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Dynamics of arsenic speciation in surface waters: As(III) production by algae

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Algae reduce and methylate arsenate [As(V)]. The end product of the overall transformation reaction can be arsenite [As(III)] or methylated arsenic. Field and laboratory data suggest a strong correlation between the end product of the reaction and the growth rate of the algae, with As(III) only produced during log (exponential, fast) growth. The result is a peak in As(III) concentration preceding or coincident with the algal bloom. This paper analyzes data from 18 different water bodies (five lakes, one river, six estuary/marine sites, six experimental sites). Algal blooms, As(III) peaks and algal blooms with preceding or coincident As(III) peaks were identified. In total, 80 algal blooms were identified, 49 (61%) of which were associated with As(III) peaks. In 78% of water bodies algal blooms were typically (>50%) associated with As(III) peaks. The average time lag between As(III) peaks and algal blooms was 20 days (standard deviation 18 days).

KEYWORDS: arsenic; arsenite; algae; phytoplankton; luxury uptake

INTRODUCTION

Arsenate [As(V), $AsO(OH)_3$] is chemically similar to phosphate [PO_4, $PO(OH)_3$], which is an essential and often growth-limiting nutrient in surface waters. As a result of this similarity, algae actively absorb As(V). Inside the algal cell, however, the similarities between the two compounds break down and As(V) cannot substitute for PO_4 and interferes in many of the metabolic reactions where PO_4 is used. In other words, As(V) is toxic and, in what is believed to be a detoxification mechanism, algae reduce As(V) to arsenite [As(III), $As(OH)_3$]. As(III) is either excreted or methylated and then excreted as methylated arsenic [$(CH_3)AsO(OH)_2$ or $(CH_3)_2AsO(OH)$].[1,2]

Previous investigators have noticed that As(III) is produced only during the log growth phase of the algae.[3,4] In natural waters this leads to an As(III) peak at the onset of blooms, when the algae are in the log growth phase. The following mechanism has been proposed to be responsible for this phenomenon. In the log growth phase the algae are P-replete and up-regulate their PO_4 transport system to assimilate phosphorus in excess of their immediate growth requirements (luxury uptake). Since As(V) is taken up by the PO_4 transport system, large quantities of As(V) are also taken up at that time. Inside the cell, the reduction to As(III) is fast, but the methylation is slower, causing As(III) to build up in the cell. The result is a peak in the intracellular As(III) concentration and, because As(III) is excreted, a peak in extracellular As(III) concentration as well.[5]

It is of interest to know if there are similarities in arsenic transformation by algae across various water types (freshwater/marine, flowing/stationary). Specifically, is there always an As(III) peak when algae are growing rapidly? If not, what are the characteristics of the water bodies (e.g. high phosphorus) where this does not happen? A first step in answering those questions is to analyze the existing database on arsenic speciation.

If similarities do exist, it would be valuable information on arsenic speciation in general, and might help direct further research. Further, if we have a good understanding of how algae transform arsenic then we can learn about the algae in the field by observing the arsenic speciation. When As(III) analytical technology improves to the point where sensors

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can be deployed permanently in the field (e.g. on a buoy), measuring As(III) concentrations could help identify algal blooms before they occur. This could be useful in research into (and management of) harmful algal blooms.

This paper presents an analysis of existing data from the literature. Algae produce various arsenic species, including As(III), various forms of methylated arsenic and higher more complex organic arsenic compounds. However, the production of As(III) appears to be the most pronounced feature in the data and this analysis therefore focuses on As(III) production. Datasets that contain time series of algae and As(III) concentration are included. The general strategy is to present time series of As(III) and algae, and to identify and count (1) algal blooms, (2) As(III) peaks and (3) algal blooms with preceding or coincident As(III) peaks. The As(III) peak is expected to precede the algal bloom, because that is when the algae are P-replete. Also, the time lag between As(III) peaks and algal blooms (Δt) is calculated.

