tendency for phosphate limitation in the Patuxent River in winter and early spring predisposes the system for arsenic transformation to DMA, whether or not *Katodinium* is present. However, the high biomass and resulting high demand on phosphate during *Katodinium* blooms probably results in greater transformation of arsenate to DMA.

MONOMETHYL ARSENIC

In the first seasonal cycle, MMA was present in significant concentrations from late June 1988 to October 1989, in concert with the arsenate maximum, reaching a maximum of about $0.3 \mu\text{g l}^{-1}$ in August. In the second seasonal cycle, MMA again had a broad peak from June to October 1990, peaking at about $0.3 \mu\text{g l}^{-1}$ in August. In both data sets, MMA exhibited a broad peak—increasing in summer and declining in fall, which closely paralleled, but was slightly later than the arsenate peak. Currently, the source of MMA remains a mystery.

MMA may be a bacterial degradation product of DMA, as suggested by Anderson and Bruland (1991), which would eventually be degraded to arsenate. Peak concentrations of MMA follow DMA peaks in both data sets. In the 1988–1989 data set, the sum of DMA and MMA continues to decline from June to November. In the second year, total methyl arsenic concentrations generally declined through June, but then tended to increase again through November. However, if small “methylation” events continued to pump DMA into the system, such a pattern could result. Again, as with arsenite, and in contrast to DMA, our results are in agreement with those of Howard et al. (1982) that MMA occurred most often at temperature of 12°C and above.

Another possibility for a source of MMA would be sediment flux. Low concentrations of MMA are found in estuarine sediments (Riedel et al. 1987, 1989), particularly those contaminated with arsenic. Sediment pore water values are rarely much higher than in the water column, and thus it is difficult to conceive that enough MMA could diffuse into the water column to raise its concentration there significantly. Again, if MMA in anoxic bottom waters is the source for the summer MMA peak, we should find significantly higher concentrations of MMA in anoxic bottom waters.

Finally, specific phytoplankton might produce monomethyl arsenic rather than dimethyl arsenic as a result of uptake and transformation (Sanders 1985). However, a recent examination of a number of algal clones for arsenic transformations determined that most of them (83%) produced predominantly DMA or arsenite, and only two (17%) produced MMA (Sanders and Riedel 1993). Among cryptophytes, the taxon implicated in MMA production by Sanders (1985), no clones were found that produced predominantly MMA. Moreover, the highest concentrations of MMA occur during summer, when phosphate concentrations are high, and thus the potential for algal uptake is relatively low.

Conclusions

Arsenic in the Patuxent River Estuary undergoes an annual cycle in both concentration and form of arsenic. A summer maximum is observed, largely composed of arsenate, reaching concentrations of about $1.0 \mu\text{g l}^{-1}$. The source of this Arsenate is unclear, but it is not likely to be from freshwater inputs or from the Chesapeake Bay. Arsenite is present at very low concentrations, with occasional spikes of slightly higher concentrations, which appear to correlate with the spring plankton bloom. Substantial concentrations of DMA may occur two or more times per year, in winter and late spring, and appears to be highly linked to dense dinofla-

gellate and perhaps other algal blooms, and resulting phosphate limitation. MMA has a broad summer maximum, similar to, but less than, arsenate. The origin of this peak is equally unknown. Thus, arsenic has diverse biogeochemistry in the estuary, with sources, internal chemical cycling, and biological transformations all influencing the concentrations and speciation of arsenic in a complex fashion.

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