

Arsenic, antimony, and germanium biogeochemistry in the Baltic Sea

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ABSTRACT

Arsenic, antimony, and germanium species concentrations have been determined from five hydrographic stations along the central axis of the Baltic Sea from the Bornholm Basin to the Gulf of Finland. Arsenic and antimony concentrations are lower than in the open oceans and in most rivers. In the oxic waters, the pentavalent species of As and Sb predominate, while in the anoxic basins, the distribution shifts to the trivalent species and possibly some sulfo-complexes. Methylated arsenic species make up a large fraction of dissolved As in the surface waters, and methylated species of As, Sb, and Ge are detectable throughout the water column. Germanic acid concentrations are about ten times higher than in the ocean and much higher than can be accounted for by fluvial input. The vertical distributions of arsenic, antimony, and germanium within the Baltic Sea are controlled by biogeochemical cycling, involving biogenic uptake, particulate scavenging and partial regeneration. A mass balance including river and atmospheric inputs, exchange with the Atlantic through the Belt Sea, and removal by sediment deposition suggests that anthropogenic inputs make a significant contribution to the budgets of all three elements, with atmospheric fluxes dominating the input of Ge to the Baltic.

1. Introduction

The Baltic Sea is a brackish, landlocked sea surrounded by highly industrialized countries. It has been considered to be one of the most seriously polluted marine areas in the world (Kullenberg, 1981), receiving pollutants from domestic and industrial sources, from river inputs, atmospheric deposition, and via inflow through the Danish Straits (Belt Sea). The lack of systematic information on the distribution of arsenic in the Baltic Sea waters, despite concern about significant contamination, led us to investigate the concentrations and chemical speciation of arsenic, antimony and germanium, including the methylated species of these elements, in vertical hydrographic profiles at five stations in the Baltic Sea. This paper presents the results of this study as well as estimates of the fluxes of these elements in and out of the Baltic.

The circulation in the Baltic is controlled by a large freshwater input and the existence of a shallow sill (17 m depth) in the Danish Straits (Kullenberg and Jacobsen, 1981). Deep water is

supplied from the North Sea to the Baltic through the Kattegat in a continuous flow along the bottom of this strait (Fig. 1); this inflow water is, however, not saline enough to enter the deepest basins in the Baltic Sea. Replacement of these bottom waters occurs only during unusual meteorological conditions, on the average every 2–5 years. In the

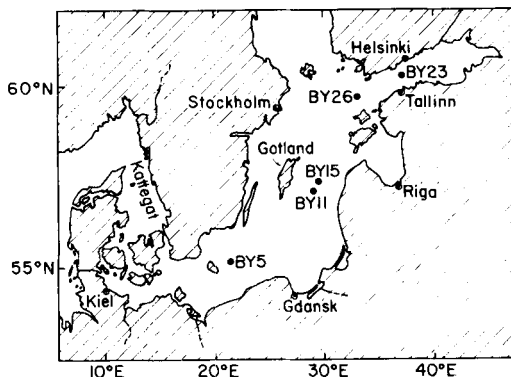


Fig. 1. Chart of the Baltic Sea with station positions.

intervening periods, oxygen becomes depleted in these deep basins, especially in the Gotland and Landsort Deep, and hydrogen sulfide is formed by bacterial sulfate reduction (Grasshoff, 1975; Fonselius, 1981). This phenomenon presents an opportunity to investigate the changes in chemical speciation of arsenic, antimony, and germanium as a function of the redox state of seawater.

2. Methods

2.1. Sampling

The seawater samples were collected on cruise no. 75 (June 10–15, 1981) of the R/V Poseidon of the Institut für Meereskunde, Kiel. Acid-cleaned samplers made from polycarbonate and stainless steel (COC sampler, Hydrobios, Kiel) were used on a standard hydrographic wire. The samplers enter the water closed to prevent contamination from the sea surface microlayer and by debris from the ship, and open at a depth of about 10 m. Samples were drawn from the samplers inside a laminar flow clean bench. One subsample for the determination of the reduced arsenic and antimony species was rapidly frozen by immersion into a dry ice/isopropyl alcohol bath; another subsample was acidified with 4 ml conc. HCl (Suprapur, Merck Inc.) per liter sample. All samples were stored in polyethylene bottles.

2.2. Analysis

The analytical methods have been previously described in detail (Andrae, 1977, 1983a; Andrae and Froelich, 1981; Andrae et al., 1981; Hambrick et al., 1984). The element species are selectively reduced with sodium borohydride to the corresponding hydrides. The hydrides are trapped at liquid nitrogen temperature; after the reaction is complete they are revolatilized by heating of the cold trap and separated by gas chromatography. They are detected by atomic absorption in either a quartz tube burner (arsenic and antimony) or in a graphite furnace modified for gaseous input (germanium). The detection limits of these methods are about 1 picomole per liter (pM) for the arsenic and antimony species; the precision at the levels observed in seawater is between 4% and 10% depending on the element species. For the germanium species, the detection limits are 8 pM,

20 pM and 40 pM for inorganic germanium, monomethylgermanium ion, and dimethylgermanium ion, respectively.

3. Results and discussion

Five stations were occupied along the axis of the Baltic Sea and the Gulf of Finland (Fig. 1) at the standard station positions established for the Baltic Year program. Stations BY11 and BY15 are in the Gotland Deep. The deepest part of this basin had been anoxic since the last flushing event in 1978 (Fonselius, 1981), with only a small addition of oxygenated bottom water in 1980 (Nehring and Franke, 1983). BY5 is in the Bornholm Basin where oxygen becomes occasionally depleted near the bottom. At the time of sampling, the oxygen levels in a layer of some 10–15 m above the bottom had been reduced to 30–40 μ M.

The hydrographic conditions in the central Baltic Sea during the study period are discussed using the example of station BY15 (Fig. 2). A seasonal thermocline at a depth of 15–25 m is present during the summer months. Most of the primary production occurs in the mixed layer above this thermocline. Salinity is almost constant at approximately 8‰ down to 50 m (upper isohaline layer), underlain by a broad halocline down to 150 m, with a deep isohaline layer (approximately 12‰) below 150 m. This stratification controls the distribution of oxygen, hydrogen sulfide, and the nutrients nitrate, phosphate and silicate. Oxygen concentrations are near saturation in the surface mixed layer, decline through the halocline, and become depleted near 180 m. H_2S first occurs near 170 m and increases in concentration towards the bottom. The depth interval of co-existing H_2S and O_2 (170–180 m) is termed the redoxcline. A nitrite maximum at approximately 160 m lies just above the sulfide zone. Nitrate concentrations are near zero in the surface mixed layer and in the anoxic zone, and show a broad maximum in the suboxic region of the halocline. Silicate and phosphate are also depleted in the isohaline upper layer and increase throughout the halocline and the anoxic zone. The distributions of the arsenic, antimony, and germanium species at BY15 are shown in Fig. 2; antimony and arsenic data for the remaining stations are given in Fig. 3. The original data (hydrography, nutrients, and arsenic, antimony,