METHODOLOGY

Time series graphs of algae (cell counts and/or chlorophyll *a*) and As(III) concentration are presented for each dataset. Datasets containing filtered and unfiltered arsenic concentrations are included because a peak in As(III) concentration is expected inside and outside the algae. However, most arsenic concentrations reported in this paper are dissolved (filtered) and can be assumed to be so unless stated otherwise. There are significant analytical difficulties in determining arsenic speciation, because As(III) can oxidize during storage.[6–8] However, any error introduced by this problem is expected to be systematic [e.g. As(III) is about 50% low in all samples], which would affect the magnitude of an As(III) peak, but not the time of the peak, which is what we are concerned with here. The As(III) concentration can be presented either as relative concentration [As(III)/total arsenic, fraction] or absolute concentration [As(III), nmol l^{-1}]. For the purpose of identifying As(III) peaks resulting from algal transformation, neither method is perfect. When presenting relative concentrations, a decrease in As(V) (due to algal uptake for example) could be falsely interpreted as an increase in As(III). When presenting absolute concentrations, an increase in total arsenic [including As(III)] from external inputs (e.g. sediment flux) could be falsely interpreted as speciation change due to algal transformation. For that reason the analysis was performed using both methods. The results do not differ appreciably (see Fig. 9, where both methods are presented), and to conserve space only the relative concentrations are presented when discussing the individual datasets. The summary table (Table 1) lists results for both methods. Based on the time series graphs, algal blooms and As(III) peaks are identified and labeled alphabetically using uppercase and lowercase letters, respectively (e.g. A, a). Algal blooms and As(III) peaks are defined as a significant increase in concentration, identified visually by the author. Readers interested in definitions of blooms are referred to Smayda.[9] The following rules were applied when identifying algal blooms and As(III) peaks:

(1) Only algal blooms with sufficient As(III) data, and As(III) peaks with sufficient algae data, are identified [e.g. the 1994 data shown in Figure 10(b)].
(2) When the algae concentration starts on a decreasing trend (e.g. chlorophyll *a* in Fig. 1), the location (peak) and onset of the bloom are not defined and no bloom is identified.
(3) When the algae concentration ends on an increasing trend (e.g. Fig. 1), the onset of the bloom can be located and the end of the time series is identified as a bloom; these blooms are termed 'beginner' blooms and labeled with an asterix (e.g. D*).
(4) When the As(III) concentration starts on a decreasing trend (e.g. Fig. 1) a peak is identified. This is considered a useful feature in the data, because the algae are expected to bloom after the As(III) peak, which would be part of the dataset. Those peaks are termed 'tail' peaks and labeled with an asterix (e.g. a*).
(5) When the As(III) concentration ends on an increasing trend [e.g. Fig. 2(c)], the location (peak) is not defined and no peak is identified.

After identifying and labeling algal blooms and As(III) peaks, the number of algal blooms with preceding or coincident As(III) peaks are identified. Algal blooms and As(III) peaks not part of a pair are labeled with brackets (e.g. [B], [d]). Note that pairs do not necessarily have the same letter identification. Algal bloom 'C' can correspond to As(III) peak 'd'. Finally, Δt is calculated for each pair, and the average for each dataset is calculated. Since the location (peak) of the 'beginner' blooms and 'tail' peaks cannot be identified, Δt cannot be calculated with certainty for those pairs. For that reason the average Δt for each water body is calculated two ways: (1) including and (2) excluding 'beginner' blooms and 'tail' peaks.

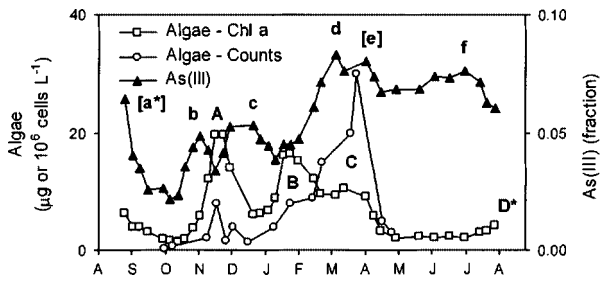

Figure 1. Marine microcosm. Data are 3 week running averages of weekly measurements for three tanks from Johnson and Burke[10] and Burke.[11] Concentrations are from unfiltered samples. As(III) fraction is based on inorganic arsenic. Cell counts were taken of Fig. 1 of Johnson and Burke[10] and are somewhat uncertain due to the scale used in the figure.

Table 1. As(III) production by algae

Dataset (figure number)	T	B	Relative concentration				Absolute concentration			
			P	M	$\Delta t(1)$	$\Delta t(2)$	P	M	$\Delta t(1)$	$\Delta t(2)$
A. Marine microcosm (1)	X	4	6	4	21	19	6	4	16	12
B. Laboratory batch experiments	X	3	3	3	—	—	—	—	—	—
C. Marine mesocosm	X	2	0	0	—	—	—	—	—	—
D. Marine mesocosm	X	1	—	—	—	—	0	0	—	—
E. Itchen Estuary and Southampton Water, UK (2)										
Woodmill	R	2	—	—	—	—	0	0	—	—
Northam Bridge	E	3	—	—	—	—	1	1	28	28
Mayflower Park	E	4	—	—	—	—	4	3	12	12
F. Davis Creek Reservoir (3)	L	1	1	1	74	74	1	1	74	74
G. Lake Greifen, Switzerland (4)	L	5	5	3	7	7	5	3	7	7
H. Field batch experiments (5)	X	10	5	5	3	3	8	6	4	4
I. Patuxent River Estuary (6)	E	7	19	6	24	23	18	6	26	22
J. Mystic Lakes										
Upper Mystic Lake (7)	L	4	3	3	16	16	6	3	11	11
K. Southampton Water, UK (8)										
Calshot Buoy	E	5	—	—	—	—	4	3	3	3
NW Netley Buoy	E	5	—	—	—	—	5	3	8	8
L. Tosa Bay and Uranouchi Inlet, Japan (9)										
Uranouchi Inlet	E	5	4	4	29	0	3	3	21	0
M. Lake Biwa, Japan (10)										
North Basin	L	6	5	4	33	28	6	4	33	28
South Basin	L	9	10	9	30	26	10	9	33	26
N. Laboratory batch experiments (11)	X	4	3	3	16	7	3	3	16	7
Total	18	80	64	45	—	—	80	52	—	—
Mean	—	—	—	—	25	20	—	—	21	17
Standard deviation	—	—	—	—	20	21	—	—	18	19

