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Biogeochemistry of arsenic and antimony in the North Pacific Ocean

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[1] The biogeochemical cycles of the metalloid elements arsenic and antimony were examined along a 15,000 km surface water transect and at 9 vertical profile stations in the western North Pacific Ocean as part of the 2002 IOC Contaminant Baseline Survey. Results show that the speciation of dissolved arsenic (As III, As V, and methylated As) was subtly controlled by the arsenate (AsV)/phosphate ratio. An additional fraction of presumed organic arsenic previously reported in coastal waters was also present (~15% of the total As) in oceanic surface waters. Dissolved inorganic antimony displayed mildly scavenged behavior that was confirmed by correlations with aluminum, but atmospheric inputs that may be anthropogenic in origin also affected its concentrations. Monomethyl antimony, the predominant organic form of the element, behaved almost conservatively throughout the water column, radically changing the known biogeochemical cycle of antimony.

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Theme: Biogeochemistry in the Northwest Pacific Ocean

Guests Editors: Michiel Rutgers van der Loeff, William M. Landing, Catherine Jeandel, and Rodney T. Powell

1. Introduction

[2] The first comprehensive study of the marine arsenic cycle occurred in the North Pacific Ocean over 27 years ago [Andreae, 1978], while investigations of its companion on the Periodic Table, antimony, began in earnest roughly 10 years later [e.g., Middelburg *et al.*, 1988; Cutter and Cutter, 1995]. The predominant form of arsenic, like phosphorus, in most oxygenated surface waters is the thermodynamically stable As(V) as arsenate (AsO_4^{3-}). However, arsenic differs from phospho-

rus by the presence of other dissolved forms of the element. Despite its thermodynamic instability in the presence of oxygen, a low background level of dissolved arsenite (As III) is ubiquitous in oxic seawater [Cutter, 1992; Cutter *et al.*, 2001]. Two methyl forms of dissolved arsenic have also been commonly observed, monomethyl arsenic (MMAs) and dimethyl arsenic (DMAs) [Braman and Foreback, 1973; Andreae, 1978]. They are usually found as minor fractions of total As in river water [Braman and Foreback, 1973; Andreae, 1977; Byrd, 1990] and seawater [Andreae, 1978, 1979;

Cutter *et al.*, 2001]. Higher molecular weight dissolved organic arsenicals have been found in coastal waters (up to 25% of the total dissolved As [Howard and Comber, 1989]), but no values for oceanic waters have been reported.

[3] In the open ocean, dissolved arsenate has nutrient-like depth profiles, with the degree of surface depletion affected by the ambient phosphate concentration [Cutter *et al.*, 2001], and a rapid increase in the thermocline to relatively constant deepwater concentrations. Between the Atlantic and Pacific, deep-water interbasin fractionation is only 36% compared to phosphate's >300% [Cutter and Cutter, 1998]. DMAs and MMAs are restricted to the upper 500 m of the oceanic water column, and correlations with chlorophyll and productivity indicate phytoplankton sources [Andreae, 1979]. Arsenite also has its highest concentrations in surface waters and correlations with chlorophyll [e.g., Cutter *et al.*, 2001] similarly argue for biotic production. However, low concentrations of arsenite in deep waters of the Atlantic and Pacific suggest other sources, or a very long residence time. For autotrophic phytoplankton, arsenate acts as a phosphate analogue, showing competitive uptake by algae [Sanders, 1979]. The toxicity of arsenic is also linked to phosphorus; arsenate can be coupled to 3-phosphoglyceraldehyde in the place of phosphate, but the bond is less stable and spontaneously breaks apart to 3-phosphoglycerate and arsenate, effectively decoupling energy metabolism [Lehninger, 1975]. Phytoplankton appear to have evolved several different strategies for ameliorating the toxic effects of As. One is to have phosphate uptake mechanisms that discriminate against arsenic [e.g., Budd and Craig, 1981]. Second, arsenate can be transformed into compounds that are less harmful and easier to excrete (arsenite, MMAs, DMAs), and then either transferred to the water column or stored innocuously [e.g., Andreae and Klumpp, 1979; Sanders and Windom, 1980].

[4] In the last 27 years, our understanding of the As cycle has expanded only incrementally. In studying the behavior of As in a phosphorus-enriched estuary, Froelich *et al.* [1985] proposed that the arsenate/phosphate ratio controlled the reduction and methylation of arsenate, and that most of the arsenate taken up by phytoplankton was transformed into the methylated fraction. Nevertheless, they also argued that much of the DMAs and MMAs could be produced via the regeneration of organic matter rather than by direct methyl-

ation and release. Such a mechanism for the production of DMAs was also invoked by Howard and Comber [1989]. With respect to the conditions under which arsenate is reduced and methylated, Hellweger *et al.* [2003] developed a simulation model to explain the production of arsenite and methyl As as a function of phosphate concentration. They assumed that arsenate is taken up with phosphate and then detoxified by rapid reduction to arsenite and slower methylation to MMAs and DMAs. For cells growing under P-replete conditions (i.e., log phase growth), arsenite is rapidly produced and excreted (arsenite predominates since methyl As is produced slowly), whereas under P limitation and slow growth, the production of methylated As is favored. This relationship with the phosphorus status of surface waters that was also postulated by Froelich *et al.* [1985] raises a compelling reason to reexamine the marine biogeochemistry of arsenic. If the ocean is becoming more phosphorus limited as hypothesized by Karl *et al.* [2001] and Ammerman *et al.* [2003], then the As/P ratio will increase and the resident phytoplankton will become more As-stressed (i.e., detoxification mechanisms employed).

[5] Although a Group V element, the oceanic behavior of antimony is quite different than that of arsenic, with depth profiles from the North and South Atlantic [Middelburg *et al.*, 1988; Cutter and Cutter, 1995, 1998; Cutter *et al.*, 2001] showing either conservative behavior, or surface maxima and slight decreases with depth, consistent with mildly scavenged behavior. Like arsenic, dissolved antimony is primarily in the pentavalent oxidation state. Antimony (III) and methyl Sb, primarily monomethyl (MMSb), are found in surface waters, but dimethyl and trimethyl antimony also have been detected [Ellwood and Maher, 2002]. Benson and Cooney [1988] reported the production of a methylated antimony lipid by a marine diatom that had an arsenic equivalent, but it was produced from Sb(III) not (V). Thus, in spite of the existence of methylated and reduced antimony in surface waters, there are no supporting studies of antimony that show a detoxification pathway equivalent to that of arsenic. The sources of reduced and methylated antimony are largely unidentified. Furthermore, if scavenging is an important process affecting antimony, then data for the Pacific Ocean will help highlight this behavior due to longer deep-water residence times.