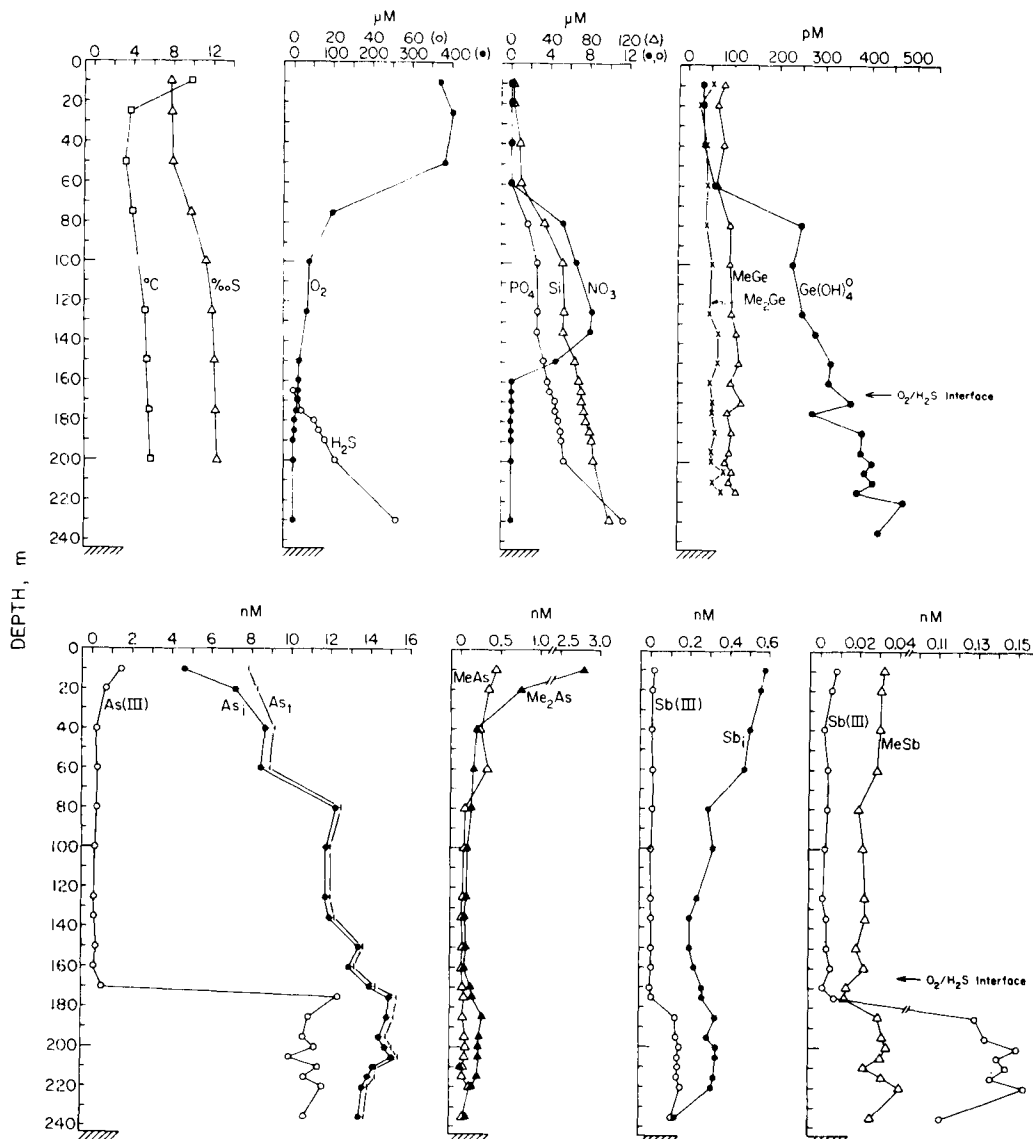


Fig. 2. Hydrographic and chemical data from station BY15 (As_t: total dissolved inorganic arsenic; As_i: total dissolved arsenic; MeAs: methylarsonic acid; Me₂As: dimethylarsinic acid; MeSb: methylstibonic acid; MeGe: mono-methylgermanium; Me₂Ge: dimethylgermanium). The bars between As_i and As_t represent the sum of the amounts of methylarsonic and dimethylarsinic acid present.

and germanium species) are tabulated in the Appendix.

3.1. Inorganic arsenic and antimony species

In the oxic zone, arsenic(V) and antimony(V) are always the most abundant oxidation states of these elements. However, the reduced forms of both

elements, arsenic(III) and antimony(III), are present at detectable levels throughout the water column (Figs. 2 and 3; antimony(III) was measured only at BY15 and BY26). There is always a maximum of arsenic(III) in the surface mixed layer, and at station BY15 and BY26 a surface maximum is evident for antimony(III) as

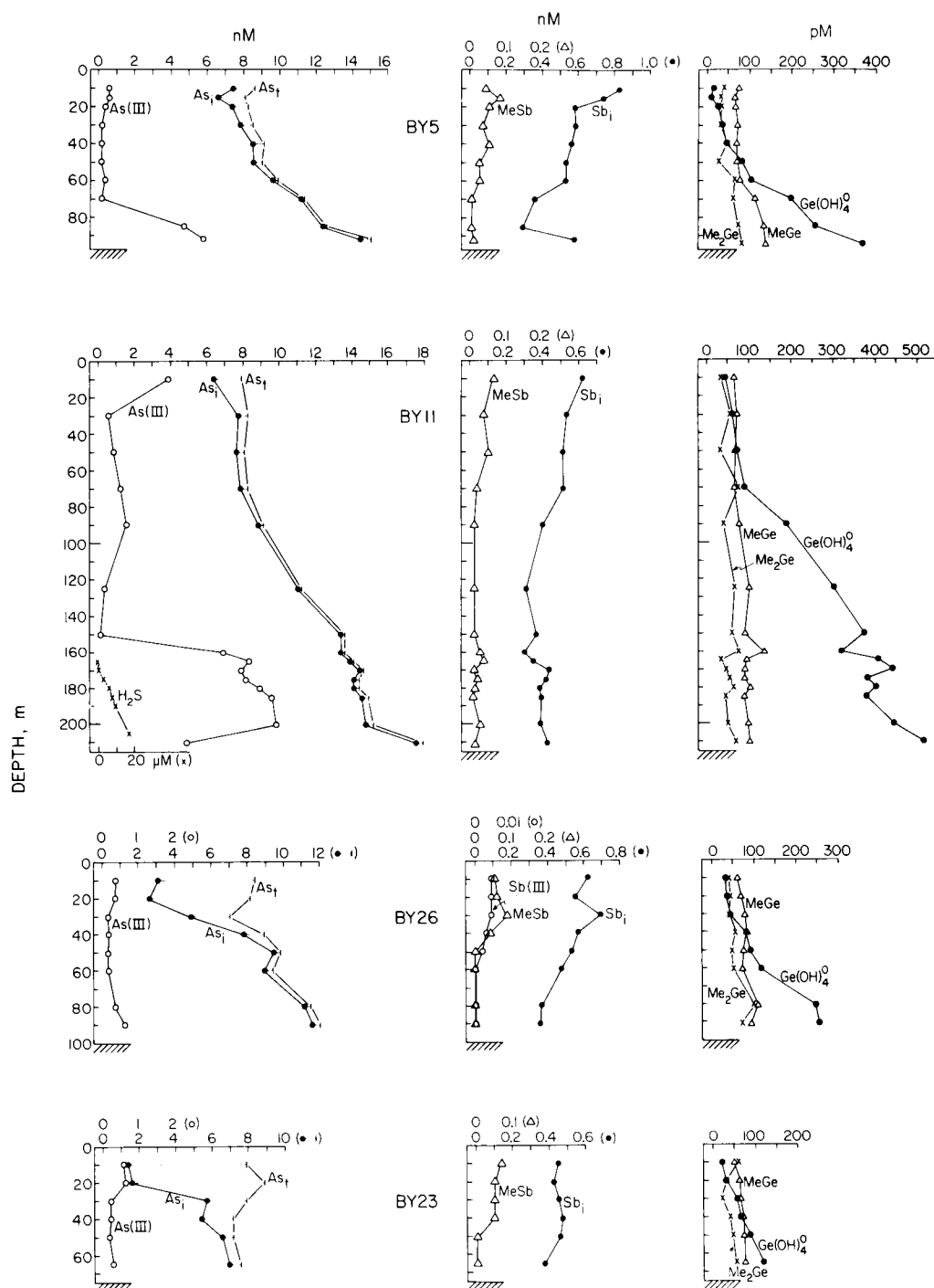


Fig. 3. Speciation of arsenic, antimony, and germanium at stations BY5, BY11, BY26, and BY23 (labelling as in Fig. 2).

well. A similar surface layer maximum has been observed for As(III) in the open ocean (Andreae, 1979) and for Sb(III) in Saanich Inlet, British Columbia (Bertine and Lee, 1983). This maximum is related to the presence of biological activity in this layer. Andreae and Klumpp (1979) have shown the ability of marine phytoplankton to reduce arsenic(V) to arsenic(III) in laboratory cultures. The presence of antimony(III) in marine macro-algae was shown by Kantin (1983), who found that up to 30% of the antimony in *Sargassum* sp. is in the trivalent form. Direct evidence for the reduction of arsenic and antimony to the trivalent form by marine phytoplankton is shown in Table 1, which reports the results of the chemical speciation analysis for arsenic and antimony in samples of phytoplankton (largely diatoms) from the eastern North Pacific. The extracts were prepared by grinding the plankton samples with 2 N HCl for 2 min in a tissue grinder. In all instances, the trivalent species are found to make up an important fraction of the inorganic arsenic and antimony in phytoplankton.

Total inorganic arsenic (As_i , the sum of As(III) and As(V)) is significantly depleted in the surface mixed layer compared to the concentration in the layer below the seasonal thermocline. Most of this apparent depletion can be accounted for by the presence of organoarsenic species (see below), so that total dissolved arsenic (As_d) does not show a strong gradient in the isohaline region between the surface and a depth of about 60 m. Below this zone, arsenate shows an increase in concentration with depth, comparable to the increase in the nutrient concentrations. The trivalent species As(III) and Sb(III) decrease to very low levels at the base of the seasonal thermocline, and their

concentrations remain low down to the sediment/water interface or the redoxcline, where increases are observed. At the shallowest stations BY23 and BY26 in the Gulf of Finland, the oxygen levels in the water column are not significantly depleted. Consequently, we only observe a small increase in As(III) near the sediment interface, which may be due to the diffusion of As(III) out of the sediments or to the remobilization of As at the sediment/water interface. The presence of high concentrations of As(III) in sedimentary pore waters and its diffusion into the overlying water column was shown by Andreae (1979). On the other hand, Carpenter et al. (1978) found only a very small flux of arsenic from the sediments in Puget Sound to the overlying water column. On the basis of a comparison between As in suspended particulates and underlying sediments, Peterson and Carpenter (1983) have suggested that As is remobilized at the sediment/water interface. At station BY5 in the Bornholm Basin, oxygen drops to 30–40 μ M in the two deepest samples below 70 m depth, but no H_2S is present. Here, As(III) increases dramatically in the O_2 -depleted zone with only a slight increase in total dissolved As, suggesting that in situ reduction of As(V) is taking place. At stations BY11 and BY15 in the Gotland Deep, As(III) remains low throughout the suboxic zone and increases only a few meters above the depth where H_2S becomes detectable. In the anoxic zone, it becomes the dominant arsenic species, but not all of the total inorganic arsenic is present as arsenite. In Saanich Inlet, an intermittently anoxic fjord on the coast of British Columbia, Peterson and Carpenter (1983) have observed similar steep gradients in the As(III)/As(V) ratio across the redoxcline.

Antimony(III) shows a behavior similar to

Table 1. Speciation of arsenic and antimony in phytoplankton from the eastern North Pacific (ng g⁻¹ dry weight)

Sample	As(III)	As(V)	MeAs*	Me ₂ As†	As _i ‡	% org.	Sb(III)	Sb(V)	Sb _i §
001	63	30	5.9	490	590	84	43	11	54
018	26	94	20	1290	1430	92	N.D.	220	220
033	27	429	27	740	1210	63	18	46	64

* As in the form of methylarsonic acid, $CH_3AsO(OH)_2$.