T = water body type, lake (L), river (R), estuary/marine (E) and experiment (X); B = number of algal blooms; P = number of As(III) peaks; M = number of algal blooms with preceding or coincident As(III) peak; Δt = mean time lag in days between As(III) peaks and algal blooms calculated (1) including and (2) excluding 'beginner' algal blooms and 'tail' As(III) peaks (see Methodology section).
(—) No estimate.

RESULTS AND DISCUSSION

A summary of the analysis is presented in Table 1, which lists the type of waterbody (e.g. lake, column T), number of algal blooms (column B), number of As(III) peaks (column P), and number of algal blooms with preceding or coincident As(III) peaks (column M) for each water body, in chronological order. Following is a discussion of each dataset included in the analysis. Datasets with sufficient data for a qualitative discussion, but not enough to warrant inclusion in the formal analysis, are discussed at the end of this section.

A. Marine microcosm[10]

The Marine Ecosystem Research Laboratory (MERL) is a stirred, flow-through, benthic/pelagic microcosm fed with water from Narragansett Bay. Cell counts, chlorophyll *a* and As(III) for the period August 1976 to August 1977 are presented in Fig. 1. The two metrics of quantifying algae (cell counts, chlorophyll *a*) were not always proportional, presumably due to variations in algal species. As a result, the relative magnitudes of the blooms defined by the two metrics were different. However, the two metrics were relatively consistent in the occurrence of blooms, which is important here.

Three blooms were defined by the two metrics (blooms A–C). Each bloom was preceded by an As(III) peak. The chlorophyll *a* concentration increased towards the end of the experiment (bloom D*), and an As(III) peak preceded this (peak f). It is unclear why the As(III) concentration remained elevated after bloom C, when the algae experienced a strong decline.

B. Laboratory batch experiments[3]

The diatom *Skeletonema costatum* was grown in axenic batch culture under three different As(V) initial conditions. Algae concentrations were not presented by Sanders and Windom,[3] but the end of the log phase and beginning of stationary phase (the time when algae are no longer growing and the algae concentration does not increase) was identified. The As(III) concentration in all three experiments peaked at the

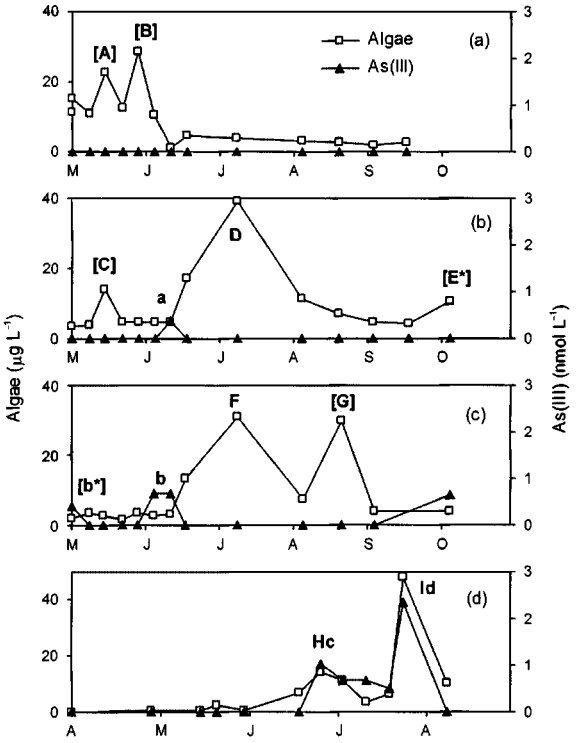

Figure 2. Itchen Estuary and Southampton Water, UK. (a) Woodmill 1983, (b) Northam Bridge 1983, (c) Mayflower Park 1983 and (d) Mayflower Park 1984. Data are from Howard and Apte.[13]

beginning of the stationary phase, 1 or 2 days after the end of the log phase. This was considered to be preceding or coincident with the algal bloom, since algae concentration typically peaked some time during the stationary phase.