[6] The 2002 IOC Contaminant Baseline Survey in the North Pacific [Measures *et al.*, 2006] traversed

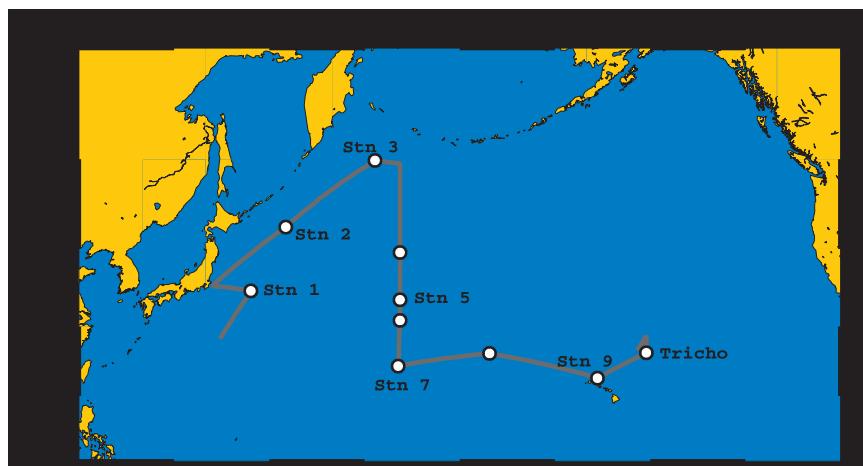


Figure 1. Ship's track for surface sampling and major vertical profile stations during the 2002 IOC Contaminant Baseline Survey, 1 May to 5 June 2002. "Tricho" is the location of visually observed blooms of the nitrogen-fixing cyanophyte, *Trichodesmium*.

waters ranging from the extremely oligotrophic North Pacific central gyre to the high nutrient-low chlorophyll region of the sub-Arctic Pacific, ideal for examining the cycling of arsenic and antimony. This paper examines antimony and arsenic behavior in the North Pacific Ocean in order to evaluate the arsenic-phosphorus relationship, as well as to evaluate whether antimony truly behaves as a mildly scavenged element.

2. Methods

2.1. Study Area and Sampling Methods

[7] The 2002 expedition used the U.S. Research Vessel *Melville* and left Osaka, Japan, on 1 May 2002 and arrived in Honolulu, Hawaii, on 5 June 2002. A total of nine vertical profile stations were occupied, and surface samples were acquired 2–3 times per day during transects between stations (Figure 1). In addition to hydrographic sampling using a CTD/rosette, trace element samples at the vertical profile stations were acquired using 12 and 30 L trace metal-clean Go Flo bottles deployed on a 5600 m, 6 mm Kevlar cable with plastic-coated weight and triggered with plastic messengers; the depth of the deepest bottle was verified using a logging pressure transducer. After recovery, the Go Flo bottles were brought into a clean room, the bottles pressurized (8 psi, filtered compressed air), the water directly passed through acid-cleaned, 0.4 μm polycarbonate filters in Teflon holders, and into sample containers (500 mL FEP Teflon); these bottles were refrigerated until analysis (within 24 hours). Additional samples for salinity, nutrients,

and chlorophyll were also taken [Measures *et al.*, 2006].

[8] For underway surface sampling, a "fish" [Vink *et al.*, 2000] was towed ~ 7 m off the port, aft quarter of the ship at 1–3 m depth depending on ship's roll. Water was peristaltically pumped through Teflon tubing and into a clean facility in the ship's analytical lab where it passed through a 0.2 μm filter and into a Teflon bottle as above; nutrient, salinity, and chlorophyll samples were also taken.

2.2. Analytical Methods

[9] Because of the instability of As and Sb species with storage [Cutter *et al.*, 1991], all analyses were made on board ship within 24 hours of sample collection. The simultaneous determinations of inorganic antimony and arsenic speciation utilized the selective hydride generation, cryogenic trapping, and gas chromatography-photoionization detection method of Cutter *et al.* [1991]. Reduced (i.e., +3) As and Sb were converted to their hydrides at pH 6.2 (TRIS-HCl buffer) using NaBH_4 in the presence of sulfanilamide (0.5 mL of a 2% solution to remove nitrite interference; see below) and determined. Hydride generation at 0.5 M HCl (+KI solution) and GC/PID detection yielded the concentrations of As and Sb (III + V); As and Sb (V) were the difference between the two separate determinations. The detection limit for inorganic As was 0.001 nmol l^{-1} while that for Sb was 0.0005 nmol l^{-1} , and precision at 0.5 nmol l^{-1} was better than 5% (relative standard