† As in the form of dimethylarsinic acid, $(CH_3)_2AsO(OH)$.

‡ Total soluble arsenic (in 2 N HCl).

§ Total soluble antimony (in 2 N HCl).

trivalent arsenic, with low concentrations below the surface layer, and an increase in the anoxic zone. The increase in Sb(III) occurs slightly deeper than for As(III); Sb(III) increases only after H_2S is already present. In addition, Sb(III) accounts for only 44% of total inorganic Sb in the anoxic zone; only in the deepest sample does this percentage increase to 93%, mostly as a result of a decrease in Sb_I rather than an increase in Sb(III). In the anoxic zone in Saanich Inlet, Bertine and Lee (1983) also found that not all of the dissolved Sb was present in the Sb(III) form. In contrast to arsenic, the total dissolved antimony concentration in the Baltic is consistently highest in the surface layer and decreases in the halocline. A slight increase in Sb_I is evident across the redoxcline at BY11 and BY15 and in the deepest sample at BY5.

The true speciation of arsenic and antimony in the anoxic zone thus remains unclear. While a sharp gradient in the ratio of the trivalent to pentavalent species is observed at the redoxcline, As(III) represents only an average of 56% and 76% of As_I at BY11 and BY15, respectively, and about 90% in Saanich Inlet, and Sb(III) makes up only 44% at BY15. On the basis of thermodynamic calculations, both elements should be completely in the trivalent form under anoxic conditions. The observed disequilibrium speciation may therefore represent a kinetically controlled condition as suggested for oxic waters by Andreae (1978) and for anoxic waters by Peterson and Carpenter (1983), or arsenic and antimony may be present in the form of thiocomplexes (thioarsenates and thioantimonates) which form in the presence of sulfide ion (Cotton and Wilkenson, 1972). Bertine and Lee (1983) have found evidence for the formation of such species when sulfide is added to seawater. Further work will be necessary to develop analytical procedures to characterize the chemical species of arsenic and antimony in anoxic waters containing hydrogen sulfide.

3.2. Methylated species of arsenic and antimony

Methylarsonic acid ($CH_3AsO(OH)_2$) and dimethylarsinic acid ($(CH_3)_2AsOOH$) are ubiquitous in the euphotic zone of the oceans (Andreae, 1979). The analogous antimony species (methylstibonic and dimethylstibinic acid) have also been observed in oceanic and estuarine waters (Andreae et al., 1981; Andreae, 1983b). In the

open ocean, the methylated species account for about 10% of the total dissolved arsenic and antimony. The methylated antimony species are present throughout the water column, while the methylarsenic compounds disappear below the euphotic zone. In the Baltic Sea, the methylantimony species showed a pattern similar to that found in the open ocean: the monomethyl species is more abundant than the dimethyl species, there is a tendency toward higher levels of methylantimony species in the surface layer (but methylstibonic acid is usually detectable throughout the water column), and the methylated forms make up about 10% of total antimony (Figs. 2 and 3). A slight secondary maximum appears in the anoxic zone at BY11 and BY15.

The methylated arsenic species show very high concentrations in the surface layer in the Baltic Sea with both the relative and the absolute concentrations increasing in a west-to-east direction (Figs. 2 and 3). In the surface water at BY5, the methylated species are 14% of total arsenic (0.4 nM methylarsonic acid, 0.77 nM dimethylarsinic acid); their concentration is similar to values observed in the open ocean. At BY23 in the Gulf of Finland, on the other hand, the methylarsenicals represent 83% of total dissolved As. The concentrations of 0.38 nM monomethyl and 6.15 nM dimethylarsinic acid are the highest we have yet observed in marine waters, three times higher than in eutrophicated waters of southern California (Andreae, 1979).

The methylarsenic species have been shown to be produced by pure cultures of marine phytoplankton (Andreae and Klumpp, 1979). In marine phytoplankton, methylarsonic and dimethylarsinic acids (or compounds which very easily hydrolyze to these species, e.g. the arsenosugars described by Edmonds and Francesconi (1981)) make up most of the soluble arsenic content (Table 1). In contrast, the methylantimony compounds were found neither by us in marine phytoplankton (Table 1) nor by Kantin (1983) in macro-algae. Digestion of the phytoplankton samples with conc. HNO_3 at 110° under pressure did not release significant additional amounts of As or Sb over those measured in a cold HCl digest. We suggest that the methylantimony compounds may be formed by bacteria, similar to the production of methylmercury compounds. This is in agreement with the observation that the methylantimony compounds are not as closely tied

to the euphotic zone as the methylarsenic compounds, which are released by phytoplankton.

The reason for the increase in the abundance of the methylarsenic compounds from west to east in the Baltic Sea is not clear, especially in view of the fact that the phytoplankton biomass decreases in the same direction (from $2.5 \mu\text{g}$ chlorophyll $a \text{ l}^{-1}$ at BY5 to $1.06 \mu\text{g}$ Chl $a \text{ l}^{-1}$ at BY23). Most likely, these differences reflect the dependence of the rate of output of methylarsenicals on phytoplankton species and the physiological state which has been observed in laboratory cultures (Andreae and Klumpp, 1979; Sanders and Windom, 1980) as well as the relative rates of methylation by algae and demethylation by bacteria which proceed concurrently in seawater (Sanders, 1979).

A second maximum in the concentration of both the methylarsenic and the methylantimony species is present in the anoxic zone (Fig. 3). The absence of a gradient near the sediment/water interface makes it unlikely that this is due to biosynthesis of methylarsenicals in the sediments as described from arsenic-polluted lakes in Ontario by Wong et al. (1977). On the basis of the data from the Baltic Sea presented here, it cannot be established with certainty whether the methylarsenicals are produced by bacteria in situ or are simply released as a consequence of the decomposition of algal matter sinking from the surface. The latter hypothesis appears more likely, since methylation of arsenic in anoxic marine environments has been observed neither in the pore waters of the Southern California Basins (Andreae, 1979) nor in laboratory experiments with marine mud (McBride et al., 1978). In view of the relatively small increase in methylarsenic levels compared to the increase of total arsenic across the redoxcline, and of the normally high proportion of methylated arsenic in marine plankton, decomposition of sinking plankton debris can readily explain the observed profiles of methylated arsenic species in the anoxic zone.

3.3. Inorganic and methylated species of germanium

Three dissolved germanium species were observed in the Baltic Sea: inorganic germanium, which is thought to exist in seawater as germanic acid ($\text{Ge}(\text{OH})_4^0$), and the organogermanium species, monomethylgermanium ($\text{CH}_3\text{Ge}^{3+}$) and dimethylgermanium ($(\text{CH}_3)_2\text{Ge}^{2+}$). The methylated species

are likely to be present in the form of the uncharged hydroxide complexes rather than the free ions, in analogy with the corresponding methyltin species (Byrd and Andreae, 1982). Trimethylgermanium was not found at a detection limit of 10 pM. The vertical distribution of inorganic germanium (Figs. 2 and 3) follows closely that of dissolved silica, suggesting congruent removal and regeneration of these two species. The methylated species, on the other hand, show only a small degree of vertical structure. This rules out the possibility of a significant production of these species in the anoxic basins of the Baltic. We have found the methylgermanium species to behave conservatively in the oceans and estuaries (within an experimental precision of approximately 15%) (Froelich et al., 1983). We have not been able to detect these species in river waters.

To test for conservative behaviour of the methylgermanium species in the Baltic, we have plotted their concentrations against salinity (Fig. 4). In the same figure, we show lines connecting a freshwater endmember which does not contain methylgermanium and a seawater endmember which contains 300 ± 40 pM of monomethylgermanium and 120 ± 40 pM of dimethylgermanium, our estimates of the average seawater concentration of these species based on data from the Pacific and Atlantic Oceans. In the case of monomethylgermanium, the points fall reasonably well within the predicted range. The fit would be improved if one allowed for a small amount of monomethylgermanium in the freshwater input (approximately 10 pM). For dimethylgermanium, there appears to be a somewhat more pronounced deviation from the values predicted on the basis of conservative mixing, especially in the less saline samples. This could be due to atmospheric input of dimethylgermanium, since we consistently detect this species at concentrations of some tens of pM in rainwater. When the effect of this atmospheric flux, based upon an average concentration of 26 pM in rainwater, is considered, the dotted lines in Fig. 4b are obtained, which give a very good fit to the data.