C. Marine mesocosm[3]

The Controlled Ecosystem Pollution Experiment (CEPEX) is a mesocosm in Saanich Inlet, British Columbia. Phytoplankton carbon and arsenic species concentrations were measured for about 3 weeks in July 1977. The algae concentration started on a decreasing trend and two weak blooms occurred on days 12 and 21. The As(III) concentration remained low (<15%) and no peaks were evident. The observational period was relatively short, which could be responsible for the lack of observed As(III) peaks. As summarized in Table 1, the average time lag between As(III) peaks and algal blooms was 20 days, so there could have been an As(III) peak preceding the 12- and 21-day blooms prior to the initiation of sampling.

D. Marine mesocosm[12]

Speciation was followed in a marine mesocosm moored in Loch Ewe, a Scottish sea loch, over a period of 18 days in April 1983. A pronounced algal bloom occurred on about day 12. The As(III) concentration did not change appreciably during the experiment and remained low (<5%). As with the dataset described in the previous section, the lack of an observed As(III) peak may be due to the short observational period.

E. Itchen Estuary and Southampton Water, UK[13]

Chlorophyll *a* and arsenic speciation in the Itchen Estuary and Southampton Water, UK, for 1983 and 1984, are presented in Fig. 2. Three stations representing freshwater (Woodmill), estuarine (Northam Bridge) and marine (Mayflower Park) conditions were presented, which, due to the different characteristics, were considered separate water bodies.

At the Woodmill site [Fig. 2(a)] the algae concentration was relatively high in March and two blooms were identified. As(III) was not detected in any of the samples. At the Northam Bridge site [Fig. 2(b)], an As(III) peak preceded the large June–August bloom (bloom D). Smaller blooms at the beginning and end of the sampling period (blooms [C] and [E*]) were not associated with As(III) peaks. At the Mayflower Park site [Fig. 2(c, d)], two large blooms occurred from June to August in 1983 (blooms F and [G]), the first of which was preceded by an As(III) peak. In 1984 [Fig. 2(d)], two algal blooms were present accompanied by two coincident As(III) peaks.

The lack of As(III) detections at the Woodmill site could be due to the low total arsenic concentrations at that site. Total arsenic was not determined in all samples, but limited measurements indicate that the concentration at the Northam Bridge and Mayflower Park sites was about 11 nmol l^{-1}, whereas at the Woodmill site it was only about 3 nmol l^{-1}. The average of the As(III) detections at the Northam Bridge and Mayflower Park sites was 0.8 nmol l^{-1}, or 7% of the total arsenic; 7% of the total arsenic concentration at the Woodmill site was 0.2 nmol l^{-1}, which was below the detection limit of 0.3 nmol l^{-1}. In other words, the same relative amount of As(III) could have been produced at the Woodmill site (7% of the total), without being detected.

F. Davis Creek Reservoir[14]

Chlorophyll *a* and As(III) concentration in Davis Creek Reservoir for 1988–1989 are presented in Fig. 3. One algal bloom is identified, which has a preceding As(III) peak.

G. Lake Greifen, Switzerland[16]

Chlorophyll *a* and As(III) concentrations for Lake Greifen are presented in Fig. 4. The As(III) concentration increased in

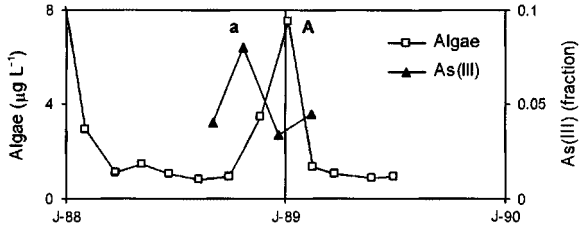

Figure 3. Davis Creek Reservoir. Arsenic data are dissolved, top-most samples (0 or 1.8 m) from Anderson and Bruland.[14] Chlorophyll *a* data are 0–6 m average from Slotton.[15]

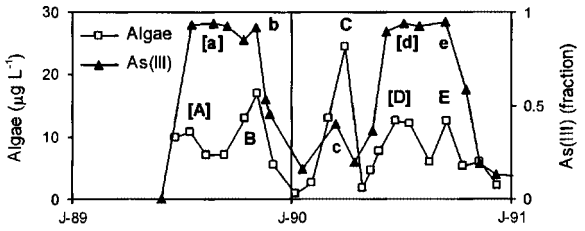

Figure 4. Lake Greifen, Switzerland. Arsenic data are from Kuhn and Sigg[16] and algae concentration are from H. Buehrer (personal communication).

the spring and remained high through the summer, whereas there was significant variability in the algae. Nevertheless, five algal blooms and five As(III) peaks were identified. The relatively weak increases in As(III) concentration during the summer (identified as peaks b and e) would be considered noise in other datasets, but since the As(III) fraction was close to 1.0, they were considered significant. During peak b, for example, 50% of the non-As(III) was converted to As(III). Peak a, as defined, occurred after bloom A and peak d occurred after bloom D. Those peaks therefore do not meet the definition of preceding or coincident peaks. However, the largest increase in As(III) concentration did occur preceding or coincident with the blooms.