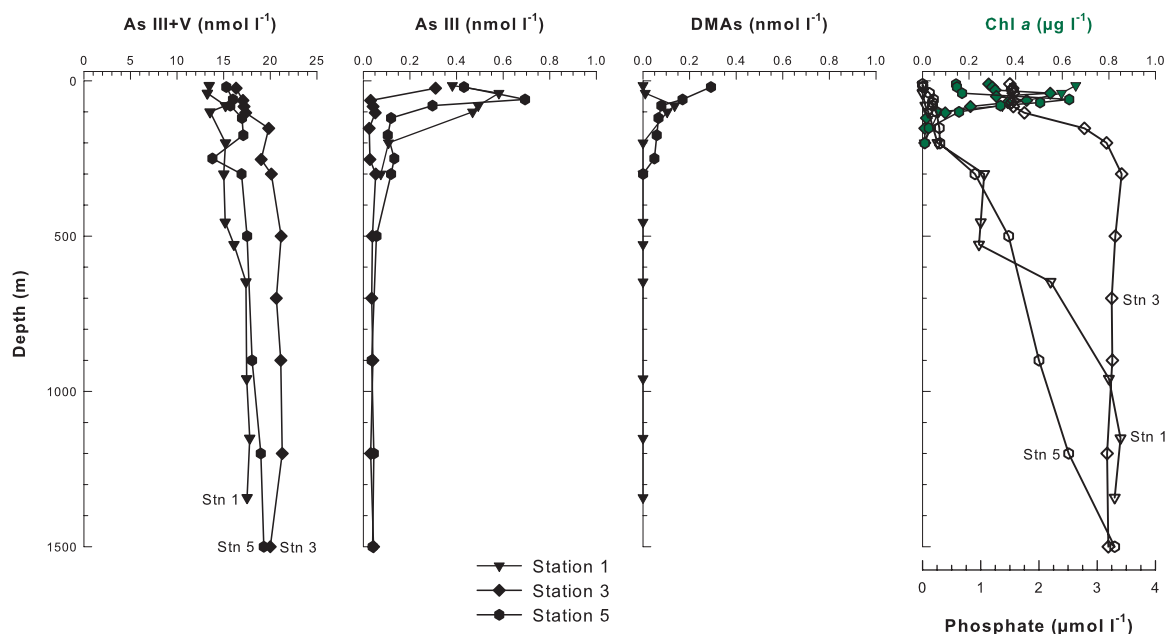


Figure 2. Vertical profiles for dissolved inorganic (As III + V and As III) and organic (dimethyl arsenic, DMAs) arsenic speciation, phosphate, and chlorophyll *a* at 2002 IOC Stations 1, 3, and 5. Note that in the right-hand panel, phosphate concentrations are plotted as the open symbols, while chlorophyll are the filled green symbols, with the shape of the symbols corresponding to the stations numbers in the legend.

deviation, RSD). The standard additions method of calibration was used to assure accuracy.

[10] Dimethyl and monomethyl arsenic and antimony (DMAs, DMSb, MMAs, and MMSb) were simultaneously determined using the total inorganic As and Sb procedures above (except no KI was added), including the addition of sulfanilamide, but using a different gas chromatography column (15% OV-3 on Chromasorb W/AW DMCS, 80/100 mesh). Detection limit for the methylated As and Sb species was $0.005 \text{ nmol l}^{-1}$ and the precision was 6% (RSD) at 0.1 nmol l^{-1} .

[11] The addition of sulfanilamide for the determinations of both the trivalent and methylated species is an update from the procedure used in the Atlantic Ocean [Cutter *et al.*, 2001], and was instituted when low recoveries (based on standard additions) were encountered in the HNLC waters north of 42°N during the expedition. The major constituent in these waters that is not present in the more oligotrophic waters is nitrate. In as much as sulfanilamide addition removes the interference (no change in the standard additions slope), it appears that some nitrate may be reduced to nitrite by borohydride. More specifically, nitrite is a strong oxidant for hydrides and sulfanilamide reacts with nitrite to form a stable diazonium compound [Cutter, 1983]. Nitrate and nitrite were determined

on board ship and sulfanilamide was available since it is a key reagent in the colorimetric procedures. The use of this sulfanilamide was instituted after Station 3 and therefore the methyl Sb data from Stations 1–3 are suspect; Sb(III) did not appear to be affected as much. As will be seen, this analytical modification profoundly changes our understanding of methyl antimony cycling.

3. Results and Discussion

3.1. Vertical Profiles

[12] For this discussion six of the nine vertical profile stations on the cruise are covered, and these represent the highest and lowest latitudes, extremes in longitude, existing time series stations, and variations in oceanographic conditions. The westernmost Station 1 (34.467°N , 146.99°E) was at the northern edge of the subtropical gyre in the Kuroshio Current, and had undetectable nutrient concentrations [Measures *et al.*, 2006] and the highest chlorophyll concentration of the vertical profiles stations (Figure 2). Total inorganic arsenic (As III + V or As_i) in the 25 m deep mixed layer had the lowest concentration encountered on the expedition, while correspondingly high concentrations of arsenite, but only low methyl arsenic concentrations, were present (Figure 2; for clarity only

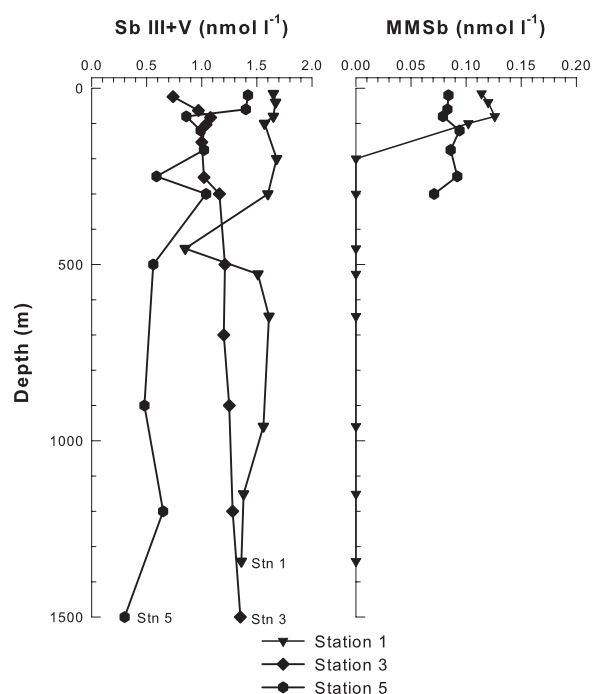


Figure 3. Vertical profiles for dissolved inorganic (Sb III + V) and organic antimony (monomethyl antimony, MMSb) at 2002 IOC Stations 1, 3, and 5.

DMA data are plotted). In contrast, total inorganic antimony (Sb III + V or Sb_i) had its highest mixed layer concentration at Station 1 (Figure 3), with a slight decrease into the thermocline. Antimony (III) was undetectable at this and all other vertical profile stations and will only be discussed for the horizontal transect. However, monomethyl antimony had its highest concentrations in the mixed layer and upper thermocline at Stn. 1, but then dropped to undetectable levels by 200 m (Figure 3); this later feature is likely an analytical artifact that will be discussed below.