3.4. Cycling of arsenic, antimony, and germanium in the Baltic Sea

The vertical distribution of arsenic suggests that it is taken up similarly to the nutrient elements by biological activity in the surface mixed layer. This

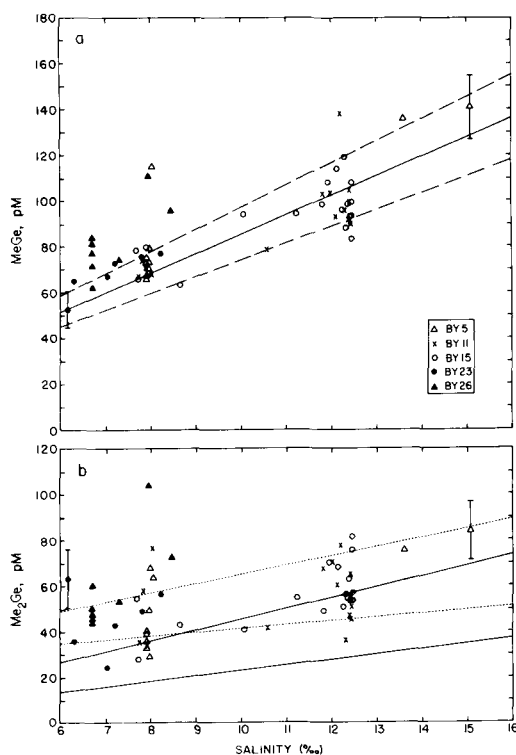


Fig. 4. Plot of the methylated germanium species versus salinity (MeGe: monomethylgermanium; Me₂Ge: dimethylgermanium). The lines represent linear mixing models between seawater and freshwater endmembers (see text). Error bars are only indicated for the highest and lowest samples; they are of proportionate size for the other samples. The dashed lines in Fig. 4a represent the range of uncertainty of the saline endmember composition. In Fig. 4b, the range of expected values is drawn in solid lines for a model without, in dotted lines for a model with atmospheric input of dimethylgermanium.

is in agreement with our previous observations of arsenic cycling in the oceans (Andreae, 1979). Arsenic is then at least partially regenerated at depth, especially near the anoxic interface. The arsenic-salinity relationships in the Baltic have been plotted in Fig. 5. The profile for each station begins at low salinities and low arsenic concentrations, and shows an increase of arsenic with depth at constant salinity, indicating rapid regeneration in the seasonal thermocline. No consistent deviations different from linear mixing are evident in the halocline region. Below the redoxcline (arrow in Fig. 5) at stations BY11 and BY15, arsenic

continues to increase at nearly constant salinity as a consequence of regeneration of arsenic in the anoxic regime.

The average total arsenic concentrations within the Baltic (8 nM As at 9‰ salinity) are much lower than can be explained by simple mixing of river waters (0‰ salinity, 19 nM As) and Atlantic surface seawater (35‰ salinity, 20 nM As). Thus, net removal of As must be occurring within the Baltic, presumably by incorporation of As into biogenic debris, a portion of which is buried without regeneration in the underlying sediment.

The highest concentrations of antimony occur at the surface (low salinity in Fig. 5) and then decrease with depth in the isohaline layer. This decrease with depth suggests that antimony is scavenged by particles throughout this layer. Antimony, therefore, does not behave like arsenic, which is taken up by phytoplankton in the surface layer due to the similarity of the arsenate ion to the phosphate ion. Phosphorus(V) and arsenic(V) both form tetraoxo-anions with coordination number 4. Antimony(V), on the other hand, due to its large ionic radius and lesser charge density, forms the hexahydroxo-anion, Sb(OH)₆⁻, which does not resemble the phosphate ion and is therefore not taken up by phytoplankton. The Sb(OH)₆⁻ ion is expected to have a moderate affinity towards particle surfaces, as the normally high surface-affinity of polyhydroxo complexes is opposed by the electrostatic repulsion from the negative charge present on estuarine particles.

As was observed for arsenic, no consistent deviations from conservative behavior are evident for antimony in the halocline region. Below the redoxcline (arrows), antimony increases slightly (with the exception of the deepest point at BY15), similar to arsenic. The minimum antimony concentrations are found at or just above the redoxcline, suggesting that antimony removal is taking place here by scavenging onto iron hydroxyoxide precipitates forming in the suboxic layer above the sulfide zone. Kremling (1983) has presented evidence for the redox-regulated removal of several transition metals in the same zone on samples collected during the same cruise.

The total antimony concentrations in the Baltic water column also imply that a significant amount of removal to particulate phases must be taking place. Even in the surface waters, the antimony concentration is lower than can be explained on the

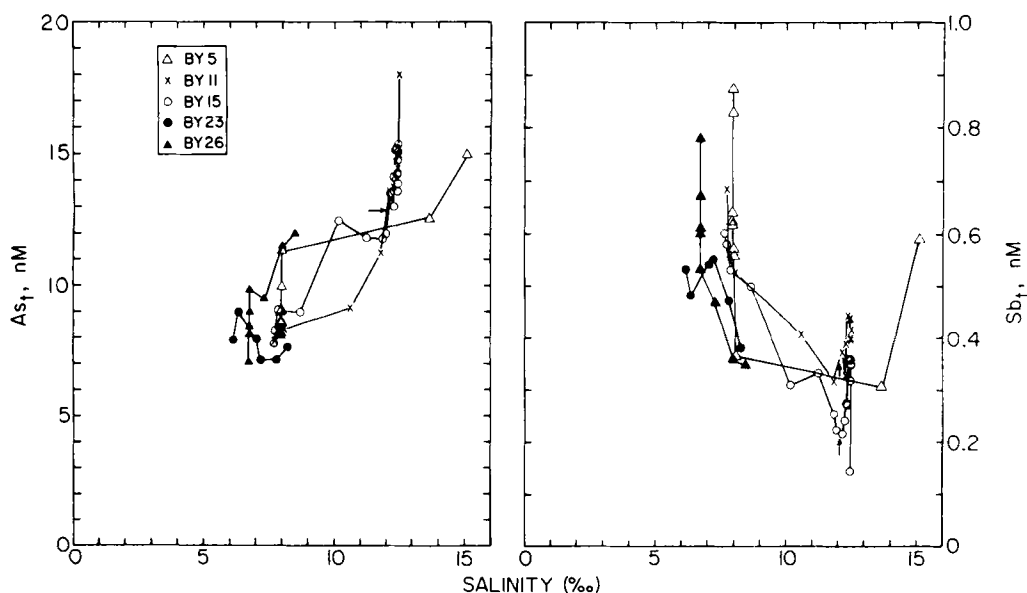


Fig. 5. Plots of total dissolved arsenic and antimony versus salinity.

Table 2. Arsenic, antimony, and germanium concentrations in European and North American rivers

	As, nM	Sb, nM	Ge, pM
Rhein, Bregenz, 12 May 82	10.9	0.66	27
Rhein, Oppenheim, 12 April 81	15.8	1.91	8.8
Rhein, Mainz, 6 December 82	18.8	4.34	233
Main, Frankfurt, 13 April 81	21.7	2.57	111
Donau (Danube), Neuberg, 10 May 82	6.03	<0.03	80
Tejo, Santarem, 30 April 82	54.7	0.84	48
Tejo, Vilafranca, 16 December 82	67.3	1.88	240
Guadalquivir, Coria, 18 December 82	127	4.43	223
Elbe, below Hamburg, 9 June 81	85.5	2.10	1900
Rhône, Arles, 5 September 81	80.0	2.75	
Isère, Domène, 2 September 81	34.6	2.68	
Average, European rivers	46	2.04	110*
	(3540)	(249)	(8.0 ng l ⁻¹)
Yukon, Pilot Station, AK, average of 8 samples, August 81–September 82	6.41	2.73	121
	(480)	(332)	(8.8 ng l ⁻¹)
St. Lawrence, Massena, NY, average of 5 samples, December 81–August 82	7.15	1.62	107
	(536)	(197)	(7.8 ng l ⁻¹)

* Geometric mean.

basis of mixing of seawater (1.2–1.4 nM Sb: Andreae, 1983b; Andreae et al., 1981; Bertine and Lee, 1983; van der Sloot et al., 1977) with river waters, which rarely show concentrations below 1.0 nM Sb (Table 2). In the deep waters of the Baltic, the dissolved Sb concentration is actually

lower than would be expected to result from the mixing of seawater with a river water totally free of antimony. These observations are in contrast to our data on the behaviour of antimony in estuaries (Andreae, 1983b; Andreae et al., 1983), which show no evidence for Sb removal by association

with particles, as well as the work on Sb in the marine water column (Andreae et al., 1981; Bertine and Lee, 1983; Brewer et al., 1972; and unpublished data), which suggests a conservative behaviour of Sb in the ocean. The removal of Sb is probably more pronounced in the Baltic compared to river estuaries because of a high particle flux and a longer water residence time.

The vertical profiles of germanium at all stations (Figs. 2 and 3) resemble those of dissolved silica, displaying low concentrations in surface water, and high concentrations in the deep and bottom waters. This distribution is similar to that observed in the open ocean and in estuaries (Froelich and Andreae, 1981) and is presumably due to uptake from surface waters by biological activity, and regeneration of the falling biogenic particulates in the deeper water. We have previously proposed that in the open ocean, siliceous organisms incorporate dissolved Ge as a fortuitous surrogate for Si (a "superheavy stable isotope"), since the chemistries of the two elements are so similar, and Ge is in such low concentrations compared to Si.

This hypothesis is supported by the results obtained in the Baltic. The close linear correlation between Ge and Si ($r^2 = 0.95$, $n = 59$, $P < 0.001$) suggests congruent removal and regeneration of these elements (Fig. 6). There is no clear systematic

change in the mole ratio Ge/Si in either the horizontal or the vertical dimensions; the best-fit value for this ratio in the Baltic is 4.8×10^{-6} . A similar ratio ($\approx 3.2 \times 10^{-6}$) has been observed in Pettaquamscutt Fjord, a small, anoxic estuary in southern Rhode Island, where atmospheric inputs also must be expected to play an important role in the supply of Ge. In the open oceans, Ge and Si are correlated to a similar high degree but the Ge/Si ratio is much lower, about 0.7×10^{-6} (Froelich and Andreae, 1981). As we show below, the high Ge/Si ratio results from an atmospheric Ge input to the Baltic about 10 times higher than that of the river input. Presumably, biological recycling within the Baltic reflects the average ratios in the inputs of Ge (mostly atmospheric) and Si (mostly rivers) which are very different from the ocean.