H. Field batch experiments[17]

A number of field batch experiments were conducted at various times of the year (late spring, early autumn, mid winter) using water from the Patuxent River, Chesapeake Bay. Each set of experiments was conducted using two to three As(V) spiked and control tanks and the results are presented together for each experiment in Fig. 5.

Experiment 1 had an algal bloom in the spiked and control tanks with preceding or coincident As(III) peaks. In experiment 2, the algae concentration in the spiked and control tanks showed short first blooms and more gradual second blooms. No As(III) peaks were associated with the first blooms. The spiked tanks showed an As(III) peak preceding the second bloom, whereas the As(III) in the control tanks was too variable to make a judgment. Experiment 3 had a strong first bloom and the beginning of a bloom towards the end of the experiment. As(III) peaks preceded the first bloom in spiked and control tanks. The As(III) concentration increased in the control tank towards the beginning of the second bloom, but this increase did not meet the definition of As(III) peak used here.

I. Patuxent River Estuary[18]

Chlorophyll *a* and As(III) concentrations in the Patuxent River Estuary (Chesapeake Bay) over 4 years (1988–1991) are presented in Fig. 6. A bloom occurred in June–August 1988 (bloom A), which was preceded by an As(III) peak. A weak As(III) peak (peak b) preceded the February 1989 bloom (bloom C).

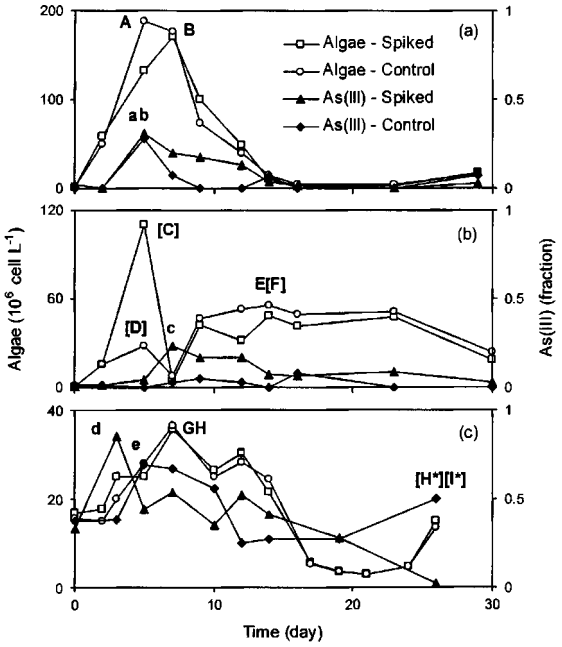

Figure 5. Field batch experiments. Data are from Sanders and Riedel.[17] (a) Experiment 1, late spring; (b) experiment 2, early autumn; (c) experiment 3, mid-winter. Symbols are means of two to three tanks.

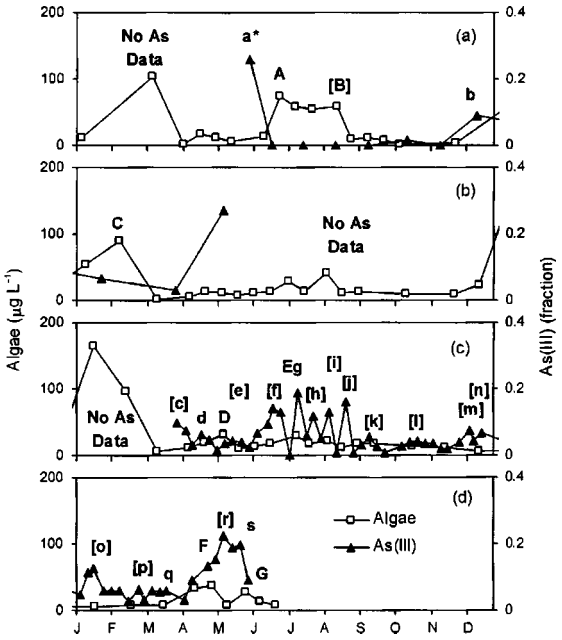

Figure 6. Patuxent River Estuary. (a) 1988; (b) 1989; (c) 1990; and (d) 1991. Data are from Riedel.[18]

The As(III) concentration increased in May 1989, when no bloom was evident in the data. However, based on the methodology employed, this increase in As(III) concentration was not considered a peak. For 1990–1991 the arsenic

sampling frequency was increased, revealing high variability and making the data difficult to interpret. There were multiple weaker algal blooms and what appeared to be unrelated higher variability in the As(III) concentration. Based on the methodology employed, numerous As(III) peaks were defined. Four algal blooms were defined (blooms D–G) and each was preceded by an As(III) peak. However, given the large number of As(III) peaks, any algal bloom would be preceded by an As(III) peak. It is questionable if any of the As(III) peaks were directly related to the algae.