[13] Station 5 (33.765°N, 170.58°E) was at nearly the same latitude as Station 1, and in the Kuroshio Current Extension and subtropical Gyre, but much farther from potential atmospheric sources of As and Sb (discussed below). Like Station 1, nutrients were below detection limits, but chlorophyll *a* concentrations were elevated [Measures *et al.*, 2006] (Figure 2). Total inorganic arsenic was not as depleted in surface waters compared to Station 1, arsenite concentrations were roughly equivalent, but DMA was twice that at Station 1 (Figure 2). Total inorganic antimony had a surface maximum and decrease into the major thermocline, but the maximum was 15% lower than the concentrations at Station 1 (Figure 3). In contrast to the Station 1

profile, MMSb had a relatively uniform concentration with depth (Figure 3; $0.084 \pm 0.007 \text{ nmol l}^{-1}$), a change that is due to the use of sulfanilamide to remove the nitrite/nitrate interference.

[14] Stations in the western sub-Arctic gyre (2 at 44.0°N, 155.0°E; and 3 at 50.0°N, 167.0°E) had properties that were quite different than those to the south, particularly their nutrient enrichment (Figures 2 and 4) in surface waters characteristic of this High Nutrient-Low Chlorophyll (HNLC) region; however, both stations still had strong subsurface (40–50 m) chlorophyll maxima (Figures 2 and 4). For arsenic, the most striking features at these stations were the lack of surface depletion of As_i relative to stations in more oligotrophic waters, and the low concentrations of arsenite and methyl As in the upper water column (Figures 2 and 4), particularly at Station 2 (Japanese JGOFS Time Series Station KNOT). For total inorganic antimony, surface maxima were absent and indeed, the vertical profiles look almost nutrient-like (surface depletion, deep water enrichment; Figures 3 and 5), with nearly identical concentrations in the major thermocline of the two stations (1000–1500 m). Data for MMSb are not available at these stations since the nitrite interference problem had not been resolved at this stage.

[15] Within the oligotrophic subtropical gyre at Stations 7 (24.25°N, 170.33°E) and 9 (US JGOFS Time Series Station ALOHA; 22.75°N, 158.0°W), nutrient concentrations dropped back to undetectable levels, while chlorophyll maxima were deeper and much lower concentration than at the other stations (Figure 4). Total inorganic arsenic displayed ~25% surface depletion relative to deep waters, typical of oligotrophic waters [e.g., *Andreae*, 1978; *Cutter et al.*, 2001], while prominent maxima in arsenite and methyl As were found in the upper 200 m of the water column (Figure 4). The deepest samples at Station 7 were composed of Antarctic Bottom Water (AABW) and it appears that As_i decreased slightly into this water mass. Interestingly, the concentration of As_i in AABW at Station 7, 20.6 nmol l^{-1} , was identical to that in the South Atlantic (20.4 nmol l^{-1} [Cutter *et al.*, 2001]).

[16] Surface maxima in total inorganic antimony were apparent at Stations 7 and 9 (Figure 5), although the actual concentrations (average of 1.05 nmol l^{-1}) were over 30% less than those at Stations 1 and 5 to the west. Using data below 2500 m at Station 9, Sb_i averaged $0.83 \pm 0.08 \text{ nmol l}^{-1}$, slightly lower, but not statistically

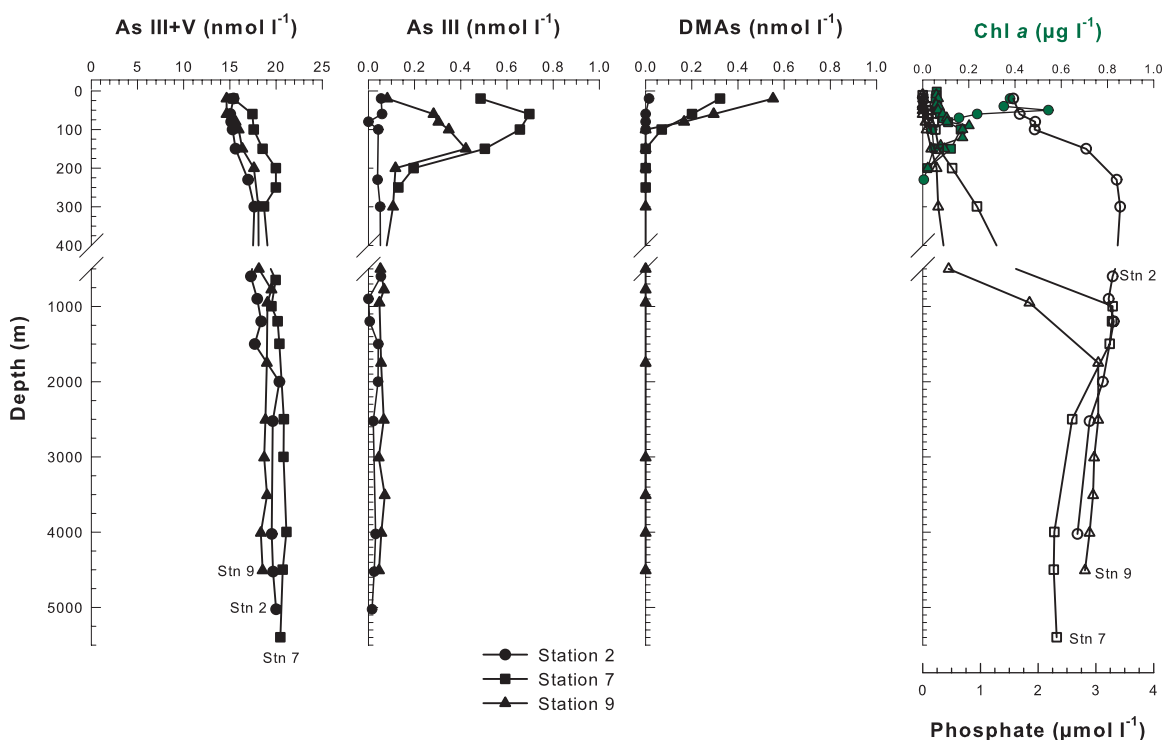


Figure 4. Vertical profiles for dissolved inorganic (As III + V and As III) and organic (dimethyl arsenic, DMAs) arsenic speciation, phosphate, and chlorophyll *a* at 2002 IOC Stations 2, 7, and 9. Note that the upper 400 m are plotted on an expanded scale. Also, in the right-hand panel, phosphate concentrations are plotted as the open symbols, while chlorophyll are the filled green symbols, with the shape of the symbols corresponding to the stations numbers in the legend.

different, than the value for deep waters in the South Atlantic [Cutter *et al.*, 2001]. However, in the AABW at Station 7, Sb_i averaged 1.14 nmol l^{-1} , over twice that in the AABW of the South Atlantic ($0.53 \pm 0.05 \text{ nmol l}^{-1}$ [Cutter *et al.*, 2001]). The most significant dissolved antimony profile for the entire data set is that of MMSb at Station 9, which displayed an essentially conservative behavior for the entire water column ($0.037 \pm 0.006 \text{ nmol l}^{-1}$). This has never been reported for any ocean or sea, and we believe that the discovery of the nitrite/nitrate interference, also previously unreported, provides an explanation. However, it also changes the role of methyl Sb in the antimony cycle, to be elaborated below.