3.5 Input flux estimates

The Baltic receives its supply of arsenic, antimony, and germanium predominantly through the rivers entering it from the surrounding countries and by atmospheric transport and deposition. Since there are no available data on the concentrations of arsenic, antimony and germanium in the rivers discharging into the Baltic, we used data obtained in our laboratory on the concentrations of these elements in rivers from Europe and North America (Table 2). To represent the rivers entering the Baltic from the Scandinavian shield area, we selected the composition of the Yukon River, Alaska. The Yukon drains a region rich in siliceous rock of Paleozoic and Precambrian age (with considerable mineralization high in As) and in a climate zone similar to northern Scandinavia. The St. Lawrence River, which drains the Great Lakes, was used to estimate the composition of the Neva River, which drains Lake Ladoga. For the rivers entering the Baltic along its southern periphery, we used the average of the European rivers in Table 2. The river discharge data were taken from Grasshoff (1975), who estimates a total discharge into the Baltic of approximately $450 \text{ km}^3 \text{ yr}^{-1}$. Estimates for the average concentrations of As, Sb, and Ge in the rivers entering the Baltic and the river inputs obtained on this basis are shown in Table 3.

The estimate of atmospheric inputs is based on measurements of the atmospheric concentrations of arsenic and antimony (3.0 and 1.4 ng m^{-3} , respectively) at a lighthouse off Kiel, Germany. The values used in Table 3 represent the averages

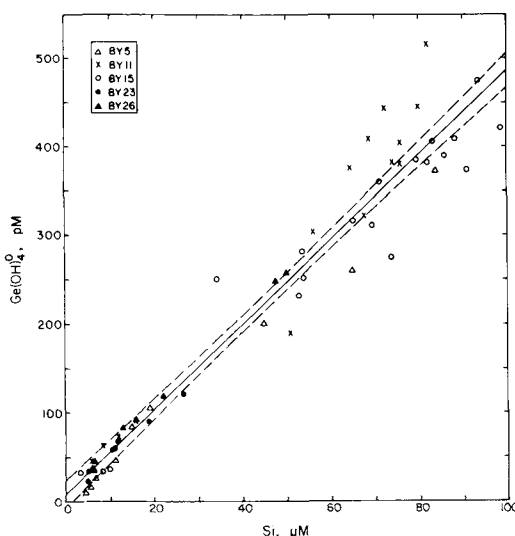


Fig. 6. Dissolved germanic acid versus dissolved silica in the Baltic Sea. The regression line is shown with 95% confidence limits for the regression.

Table 3. *Inputs of arsenic, antimony, and germanium to the Baltic Sea*

	Rivers		Atmospheric deposition						
			Aerosol conc.	Dry depos. velocity	Dry depos. flux	Washout ratio	Wet depos.	Total atmospheric depos.	Atmos- pheric/ fluvial flux
	Av. conc.* (ng l ⁻¹)	Flux (10 ⁶ g yr ⁻¹)	conc. (ng m ⁻³)		flux (10 ⁶ g yr ⁻¹)				
As	1440	648	3.0	0.37	130	0.22	151	281	0.43
Sb	269	121	1.4	0.15	24	0.16	51	75	0.62
Ge	8.1	3.6	0.6	0.25	18	0.2	28	46	12.8

* Weighted mean of rivers representing geochemically similar regions in Europe and North America.

of 12 samples collected from May to October 1981 (Schneider [Institut für Meereskunde, Kiel], personal communication, 1982). They are in agreement with data from other sites in northern Europe: the average As and Sb concentrations from a large number of samples from northern Europe (north and central Norway, Denmark, Shetland, and the North Sea: Rahn, 1976) are 3.1 and 1.3 ng m⁻³. These sites have been selected to represent areas remote from sources of these elements. No data on the atmospheric germanium concentrations in the Baltic region were available. We estimated this concentration on the basis of the Ge/As ratio observed in urban aerosols (0.21 ng m⁻³; Rahn, 1976) and the arsenic concentrations measured at Kiel lighthouse. We considered two modes of deposition of atmospheric particulates to the Baltic: dry deposition, estimated on the basis of the deposition velocities given by Slinn et al. (1978), and wet deposition, which we calculated on the basis of the washout ratio (rainwater concentration divided by aerosol concentration) given by the same authors. The area of the Baltic was taken to be 370,000 km² (Grasshoff, 1975) and the annual rainfall amount 229×10^{12} l (Rodhe et al., 1980). The resulting fluxes are given in Table 3. In view of the uncertainties in the estimates of the atmospheric concentrations, the deposition velocities and the washout ratios, the resulting fluxes must be considered rough estimates only. In order to obtain a check on the validity of these flux estimates we calculated an emission inventory for arsenic and antimony for the countries which represent the source regions for air pollutants to the Baltic: Belgium, Denmark, Finland, East and West Germany, Ireland, the Netherlands, Norway, Poland, Sweden, and the United Kingdom (Rodhe et al., 1980). The emission rates for the different countries

Table 4. *Comparison of emissions in airmass source areas with deposition in Baltic (10⁶ g yr⁻¹)*

	Emissions	Deposition to Baltic	% deposited in Baltic
As	2,423	281	11.6
Sb	367	75	20
Ge	180	46	26
Ca	1,084	80	7.4
Pb	38,800	2,400	6.2
Ni	4,722	700	15
Cu	4,524	1,400	31
Zn	33,470	6,000	18
Cr	6,518	270	4.1
V	10,408	600	5.8

were based on the compilation of Pacyna (1982). For comparison, we calculated the emission rates for the same countries for cadmium, lead, nickel, copper, zinc, chromium and vanadium.

The emissions of germanium from the European countries were not estimated by Pacyna (1982). Since most of the atmospheric germanium input is from the combustion of coal, we used the amount of coal burned in the states listed above (520 million tons per year in 1977: Wilson, 1980), the emission factor for the production of flyash (0.014: National Academy of Sciences, 1981), and the content of germanium in flyash (25 p.p.m.: Smith et al., 1979) to predict the germanium emission. The results of these calculations are summarized in Table 4. Comparison of the amounts emitted in the airmass source regions to the Baltic and the deposition estimates of Rodhe et al. (1980) shows that between about 4% and 30% of the emitted heavy metals end up in the Baltic. Our deposition estimates represent a similar proportion of the As, Sb, and Ge emissions being deposited in the Baltic.

It must be recognized of course that all the estimates given in Tables 3 and 4 represent only the order of magnitude of the flux (the values in Tables 2–4 have not been rounded only to prevent the introduction of numerical errors in subsequent calculations).

The ratio between the atmospheric and riverine fluxes shows a progression from arsenic, for which the flux to the Baltic is carried mostly by the rivers, to germanium, for which the atmospheric transport predominates. This strong atmospheric component in the transport of germanium may explain the anomalously high Ge/Si ratios in the Baltic. The average Ge concentration in the European rivers in Table 2 is 8.0 ng l^{-1} (110 pM). Using the average silicate concentration in rivers from the north-eastern U.S. and Alaska (approximately $70 \text{ } \mu\text{M}$: Briggs and Fickes, 1977), we estimate the molar Ge/Si ratio of the riverine input to be about 1.6×10^{-6} . A significant atmospheric input of Ge is therefore required to raise the Ge/Si ratio in the Baltic to the observed value of about 5×10^{-6} .

Since the atmospheric flux makes a significant contribution to the input of all three elements into the Baltic, and since practically all of the atmospheric burden of these elements in this region is anthropogenic, we must conclude that anthropogenic inputs are an important component in the mass balance of arsenic and antimony, and probably are dominant in the case of germanium. The anthropogenic component in the river transport of arsenic, antimony, and germanium is also likely to be considerable, but cannot be documented on the basis of present data.

3.6. Mass balance

We can further test our input model by attempting a mass balance for As, Sb, and Ge in the Baltic. The fluxes we will consider here are the river and atmospheric inputs discussed above, exchange through the Belt Sea with Atlantic Ocean surface water, and removal by sedimentation within the Baltic. The box model in Fig. 7 depicts our simplified idea. River flow into the Baltic is about $450 \times 10^{12} \text{ l yr}^{-1}$ (Grasshoff, 1975). Since the Baltic has an average salinity of 9‰ (Kullenberg and Jacobsen, 1981), we take the export as this salinity. Salt balance then requires that input to the deep Baltic of Atlantic surface water (at 35‰) be $116 \times 10^{12} \text{ l yr}^{-1}$, and export of Baltic water (at 9‰) on the surface be about $566 \times 10^{12} \text{ l yr}^{-1}$. It must be emphasized that these fluxes do not represent the

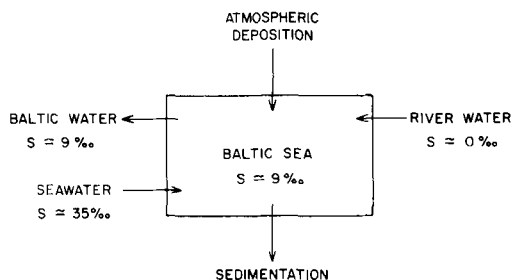


Fig. 7. Simplified one-box model for the mass balance in the Baltic Sea.

actual exchange of water across a given section, e.g. through the Kattegat, but rather the flux of the endmembers of the mixing process in a simple one-box model. They are therefore appropriate for the net transport of solutes rather than for the gross water exchange.