J. Mystic Lakes[19,20]

Arsenic speciation in the Upper and Lower Mystic Lakes (Boston) were measured in 1991–1994 and 1991–1992, respectively. Algae concentrations were only measured in Upper Mystic Lake in 1994, limiting this analysis to that specific lake and year. However, Aurilio *et al*.[19] noticed 'two distinct peaks in As(III) concentration [. . .] one in June/July and the other in October' 1992. There was also a strong As(III) peak in the spring and a weaker peak in the autumn of 1993. These observations were consistent with As(III) peaks preceding or coincident with spring and autumn blooms, respectively. The 1994 data set (Fig. 7) showed four blooms. As(III) peaks occurred before the first three, but not the last.

K. Southampton Water, UK[21]

Algae and arsenic speciation at two locations in Southampton Water, UK for 1988 are presented in Fig. 8. At the Calshot Buoy [Fig. 8(a)], the first two blooms (blooms A and B) were not accompanied by an As(III) peak. The following three blooms (blooms C–E) had a coincident As(III) peak. There was a weak As(III) peak towards the end of the year, when there was no algal bloom. At the NW Netley Buoy [Fig. 8(b)], five blooms were identified, three of which had preceding or coincident As(III) peaks.

L. Tosa Bay and Uranouchi Inlet, Japan[22]

Chlorophyll *a* and arsenic species were analyzed in Tosa Bay and Uranouchi Inlet during 1994–1995. Seasonal As(III) concentration for Tosa Bay were not presented by Hasegawa,[22] so the analysis could not be performed on that waterbody. Uranouchi Inlet data are presented in Fig. 9. As(III) concentrations are presented using both methods (relative and absolute, see Methodology section). A bloom occurred in the summer of 1994 (bloom A) and there was a preceding As(III) peak. A bloom occurred in December 1994, with a coincident As(III) peak. In 1995 three blooms were present, the first (bloom C) was accompanied by a coincident As(III) peak. No As(III) peak was associated with the weak second bloom (bloom [D]). The As(III) concentration increased slightly (7.4–7.5%) prior to the third bloom (bloom E*). Although this increase was small (and only visible in the relative concentrations), it was significant when viewed in light of the otherwise monotonically decreasing As(III) concentration.

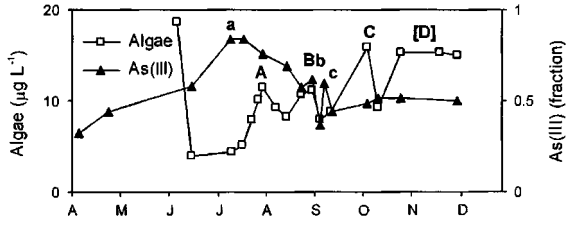

Figure 7. Upper Mystic Lake. Data are surface concentrations for 1994 from Spliethoff *et al*.[20]

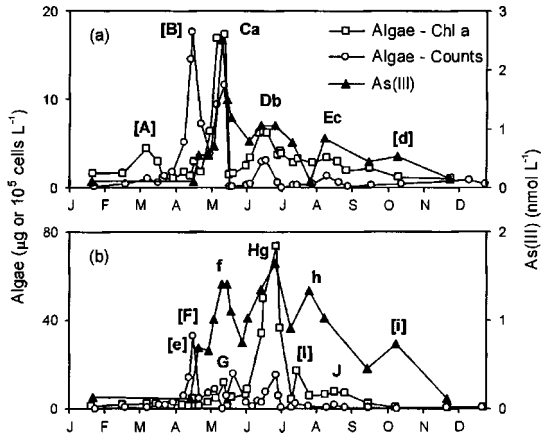

Figure 8. Southampton Water, UK. (a) Calshot Buoy and (b) NW Netley Buoy. Data are from Howard *et al*.[21]

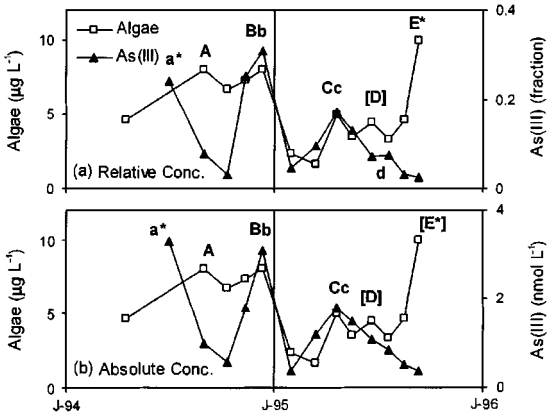

Figure 9. Uranouchi Inlet, Japan. As(III) concentrations are from unfiltered samples. Data are averaged 0–4 m, station A, from Hasegawa.[22]