3.2. Horizontal Transect

[17] The surface water transect from Osaka to Honolulu between the vertical profile stations covered almost 15000 kilometers, and crossed, in order, the subtropical gyre, the Kuroshio Current, the Oyashio Current, the western sub-Arctic gyre, back across the 2 major current systems, and into the subtropical gyre (Figure 1). Data for dissolved arsenic, phosphate, and chlorophyll *a* are plotted in

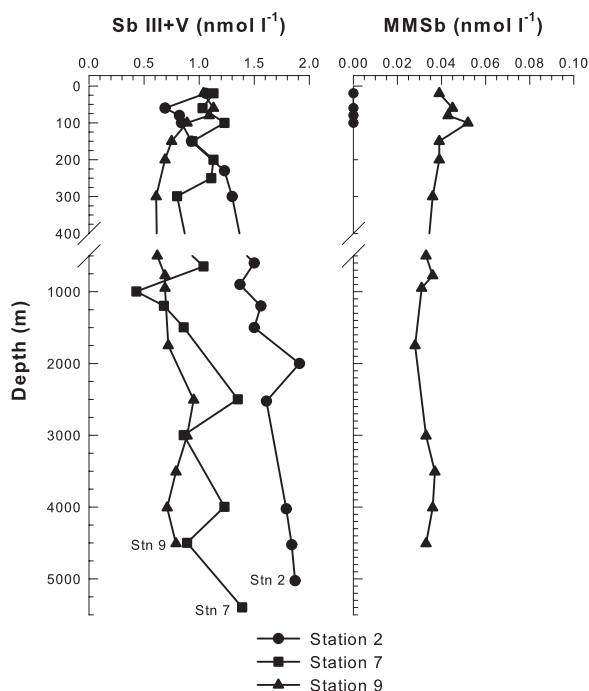


Figure 5. Vertical profiles for dissolved inorganic (Sb III + V) and organic antimony (monomethyl antimony, MMSb) at 2002 IOC Stations 2, 7, and 9. Note that the upper 400 m are plotted on an expanded scale.

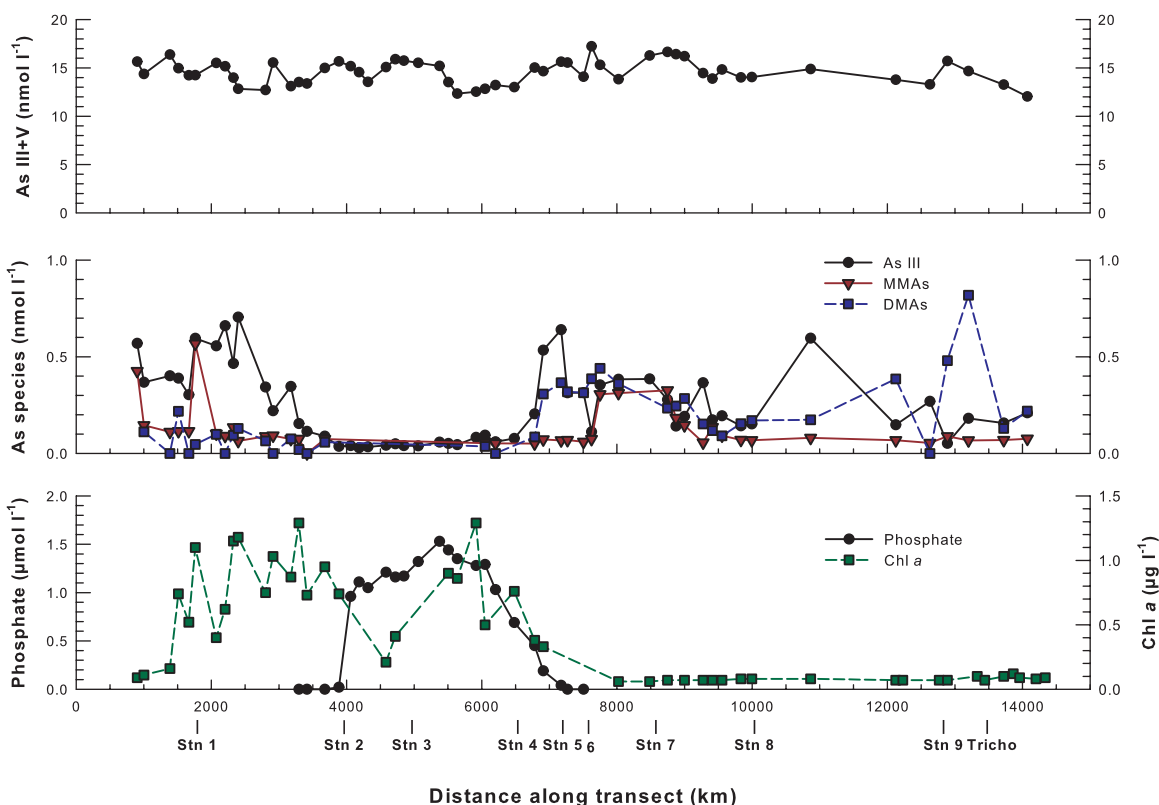


Figure 6. Dissolved arsenic speciation (As III + V, As III, monomethyl arsenic or MMAs, and dimethyl arsenic or DMAs), phosphate, and chlorophyll *a* as a function of distance along the surface transect depicted in Figure 1. The positions of the vertical profile stations and the *Trichodesmium* blooms (“Tricho”) are shown for reference (see Figure 1).

Figure 6. For the entire transect, As_i averaged $14.6 \pm 1.2 \text{ nmol l}^{-1}$, and had little variation with the oceanographic regimes crossed (Figure 6). In comparison to As_i in the Atlantic Ocean ($16.3 \pm 2.1 \text{ nmol l}^{-1}$ [Cutter *et al.*, 2001]) and South Pacific ($18 \pm 2 \text{ nmol l}^{-1}$ [Ellwood and Maher, 2002]), these North Pacific arsenic concentrations are noticeably lower.