Our mass balance estimate is shown in Table 5. The river concentrations and fluxes and the atmospheric fluxes are taken from Table 3. The concentrations of As, Sb, and Ge in inflowing Atlantic surface waters are taken as $\text{As} = 1.5 \text{ } \mu\text{g l}^{-1}$ (Burton et al., 1983; van der Sloot et al., 1977; Waslenchuk, 1978; and unpublished data), $\text{Sb} = 0.16 \text{ } \mu\text{g l}^{-1}$ (Andreae, 1983b; Andreae et al., 1981; Bertine and Lee, 1983; van der Sloot, 1977), and $\text{Ge} \leq 1 \text{ ng l}^{-1}$ (Froelich and Andreae, 1981). Concentrations of surface waters at station BY5 are used to represent the composition of out-flowing Baltic waters. Thus our model predicts the net flux imbalance for each element, which we take to represent the predicted sedimentation flux (Table 5).

We estimate the observed rate of removal by sedimentation (to compare with our predicted rates) by assuming a sedimentation rate for the Baltic of 0.5 mm yr^{-1} . Higher rates have been observed for some areas in Kiel and Eckernförde Bays (1.2 mm yr^{-1} : Erlenkeuser et al., 1974), but rates of a few tenths of a millimeter per year have been estimated for the Baltic proper (Hallberg, 1979). The wet bulk density of the sediment is assumed to be 0.4 g cm^{-3} , in agreement with data quoted by Erlenkeuser et al. (1974). These data result in an estimate for the sediment deposition rate in the Baltic of $74 \times 10^{12} \text{ g yr}^{-1}$. Boström et al. (1983) derived a similar value of $66 \times 10^{12} \text{ g yr}^{-1}$ for the total dry matter deposition of the Baltic. With concentrations of 15 p.p.m. for arsenic (average of 163 samples from the Baltic: Hallberg,

Table 5. Mass balance for arsenic, antimony, and germanium in the Baltic Sea; fluxes are expressed in units of 10^6 g yr^{-1}

	Inputs				Outflow†	Sedimentation predicted from mass balance	Sedimentation observed‡
	Rivers	Atmosphere	Seawater inflow*	Total inputs			
As	650	280	170	1100	380	720	1100
Sb	120	75	20	220	50	160	110
Ge	3.6	45	<0.1	50	1.4	50	?

* $116 \times 10^{12} \text{ l yr}^{-1}$; 35‰S, $1.5 \mu\text{g As l}^{-1}$, $0.16 \mu\text{g Sb l}^{-1}$, $<1 \text{ ng Ge l}^{-1}$.

† $566 \times 10^{12} \text{ l yr}^{-1}$; 9‰S, 675 ng As l^{-1} , 85 ng Sb l^{-1} , 2.5 ng Ge l^{-1} .

‡ $74 \times 10^{12} \text{ g sediment yr}^{-1}$; 15 ppm As, 1.5 ppm Sb.

1979) and 1.5 p.p.m. for antimony (average concentration in recent sediments from Puget Sound: Crecelius et al., 1975), the sedimentation fluxes presented in Table 5 have been calculated. The mass balance shows good agreement (better than a factor of two) for As and Sb in view of the uncertainties of the individual estimates. There are no Ge or opaline Si data for sediments in the Baltic, so our predicted sedimentation flux for Ge cannot be tested. We would predict on the basis of the model that the non-detrital Ge concentration of these sediments is about 0.6 p.p.m.

In a study on the mass balance of the major crustal elements and some trace elements in the Baltic, Boström et al. (1983) found poor agreement between inputs and sedimentation outputs for the crustal elements and attributed this to the remobilization of glacial materials in the shallow regions of the Baltic and their redeposition in deeper areas. On the other hand, for copper and zinc, two elements for which pollutant inputs are likely to be of importance, they observed a rather good closure of the mass balance, similar to the conclusions reached for arsenic and antimony in this paper.

4. Conclusions

The speciation of arsenic and antimony in the Baltic Sea is controlled by the biogeochemical cycling of these elements. Methylated and reduced species are present in the biologically active surface layer. In the anoxic basins, both elements are reduced to a large extent to the trivalent species, but uncertainty persists with regard to the role of sulfocomplexes of arsenic and antimony in the sulfide zone. Germanium is present as dissolved germanic acid and as mono- and dimethyl-

germanium species. The methylated species show essentially conservative mixing behavior with no evidence of inputs by methylation processes in the anoxic zone.

Arsenic is removed by biological uptake and antimony by particulate scavenging in the water column, they are only partly regenerated in the anoxic environment. Inorganic germanium follows very closely the distribution of dissolved silica. Anthropogenic inputs resulting from atmospheric transport and deposition make substantial contributions to the budgets of arsenic, antimony, and especially germanium in the Baltic Sea. In the case of germanium, the atmospheric input predominates over the river flux by an order of magnitude.

A mass balance for arsenic and antimony in the Baltic based on river and atmospheric transport, exchange with the Atlantic through the Belt Sea, and sedimentation yields consistent results.

5. Acknowledgments

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6. Appendix

Hydrographic and chemical data from the June 1981 cruise of the R/V Poseidon in the Baltic Sea. "—" indicates "not determined". Hydrographic, nutrient, and chlorophyll data were determined on board by members of the Institut für Meereskunde, Kiel

Station B75 (11 June 1981; 55°15'N, 15°59'E; water depth 98 m)

Sample no.	Depth (m)	T (°C)	S (‰)	O ₂ (μM)	ΣH ₂ S (μM)	pH	NH ₄ ⁺ (μM)	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	PO ₄ ³⁻ (μM)	SiO ₂ (μM)	Chl <i>a</i> (μg l ⁻¹)	MeAs (nM)	MeAs (nM)	As(III) (nM)	As(V) (nM)	As ₅ (nM)	As ₇ (nM)	MeSb (nM)	MeSb (nM)	Sb(III) (nM)	Sb(V) (nM)	Sb ₅ (nM)	Sb ₇ (nM)	Ge(OH) ₂ (pM)	MeGe (pM)	MeGe (pM)
1	10	11.91	7.91	388	—	8.29	0.2	0.05	<0.05	0.14	5.6	—	0.40	0.77	0.57	6.87	7.44	8.62	0.045	0.006	—	—	0.82	0.87	16.1	75.2	40.8
2	15	11.72	7.91	382	—	8.38	0.2	0.05	<0.05	0.14	4.5	2.50	0.40	1.12	0.58	6.01	6.59	8.11	0.082	0.007	—	—	0.74	0.83	10.2	66.0	33.2
3	20	9.58	7.91	380	—	8.39	0.2	0.05	<0.05	0.22	6.7	1.92	0.36	0.50	0.34	7.07	7.41	8.26	0.054	0.005	—	—	0.58	0.64	26.2	67.6	36.2
4	30	7.48	7.91	388	—	8.23	0.2	0.05	<0.05	0.42	5.9	1.79	0.36	0.36	0.18	7.64	7.82	8.54	0.036	<0.004	—	—	0.58	0.62	37.4	73.1	33.1
5	40	—	7.96	380	—	8.10	0.2	0.02	<0.05	0.63	11.2	0.96	0.36	0.28	0.11	8.39	8.54	9.18	0.054	<0.006	—	—	0.56	0.62	46.7	70.5	49.5
6	50	3.99	7.97	372	—	7.78	0.2	<0.02	<0.05	0.68	14.9	0.74	0.37	0.11	0.14	8.43	8.57	9.05	0.026	<0.006	—	—	0.53	0.56	84.1	73.3	29.6
7	60	3.40	7.98	363	—	7.70	0.2	<0.02	<0.05	0.90	19.1	0.41	0.14	0.17	0.31	9.30	9.61	9.93	0.027	<0.006	—	—	0.52	0.56	106	79.5	68.2
8	70	3.77	8.04	360	—	7.65	0.2	<0.02	<0.05	0.61	44.9*	0.40	0.02	0.08	0.20	11.1	11.3	12.6	0.006	<0.006	—	—	0.35	0.37	201	115	63.9
9	85	6.16	13.60	44	—	7.12	0.3	<0.02	<0.05	0.67	64.9*	—	0.02	0.17	4.71	7.70	12.4	12.6	<0.006	<0.006	—	—	0.30	0.31	260	136	75.5
10	95	6.05	15.08	32	—	7.12	0.3	<0.02	<0.05	0.78	83.8*	—	0.04	0.52	5.79	8.71	14.5	15.1	0.012	<0.006	—	—	0.57	0.59	373	141	83.8

* SiO₂ data determined at Florida State University.