M. Lake Biwa, Japan[23]

Lake Biwa consists of a larger oligotrophic/mesotrophic north basin and a smaller eutrophic south basin, which, due to their different eutrophic status, are considered different waterbodies. Figure 10 shows surface chlorophyll *a* and As(III) concentration for two north basin [Fig. 10(a,b)] and three south basin [Fig. 10(c,d)] stations for 1993 and 1994.

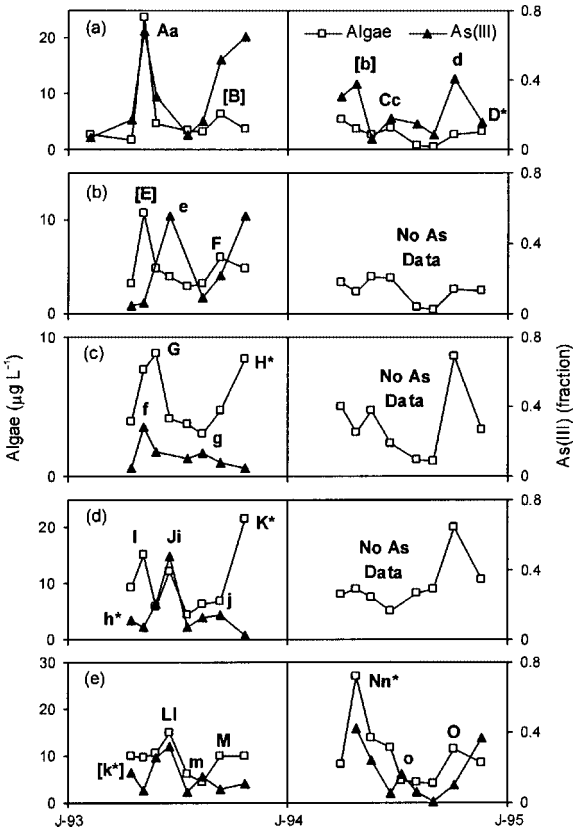

Figure 10. Lake Biwa, Japan. As(III) concentrations are from unfiltered samples. Data are surface samples from Sohrin *et al*.[23] Station (a) N1, (b) N2, (c) S1, (d) S2 and (e) S3.

Limited data are also available for 1992 and 1995, but they are too few to be useful in this analysis. A total of 15 algal blooms and As(III) peaks were identified. The blooms were too numerous to discuss individually, but the data for Station N1 [Fig. 10(a)] will be discussed.

The spring 1993 bloom (bloom A) had a coincident As(III) peak. The As(III) concentration increased at the onset of the autumn 1993 bloom (bloom [B]). Since the As(III) time series ended on an increasing trend, this feature in the data was not considered a peak. Even if it would meet the criteria of a peak, it would not be matched by bloom [B], because the As(III) concentration continued to rise as the algae concentration decreased.

The algae concentration in 1994 started on a decreasing trend and this therefore did not constitute a bloom. A smaller bloom occurred in summer 1994 (bloom C), which had a coincident As(III) peak. The algae concentration ended on an increasing trend (bloom D*) and As(III) concentration peaked at the onset of that bloom. A model application to the lake was presented by Hellweger and Lall.[24]

N. Laboratory batch experiments[4]

The green algae *Closterium aciculare* isolated from Lake Biwa, Japan were grown in axenic (bacteria-free) batch

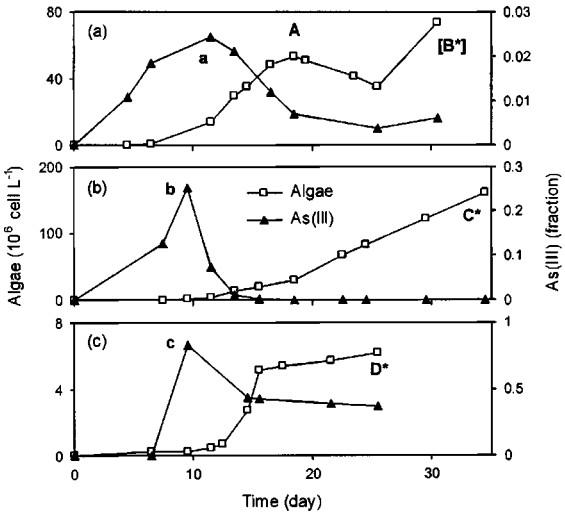

Figure 11. Laboratory batch experiments. Conditions: (a) phosphate-deficient arsenic-high; (b) phosphate-deficient arsenic-low; and (c) nutrient-deficient arsenic-low. Data are from Hasegawa *et al*.[4]

culture under different initial conditions of As(V) and nutrients. The results, presented in Fig. 11, showed a peak in As(III) concentration during the log growth phase of each experiment. The phosphate-deficient experiment showed increasing algae concentration towards the end of the experiment [Fig. 11(a), bloom B*], which was also accompanied by an increase in As(III). However the increase did not meet the definition of peak used in this study. Additional discussion and a model application to this data set were presented by Hellweger *et al*.[5]