[18] The speciation of dissolved arsenic on the horizontal transect displayed variations through the various oceanic regimes that may be diagnostic of processes controlling it. The most notable were the low concentrations of arsenite and methylated As in the HNLC region where elevated phosphate concentrations were present (Figure 6). In the region of mixed waters that are the transition between the subtropical and sub-Arctic gyres (and Kuroshio and Oyashio Currents) from Station 1 to Station 2, the highest chlorophyll *a* concentrations (biomass) were found in the same waters where arsenite reached its highest concentrations and methylated As was generally low (Figure 6). The equivalent transition region going into the subtrop-

ical gyre further to the east (Stations 4–6) also had elevated arsenite concentrations, but methylated arsenic was at equivalent concentrations. In the subtropical gyre east of Station 7, the 3 reduced forms of arsenic remained at relatively similar concentrations. The one exception was the high DMAs concentration northeast of Station 9 in the vicinity of blooms of the nitrogen-fixing cyanophyte, *Trichodesmium*. Although the discrete chlorophyll concentrations did not mark these blooms, they were recorded in the flow-through fluorometer, as well as visually observed [Measures *et al.*, 2006].

[19] In contrast to As_i , Sb_i had considerably more variability along the transect ($1.16 \pm 0.35 \text{ nmol l}^{-1}$; Figure 7), with the highest concentrations found on the western south-north leg downwind of Asia ($1.33 \pm 0.42 \text{ nmol l}^{-1}$); these results are consistent with the surface water trends at the vertical profile stations (Figures 3 and 5). The concentrations of Sb_i on the transect were substantially lower than in North and Equatorial Atlantic ($1.87 \pm 0.38 \text{ nmol l}^{-1}$, high latitude North Atlantic;

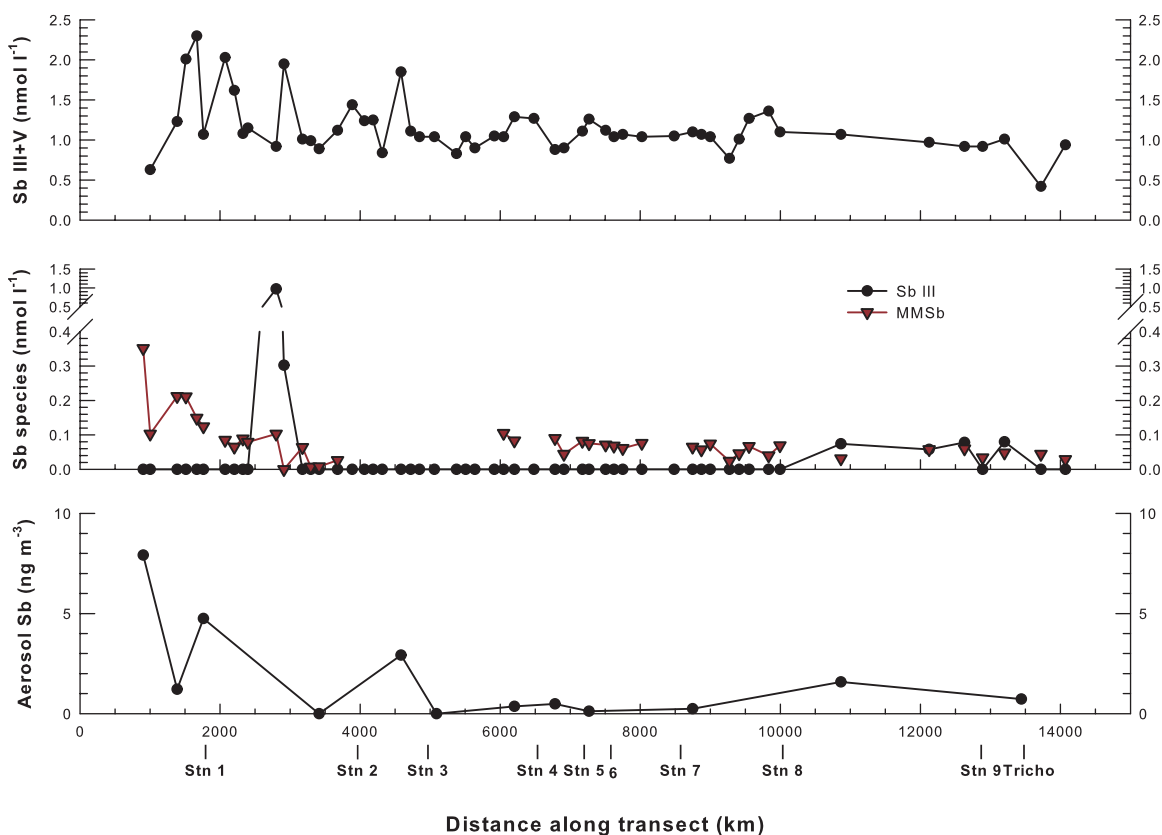


Figure 7. Dissolved antimony speciation (Sb III + V, Sb III, monomethyl antimony, or MMSb) and leachable/easily soluble aerosol antimony (see text for extraction method) as a function of distance along the surface transect depicted in Figure 1. The positions of the vertical profile stations and the *Trichodesmium* blooms (“Tricho”) are shown for reference (see Figure 1). Note that the middle panel has an expanded concentration scale for Sb species $<0.4 \text{ nmol l}^{-1}$.

Cutter and Cutter, 1998; $1.25\text{--}1.44 \text{ nmol l}^{-1}$, Equatorial Atlantic [Cutter et al., 2001]), but higher than those reported for the South Pacific ($0.99 \pm 0.06 \text{ nmol l}^{-1}$ [Ellwood and Maher, 2002]). For the entire transect, Sb (III) was only detected in 6 samples, with an unusually high concentration off of Japan and detectable levels to the northwest of Station 9 (Figure 7). Other than this one Sb (III) anomaly, monomethyl Sb was the predominant form of reduced and methylated antimony in surface waters, particularly early in the expedition when transiting along the Japanese coast (recall that there were no determinations in the HNLC waters due to the interference problem that was subsequently remedied); these results are consistent with those from the South Pacific [Ellwood and Maher, 2002].