Station B77 (12 June 1981; 57°04'N, 19°50'E; water depth 215 m)

Sample no.	Depth (m)	T (°C)	S (‰)	O ₂ (μM)	ΣH ₂ S (μM)	pH	NH ₄ ⁺ (μM)	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	PO ₄ ³⁻ (μM)	SiO ₂ (μM)	Chl <i>a</i> (μg l ⁻¹)	MeAs (nM)	Me-A ₅ (nM)	As(III) (nM)	As(V) (nM)	As ₅ (nM)	As ₇ (nM)	MeSb (nM)	Me-Sb (nM)	Sb ₅ (nM)	Sb ₇ (nM)	Sb ₃ (V) (nM)	Sb ₃ (III) (nM)	Ce(OH) ₃ ² (pM)	MeCe (pM)	Me-Ge (pM)	
1	10	9.84	7.74	381	—	8.24	0.12	0.06	0.12	0.17	5.9	1.64	0.43	1.07	3.88	2.51	6.39	7.89	0.066	<0.006	0.014	0.60	0.62	0.68	45.6	66.8	35.5	
2	30	3.01	7.82	407	—	7.88	0.36	0.03	0.43	0.34	8.3	0.29	0.32	0.16	0.57	7.15	7.72	8.20	0.036	<0.006	—	—	0.53	0.56	62.9	73.8	57.8	
3	50	2.81	7.91	383	—	7.77	0.20	0.03	0.12	0.40	11.9	0.29	0.31	0.15	0.87	7.15	7.72	8.20	0.036	<0.006	0.009	0.50	0.51	0.56	73.7	71.0	33.5	
4	70	2.52	8.03	361	—	7.63	0.16	0.03	<0.05	0.46	15.7	—	0.28	0.13	1.27	6.73	7.60	8.05	0.048	<0.006	—	—	0.51	0.53	91.1	68.1	76.6	
5	90	4.44	10.58	37	—	7.00	0.10	0.03	6.36	2.71	50.9	—	0.12	0.12	1.55	7.31	8.86	9.10	0.011	<0.006	—	—	0.40	0.41	190	78.7	41.4	
6	125	—	11.81	35	—	6.99	0.15	0.03	7.42	2.82	56.0	0.10	0.05	0.05	0.36	10.7	11.1	11.2	0.011	<0.006	—	—	0.31	0.32	303	103	67.3	
7	150	5.30	12.12	21	—	6.97	<0.05	<0.02	5.16	3.12	64.5	—	0.05	0.12	0.11	13.3	13.4	13.6	0.011	<0.006	—	—	0.36	0.37	375	92.9	60.1	
8	165	—	—	9	—	—	<0.05	0.46	1.99	3.53	65.4	—	—	—	—	6.94	6.45	13.4	13.6	0.029	<0.006	—	—	—	—	—	—	—
9	165	—	—	10	<0.1	—	0.19	<0.02	0.05	3.28	68.7	—	0.08	0.13	8.32	5.58	13.9	14.1	0.039	<0.006	—	—	0.30	0.33	321	138	77.5	
10	170	—	—	10	1.0	—	1.48	0.02	<0.05	4.71	72.3	—	0.12	0.08	7.90	6.54	14.4	14.6	0.014	<0.006	—	—	0.35	0.39	408	95.7	35.9	
11	175	5.55	12.41	6	3.5	7.08	3.19	<0.02	<0.05	4.80	74.1	0.00	0.15	0.16	8.13	5.97	14.1	14.4	0.021	<0.006	—	—	0.43	0.44	443	91.4	46.6	
12	180	—	—	4	6.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.42	0.44	382	90.4	55.1	
13	185	—	—	5	8.0	—	5.42	<0.02	<0.05	4.88	75.9	—	0.16	0.17	8.94	5.16	14.1	14.4	0.014	<0.006	—	—	0.38	0.40	404	104.5	64.9	
14	190	5.58	12.43	0	10.5	7.06	6.37	<0.02	<0.05	5.06	77.1	0.06	—	0.17	9.60	4.98	14.6	14.9	0.008	<0.006	—	—	0.39	0.40	380	90.0	45.3	
15	205	5.64	—	0	17.5	7.06	7.48	0.02	<0.05	5.46	81.9	0.09	0.16	0.20	9.86	4.94	14.8	15.2	0.028	<0.006	—	—	0.39	0.42	445	99.3	50.0	
16	210	—	—	—	—	—	—	—	—	—	—	—	0.17	0.20	4.95	12.6	17.6	17.9	0.014	<0.006	—	—	—	—	—	103	70.0	

Station B715 (13 June 1981; 57°20'N, 20°03'E; water depth 244 m) (* = SiO_2 data determined at Florida State University)

Sample no.	Depth (m)	T (°C)	S (‰)	O ₂ (μM)	ΣH ₂ S (μM)	pH	NH ₄ ⁺ (μM)	NO ₂ ⁻ (μM)	NO ₃ ⁻ (μM)	PO ₄ ³⁻ (μM)	SiO ₂ (μM)	Chl <i>a</i> (μg l ⁻¹)	MeAs (nM)	MeAs-As (nM)	As(III) (nM)	As(V) (nM)	As _T (nM)	MeSb (nM)	MeSb-Sb(III) (nM)	Sb(V) (nM)	Sb _T (nM)	Ge(OH) ₂ (pM)	MeGe (pM)				
1	10	9.75	7.68	370	—	8.40	0.13	0.02	0.05	0.06	3.2*	—	0.43	2.79	1.44	3.12	4.56	7.78	0.032	<0.006	0.008	0.56	0.57	0.60	33.5	78.4	54.5
2	20	—	—	—	—	—	0.09	0.02	<0.05	0.06	8.3*	0.24	0.35	0.76	0.63	6.56	7.19	8.30	0.031	<0.006	0.006	0.54	0.55	0.58	34.5	65.9	28.0
3	40	—	—	—	—	7.93	—	—	—	—	—	—	0.23	0.20	0.18	8.46	8.64	9.07	0.030	<0.006	0.002	0.50	0.50	0.53	36.8	79.6	39.6
4	50	3.03	7.93	383	—	7.75	—	—	—	—	—	—	—	—	0.22	8.22	8.44	8.94	0.029	<0.006	0.004	0.47	0.47	0.50	59.8	63.6	43.0
5	75	3.85	9.76	99	—	7.07	0.23	0.02	0.10	0.33	10.9	0.42	0.33	0.17	0.22	8.22	8.44	8.94	0.029	<0.006	0.004	0.47	0.47	0.50	59.8	63.6	43.0
6	100	—	—	—	—	—	<0.05	0.17	5.28	1.79	34.3	—	0.05	0.13	0.21	12.0	12.2	12.4	0.020	<0.006	0.004	0.29	0.29	0.31	251	94.1	40.9
7	125	5.08	11.82	35	—	6.99	<0.05	0.04	6.60	2.69	52.9	0.00	0.04	0.07	0.11	11.6	11.7	11.8	0.022	<0.006	0.003	0.31	0.31	0.33	232	94.3	54.6
8	135	—	—	—	—	—	0.13	0.02	8.17	2.65	53.9	0.17	<0.04	0.05	0.08	11.6	11.7	11.8	0.023	<0.006	0.002	0.23	0.23	0.25	252	98.4	48.7
9	150	5.25	12.14	15	—	6.96	0.09	0.04	7.97	2.62	53.6	—	<0.04	0.05	0.09	11.8	12.0	12.0	0.023	<0.006	0.004	0.20	0.20	0.22	282	108	69.8
10	160	—	—	—	—	—	0.14	0.09	4.56	3.33	65.1	—	<0.04	0.07	0.18	13.2	13.4	13.5	0.019	<0.006	0.004	0.20	0.20	0.22	316	114	67.8
11	165	—	—	—	—	—	0.67	0.11	0.48	3.69	69.3	—	<0.04	0.05	0.07	12.8	12.9	13.0	0.023	<0.006	0.006	0.21	0.22	0.24	311	96.1	50.4
12	170	—	—	—	—	—	0.79	0.05	<0.05	3.96	70.2	—	0.04	0.13	0.45	13.5	14.0	14.1	0.014	<0.006	0.002	0.26	0.26	0.27	360	119	55.9
13	180	—	—	—	—	—	2.65	0.04	<0.05	4.53	71.2	—	0.06	0.15	12.3	2.63	14.9	15.2	0.013	<0.006	0.008	0.25	0.26	0.27	275	88.2	54.3
14	200	5.49	12.34	7	3.7	6.99	5.48	0.02	<0.05	4.78	75.6	—	0.05	0.27	10.9	3.99	14.9	15.2	0.030	<0.006	0.129	0.20	0.33	0.36	385	98.9	62.6
15	215	—	—	—	—	—	6.32	<0.02	<0.05	5.02	79.5	—	0.07	0.24	10.6	3.83	14.4	14.7	0.032	<0.006	0.134	0.16	0.29	0.32	382	93.0	53.2
16	220	—	—	—	—	—	0.06	0.22	9.87	5.21	15.1	—	0.08	0.21	11.2	3.55	14.8	15.1	0.034	<0.006	0.150	0.18	0.33	0.36	406	83.3	53.4
17	235	—	—	—	—	—	0.04	0.03	11.4	2.75	14.1	—	0.06	0.22	9.87	5.21	15.1	15.4	0.031	<0.006	0.140	0.19	0.33	0.36	390	99.5	81.3
18	240	—	—	—	—	—	0.04	0.24	10.7	3.30	14.0	—	0.04	0.24	10.7	3.30	14.0	14.2	0.032	<0.006	0.145	0.18	(0.02)	—	409	93.5	56.7
19	250	—	—	—	—	—	0.04	0.24	10.7	3.30	14.0	—	0.04	0.24	10.7	3.30	14.0	14.2	0.032	<0.006	0.137	0.18	0.32	0.35	374	108	75.3
20	260	—	—	—	—	—	0.14	0.12	11.6	3.24	13.6	—	0.14	0.12	11.6	3.24	13.6	13.9	0.041	<0.006	0.154	0.16	0.31	0.35	475	—	—
21	270	—	—	—	—	—	0.04	0.08	10.6	2.78	13.4	—	0.04	0.08	10.6	2.78	13.4	13.6	0.026	<0.006	0.112	0.01	0.12	0.15	422	—	—

Station B726 (14 June 1981; 59°22'N, 22°28'E; water depth 100 m)