Water bodies without algae data

Following are some data sets that were included in the paper for completeness, but for which algae concentration data were not available. Arsenic speciation in the River Beaulieu, UK, was analyzed in 1980–1982.[25] As(III) concentration in the River Beaulieu consistently peaked in the spring, which is consistent with As(III) peaks preceding or coincident with spring algal blooms. Arsenic speciation in the Tamar Estuary, UK, was analyzed in from July 1980 to August 1981 at a high spatial resolution from the freshwater to the seawater portion of the estuary.[26] As(III) concentrations in March 1981 were very high, but the authors suggest the reason is high freshwater flow at that time. In Crowley Lake, California, no appreciable amount of As(III) was found in the epilimnion at two stations during three sampling events.[27] It could be that As(III) peaks were present, but not captured by the three sampling events or that As(III) was not produced, maybe because of the high naturally occurring phosphate. This could be a due to phosphate out-competing As(V) for uptake by the algae. Another possibility is that the algae do not find it necessary to induce the luxury uptake system due to the consistent abundance of phosphate.

DISCUSSION

The results of the analysis for all water bodies are summarized in Table 1. Out of all the algal blooms identified across all water bodies, the majority (61%, based on average of relative and absolute methods) were associated with As(III) peaks. Out of the 18 water bodies, 14 (78%) had more than 50% of their algal blooms associated with As(III) peaks. For the cases where clearly no As(III) peaks were observed preceding or coincident with algal blooms, no consistent characteristic (i.e. high phosphate concentration) could be identified. Various reasons were postulated, including too short an observational period (marine mesocosms), low detection limit (Woodmill) and low sampling frequency or high phosphate concentrations (Crowley Lake). In all cases the lack of observed As(III) peaks could be due to experimental set-up (i.e. duration of observations) or sampling strategy (i.e. detection limit, observation frequency). It is entirely possible that As(III) was produced in all the water bodies reviewed here and it would be useful to confirm the original observations.

The average time lag between As(III) peaks and algal blooms (Δt) for all the water bodies was 20 days. The only dataset to completely isolate the effect of algae and eliminate all other factors (e.g. transport, bacteria) is that of Hasegawa *et al*.[4] In these experiments the time lag between As(III) peaks and algal blooms was 7 or 16 days (depending on the method of calculation), which is close to the 20 day average over all the datasets. The standard deviation of the time lag for all the water bodies was 18 days, which is large, but expected due to the many different waterbodies with different characteristics included in the analysis and the various sampling and analysis techniques used. The large variability could be an artifact of a low sampling frequency (i.e. the only possible time lags for a monthly sampling interval are 0, 30, 60, etc. days) or a result of algal species variability. A species with a fast specific growth rate would rapidly consume its P stores obtained during the luxury uptake phase. This would mean a short time between the luxury uptake phase and beginning of stationary phase and consequently a short time lag. A species with a slow specific growth rate would be able to make the P stores last longer, which would result in a longer time lag.

The analysis presented in this paper leads to some useful conclusions. Nevertheless, the study is limited by the available data (e.g. high variability, detection problems). Specifically, the temporal density of the algae and arsenic data is typically not sufficient to fully define the dynamics. Many of the algal blooms and As(III) peaks are defined by only one data point (e.g. Lake Biwa, Fig. 10), a clear violation of Nyquist's sampling theorem. Future field studies should recognize the temporal variability in the algae and arsenic speciation and include weekly or even daily sampling intervals.

Another problem is the lack of an objective methodology for defining algal blooms and As(III) peaks, and connecting As(III) peaks to algal blooms. Should increased As(III) concentrations over several months (e.g. Fig. 7, peak a) and several days [e.g. Fig. 11(b), peak b] both be considered a peak? Before an objective methodology can substitute for the qualitative judgment used in this study, the data density has to be increased significantly.

Lastly, in natural waters arsenic speciation can change in response to many factors (e.g. spatial heterogeneity and transport, sediment flux, bacteria transformation). How can the effect of algal transformation be isolated from other factors? Here more advanced analysis tools considering a multitude of factors (i.e. models) are needed. Also, statistical multiple-component analysis could help isolate the effect of algae from other factors, but this type of analysis is not feasible given the presently available database.

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