3.3. Arsenic Biogeochemistry in the North Pacific

[20] All past studies of arsenic biogeochemistry have clearly shown linkages with phosphate

cycling [e.g., Andreae, 1978; Cutter et al., 2001] as well as processes unique to arsenic (e.g., redox changes [Cutter, 1991]. The stark contrast between the high phosphate/low reduced and methylated As of the HNLC region (atomic $\text{As}_i/\text{PO}_4 = 0.01$) and low phosphate/elevated reduced and methylated As concentrations in oligotrophic waters (atomic $\text{As}_i/\text{PO}_4 > 1.0$) is clearly apparent in the horizontal transect data (Figure 6). As has been noted by many studies [e.g., Andreae, 1978; Andreae and Klumpp, 1979; Sanders and Windom, 1980; Froelich et al., 1985; Cutter et al., 2001], the ratio of arsenate (the major portion of As_i) to phosphate affects the production of reduced and methylated arsenic. However, the finer detail afforded by the vertical profile stations allows an evaluation of factors affecting their production. Again, in the HNLC region (e.g., Station 2; Figure 4) phosphate concentrations were elevated and the As_i/P ratio was very low, and both arsenite and methyl As concentrations were low; this behavior has been well established [e.g., Andreae, 1978, 1979].

[21] In the transition waters where phosphate concentrations were low, there were still substantial biomass and presumably higher growth rates (i.e., chlorophyll *a*; Stations 1 and 5; Figure 2; no productivity data were obtained), arsenite concentrations were higher than those of the methyls. This is consistent with the model of *Hellweger et al.* [2003] where arsenite production is favored during higher growth rates before phosphate is completely depleted (but still low concentrations). They also proposed that methyl production is favored under phosphate-depleted conditions and slow growth rates, typical of oligotrophic gyres. The data from Stations 7 and 9 (Figure 4) and the horizontal transect (Figure 6) do not completely agree with this proposition, but the ratio of reduced to methylated As certainly was less in the gyre samples ($\text{AsIII/MMAs} + \text{DMAs} = 1.0 \pm 1.2$, $n = 17$) compared to those near the HNLC region ($\text{AsIII/MMAs} + \text{DMAs} = 3.1 \pm 1.9$, $n = 7$).

[22] It appears that *Hellweger et al.* [2003] may be correct that phytoplankton growth rate relative to As/P “stress” (i.e., when detoxification processes are invoked) may be a factor controlling the relative production of arsenite and methyl As. However, residence times of these species also affect their abundances in the water column (i.e., what was measured), and in this respect, previous works [e.g., *Johnson and Pilson*, 1975; *Cutter*, 1992; *Cutter et al.*, 2001] suggest that methyl As has a 2–3 \times longer residence time than that of arsenite. Moreover, photochemical studies conducted on this expedition (*Cutter*; unpublished) show that arsenite had a residence time of ~ 3 days due to photooxidation, while methyl As showed no photochemical reactivity. Thus the relative abundances of methylated As and arsenite in the upper ocean are not just due to production rates alone.

[23] While the data for methylated As on this expedition have increased our understanding of the conditions under which they are produced, there are other higher molecular weight organic arsenicals for which there are very little data from the open ocean. *Howard and Comber* [1989] found a nonhydride labile dissolved arsenic fraction (up to 25% of As_i) that must consist of a higher molecular weight organic compounds containing As (e.g., arsenobetaine, arsenocholine, arsenosugars). To investigate whether such a compound class was present in the North Pacific, four 0.2 μm filtered, surface transect samples (between Stations 1 and 2; Figure 1) were photo-oxidized (1000 W UV; 6 hour irradiation in quartz tubes). The excess

As averaged $16.3 \pm 4.7\%$ of the nonirradiated As_i (or, $2.42 \pm 0.63 \text{ nmol l}^{-1}$ organic As). At Station 2, seven samples from the depth profile (4 in the upper 230 m, 3 from 900 to 4525 m) were treated similarly. The concentration of excess As was constant in the upper 230 m ($2.73 \pm 0.20 \text{ nmol l}^{-1}$, or $17.5 \pm 1.4\%$ of As_i), but then dropped to nondetectable levels (approximately $<0.4 \text{ nmol l}^{-1}$) in the deeper water samples. These data document a presumably organic form of dissolved As that is not determined by direct hydride generation was present in oceanic surface waters. On the basis of its absence in the major thermocline (and therefore North Pacific Intermediate Waters that have ages of ~ 20 years and likely ventilated in the Sea of Okhotsk [*Warner et al.*, 1996; *Yamamoto-Kawai et al.*, 2004]) and deep ocean, this excess arsenic must have a residence time on the order of years (i.e., similar to the methyl species). With such reactivity, the unknown, but presumably organic, fraction should play a role in arsenic’s oceanic cycle and deserves further attention, particularly if it is a source of MMAs and DMAs [*Howard and Comber*, 1989].

3.4. Antimony Biogeochemistry in the North Pacific Ocean

[24] Most of the previous studies of antimony have been in the Atlantic Ocean and adjacent seas, but these showed either conservative or mildly scavenged behavior for dissolved inorganic antimony (not the individual species) and the importance of atmospheric deposition on both vertical and horizontal profiles [*Andreae and Froelich*, 1984; *Middelburg et al.*, 1988; *Cutter and Cutter*, 1995, 1998; *Takayanagi et al.*, 1996; *Cutter et al.*, 2001]. The most complete data set for antimony in the South Pacific [*Ellwood and Maher*, 2002] showed that Sb_i behaved conservatively in the subtropical to sub-Antarctic waters. Aluminum is the classic example of a trace element with scavenged behavior [*Hydes*, 1979; *Measures et al.*, 1986; *Orians and Bruland*, 1986], so comparing the vertical profiles of the two elements should illuminate processes affecting dissolved inorganic antimony. In this respect, the older deep waters of the North Pacific relative to those in the Atlantic facilitate comparisons between Al and Sb_i , but a confounding issue is that anthropogenic emissions increase the concentration of Sb in atmospheric deposition [*Nriagu and Pacyna*, 1988; *Arimoto et al.*, 1989, 1996; *Cutter*, 1993]. Since Station 9 had full vertical profiles of both elements (Al from *Measures et al.* [2005]; Sb_i in Figure 5) and was

farthest away from potential anthropogenic inputs (to be discussed next), it was used for the comparison; the linear correlation coefficient (r) was 0.768 ($n = 16$, $m = 0.09$ atomic Sb/Al). This correlation strongly supports the interpretation of inorganic antimony acting as a scavenged element. In this respect, Sb_i in the AABW at Station 7 was much higher than AABW in the South Atlantic [Cutter *et al.*, 2001], consistent with the behavior of Al in the same waters [Measures *et al.*, 2005].

[25] For stations on the western side of the basin (1–5), the correlation between Sb_i and Al begins to decrease, largely due to the apparent enrichment of Sb_i relative to Al. At Station 2 in the western North Pacific (and with a full profile), the linear correlation coefficient (r) decreased to 0.592 ($n = 16$), but more significantly, the atomic Sb/Al slope rose by a factor of 6 to 0.53, largely due to higher Sb_i in surface waters. This apparent enrichment of Sb_i in the western North Pacific was also present in the horizontal transect (Figure 7). The atmosphere may be one source of this antimony and during the cruise easily leachable/soluble Sb_i in 12 aerosol samples was determined using the method described by Buck *et al.* [2006]. Briefly, 100 mL of 0.2 μm -filtered seawater was passed through the aerosol filter and Sb_i determined before and after the filter. Soluble Sb_i in these aerosols was highest in the atmosphere overlying the higher surface water Sb_i region (Figure 7). Although we did not determine total aerosol Sb during the cruise, these soluble results are consistent with measurements of aerosol Sb at island sites in the northwestern Pacific that bound the IOC transect area (Okinawa, Midway, Shemya, Oahu [Arimoto *et al.*, 1989, 1996]). Moreover, Arimoto *et al.* [1996] attribute most of the aerosol Sb enrichment to anthropogenic emissions from Asia. Significantly, Ranville and Flegal [2005] made a similar argument for dissolved silver on the 2002 IOC cruise.

[26] While the North Pacific results confirm the previous assertion that Sb_i behaves as a scavenged element, the results for methyl antimony radically change the understanding of its behavior: from a relatively reactive species like methylated arsenic restricted to the upper water column [Cutter *et al.*, 2001; Ellwood and Maher, 2002] to one that behaves more like a conservative tracer (Figures 3 and 5). The only other metalloid displaying such behavior is germanium, for which the lack of reactivity leads to an oceanic residence time on the order of 10^6 years [Lewis *et al.*, 1985, 1989]. While the vertical profile at Station 9

(Figure 5) suggests a very long residence time ($>10^5$ y), concentrations in surface waters (Figure 7) showed some variation, with higher levels nearshore. This implicates a shorter residence time on the order of 10^3 – 10^4 y to minimize the effects from mixing. What is needed are profiles for the Atlantic Ocean using proper interference procedures (as above) to evaluate the amount of inter-basin fractionation and therefore a better estimate of methyl antimony's oceanic residence time. Although Benson and Cooney [1988] found a diatom-produced methylated antimony lipid, there have not been reports of free methyl Sb (e.g., MMSb) production by marine phytoplankton like arsenic [Andreae and Froelich, 1984]. However, fungus [e.g., Craig *et al.*, 1999] and bacteria [e.g., Jenkins *et al.*, 2002] do produce minor amounts under aerobic conditions. Nevertheless, if methyl antimony, like germanium, has a long oceanic residence time, its sources and sinks do not have to be readily detectable to explain the observed concentrations. Similarly, no removal processes (e.g., oxidation or demethylation) have been identified, but need to be examined to understand the cycling of these now enigmatic species.

4. Conclusions

[27] The use of combined surface water and vertical profile sampling allows the inputs and cycling of trace elements to be carefully examined, particularly in the North Pacific where potentially large atmospheric sources from Asia (mineral aerosols and anthropogenic emissions) enter an ocean that ranges from mesotrophic on its western boundary, to oligotrophic in the central gyres, to the rather special HNLC environment of the sub-Arctic gyre. For arsenic, this approach refines the relationship between As, P, and the production of presumed arsenate detoxification products, reduced and methylated arsenic. With surface water phosphate varying from <10 – 1500 nmol l^{-1} , the relative amounts of arsenite and methyl As appeared to support the model of Hellweger *et al.* [2003] that predicts primarily methyl As in oligotrophic waters and a predominance of arsenite in low phosphate/moderate productivity (transitional) waters. However, it should be noted that other mechanisms such as the regeneration of organic matter [e.g., Froelich *et al.*, 1985] or degradation of arsenosugars [Howard and Comber, 1989] could slowly produce methyl As and thus fit into the production scheme simulated by the Hellweger *et al.* [2003] model.

[28] The biogeochemical and perhaps ecological relevance of these findings is that since the residence times of these detoxification by-products with respect to oxidation back to arsenate is days (arsenite) to years (MMAs and DMAs), expenditure of metabolic energy by phytoplankton to perform these conversions varies with arsenic species produced (i.e., since arsenite is rapidly cycled back to arsenate in surface waters, the detoxification is not efficient). Other organic arsenic metabolites like arsenobetaine may be contained in the newly quantified dissolved As fraction in the upper water column of the western North Pacific. While this “extra” arsenic has been reported in coastal waters [Howard and Comber, 1989], the observations that it was 15–17% of the total inorganic arsenic in the open ocean, but apparently turned over on the same timescales as the lower molecular weight methyl As species, suggest that this arsenic fraction requires further examination.

[29] The data on the 2002 IOC cruise yielded data to refine the understanding of arsenic biogeochemistry. The dissolved inorganic antimony data provided more detail on its biogeochemical cycling; it does appear to be a mildly scavenged element and atmospheric input is a major controller of its abundance. However, the discovery of an analytical interferent and its resolution on the cruise, provided data for the Pacific that completely changes our understanding of methylated antimony. The findings of largely conservative depth profiles and the increase in methyl Sb’s residence time by a factor of $>10^3$ clearly indicate that this element is even less like arsenic than previously believed. Indeed, sources of these forms do not have to be large or even coupled to processes analogous to those for arsenic (i.e., in situ bioreduction and methylation). Methyl antimony data for other ocean basins using methods that can accurately quantify these forms will reveal how rapidly they are cycled. If they are as inert as methyl germanium forms, their importance to the antimony cycle will diminish and become more of an intellectual curiosity.

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