Sample no.	Depth (m)	T (°C)	S (‰)	O ₂ (μM)	ΣH ₂ S (μM)	pH	NH ₄ ⁺ (μM)	NO ₂ ⁻ (μM)	NO ₃ ⁻ (μM)	PO ₄ ³⁻ (μM)	SiO ₂ (μM)	Chl <i>a</i> (μg l ⁻¹)	MeAs (nM)	Me-As (nM)	As(III) (nM)	As(V) (nM)	As _T (nM)	MeSb (nM)	Me-Sb (nM)	Sb(III) (nM)	Sb _T (nM)	Sb _V (nM)	Sb _T (nM)	Ge(OH) ₂ (pM)	MeGe (pM)	Me-Ge (pM)	
1	10	8.54	6.71	371	—	8.28	0.09	0.02	<0.05	0.06	5.9	1.00	0.43	4.92	0.44	2.65	3.09	8.45	0.05	<0.01	0.009	0.61	0.62	0.67	34.8	62.3	44.3
2	20	8.53	6.71	368	—	8.42	<0.05	0.02	<0.05	0.03	5.9	0.76	0.46	5.03	0.37	2.30	2.67	8.45	0.06	<0.01	0.008	0.54	0.55	0.61	37.7	71.8	47.5
3	30	—	6.71	368	—	8.43	0.14	0.02	<0.05	<0.02	6.5	0.07	0.40	1.74	0.18	4.73	4.91	7.05	0.09	<0.01	0.008	0.68	0.69	0.78	45.7	81.4	45.6
4	40	3.77	6.71	377	—	8.44	0.26	0.02	0.12	0.40	12.8	0.04	0.38	0.74	0.19	7.65	7.84	8.96	0.04	<0.01	0.006	0.55	0.56	0.60	83.4	77.1	60.4
5	50	3.16	6.71	367	—	8.44	0.20	0.15	2.54	0.65	15.9	0.86	0.21	0.14	0.18	9.30	9.48	9.83	<0.005	<0.01	0.005	0.52	0.53	0.53	93.0	84.3	50.4
6	60	2.32	7.31	398	—	8.00	0.10	0.18	4.72	1.05	22.2	0.15	0.26	0.19	0.19	8.79	8.98	9.43	<0.005	<0.01	—	—	0.47	0.47	119	74.5	53.5
7	80	2.73	7.96	341	—	7.65	<0.05	0.04	5.57	2.44	47.5	0.05	0.10	0.27	0.37	10.8	11.2	11.5	<0.005	<0.01	—	—	0.36	0.36	249	111.0	104
8	90	3.31	8.46	274	—	7.45	—	—	—	—	—	—	0.11	0.30	0.64	11.0	11.6	12.0	<0.005	<0.01	—	—	0.35	0.35	258	95.7	72.8

Station B723 (15 June 1981; 59°51'N, 24°50'E; water depth 75 m)

Sample no.	Depth (m)	T (°C)	S (‰)	O ₂ (μM)	ΣH ₂ S (μM)	pH	NH ₃ (μM)	NO ₂ (μM)	NO ₃ (μM)	PO ₄ (μM)	SiO ₂ (μM)	Chl <i>a</i> (μg l ⁻¹)	MeAs (nM)	Me ₂ As (nM)	As(III) (nM)	As(V) (nM)	As _T (nM)	MeSb (nM)	Me ₂ Sb (nM)	Sb(III) (nM)	Sb _T (nM)	Sb ₂ (nM)	Ge(OH) ₂ (pM)	MeGe (pM)			
1	10	9.10	6.17	368	—	8.62	0.05	0.02	<0.05	0.09	5.0	1.06	0.38	6.15	0.57	0.79	1.36	7.90	0.07	0.01	—	—	0.45	0.53	23.3	52.6	63.3
2	20	8.34	6.31	379	—	8.53	0.10	0.02	<0.05	0.06	5.0	0.52	0.38	6.98	0.62	0.95	1.57	8.93	0.05	0.01	—	—	0.42	0.48	34.2	65.2	36.1
3	30	2.58	7.04	377	—	7.85	0.30	0.02	0.12	0.30	10.4	0.09	0.37	1.86	0.20	5.50	5.70	7.92	0.05	0.04	—	—	0.45	0.54	58.4	67.0	24.7
4	40	2.21	7.21	384	—	7.77	0.31	0.02	0.40	0.39	11.7	0.28	0.42	1.27	0.20	5.21	5.41	7.16	0.05	0.03	—	—	0.47	0.55	68.0	72.9	43.0
5	50	1.82	7.80	327	—	7.51	0.12	0.08	4.07	0.84	18.7	—	0.30	0.35	0.17	6.35	6.52	7.17	<0.005	<0.01	—	—	0.46	0.47	90.1	75.7	49.0
6	65	2.21	8.22	247	—	7.28	<0.05	0.25	5.22	1.33	26.7	0.30	0.25	0.42	0.27	6.67	6.94	7.61	<0.005	<0.01	—	—	0.37	0.38	121	77.1	56.4

REFERENCES

- Andreae, M. O. 1977. Determination of arsenic species in natural waters. *Anal. Chem.* **49**, 820–823.
- Andreae, M. O. 1978. Distribution and speciation of arsenic in natural waters and marine algae. *Deep-Sea Res.* **25**, 391–402.
- Andreae, M. O. 1979. Arsenic speciation in seawater and interstitial waters: the influence of biological-chemical interactions on the chemistry of a trace element. *Limnol. Oceanogr.* **24**, 440–452.
- Andreae, M. O. 1983a. Arsenic (by hydride generation/AAS). Antimony (by hydride generation/AAS). Germanium (by hydride generation/AAS). In *Methods of seawater analysis* (eds. K. Grasshoff, M. Ehrhardt and K. Kremling). Weinheim: Verlag Chemie, 2nd edition. Chapters 10.6–10.6.8, 218–236.
- Andreae, M. O. 1983b. The determination of the chemical species of some of the “hydride elements” (arsenic, antimony, tin, and germanium) in seawater: methodology and results. In *Trace metals in sea water* (eds. C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg). New York: Plenum, 1–19.
- Andreae, M. O. and Froelich, P. N. 1981. Determination of germanium in natural waters by graphite furnace atomic absorption spectrometry with hydride generation. *Anal. Chem.* **53**, 287–291.
- Andreae, M. O. and Klumpp, D. W. 1979. Arsenic uptake and metabolism by marine phytoplankton. *Environ. Sci. Technol.* **13**, 738–741.
- Andreae, M. O., Asmodé, J.-F., Foster, P. and Van’t dack, L. 1981. Determination of antimony(III), antimony(V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation. *Anal. Chem.* **53**, 1766–1771.
- Andreae, M. O., Byrd, J. T. and Froelich, P. N. 1983. Arsenic, antimony, germanium, and tin in the Tejo Estuary, Portugal: modeling a polluted estuary. *Environ. Sci. Technol.* **17**, 731–737.
- Bertine, K. K. and Lee, D. S. 1983. Antimony content and speciation in the water column and interstitial waters of Saanich Inlet. In *Trace metals in sea water* (eds. C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg). New York: Plenum, 21–38.
- Boström, K., Burman, J.-O. and Ingri, J. 1983. A geochemical mass balance for the Baltic. *Ecol. Bull. (Stockholm)* **35**, 39–58.
- Brewer, P. G., Spencer, D. W. and Robertson, E. D. 1972. Trace element profiles from the GEOSECS II test station in the Sargasso Sea. *Earth Planet. Sci. Lett.* **16**, 111–116.
- Briggs, J. C. and Fickes, J. F. 1977. *Quality of rivers of the United States, 1975 Water Year: Based on the National Stream Quality Accounting Network (NASQAN)*. Reston/Virginia: U.S. Geological Survey, Report 78–200.
- Burton, J. D., Maher, W. A. and Statham, P. J. 1983. Some recent measurements of trace metals in Atlantic Ocean waters. In *Trace metals in sea water* (eds. C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg). New York: Plenum, 415–426.
- Byrd, J. T. and Andreae, M. O. 1982. Tin and methyltin species in seawater: concentration and fluxes. *Science* **218**, 565–569.
- Carpenter, R., Peterson, M. L. and Jahnke, R. A. 1978. Sources, sinks and cycling of arsenic in the Puget Sound region. In *Estuarine interactions* (ed. M. L. Wiley). New York: Academic, 459–480.
- Cotton, F. A. and Wilkinson, G. 1972. *Inorganic chemistry*. New York: Wiley.
- Crecelius, E. A., Bothner, M. H. and Carpenter, R. 1975. Geochemistries of As, Sb, Hg and related elements in the sediments of Puget Sound. *Environ. Sci. Technol.* **9**, 325–333.
- Edmonds, J. S. and Francesconi, K. A. 1981. Arsenosugars from brown kelp (*Ecklonia radiata*) as intermediates in cycling of arsenic in a marine ecosystem. *Nature* **289**, 602–604.
- Erlenkeuser, H., Suess, E. and Willkomm, H. 1974. Industrialization affects heavy metal and carbon isotope concentrations in recent Baltic sediments. *Geochim. Cosmochim. Acta* **38**, 823–842.
- Fonselius, S. 1981. Oxygen and hydrogen sulphide conditions in the Baltic Sea. *Marine Pollut. Bull.* **12**, 187–194.
- Froelich, P. N. and Andreae, M. O. 1981. The marine geochemistry of germanium: ekasilicon. *Science* **213**, 205–207.
- Froelich, P. N., Hambrick, G. A. and Andreae, M. O. 1983. Geochemistry of inorganic and methyl germanium species in three estuaries. *Eos* **64**, 715.
- Grasshoff, K. 1975. The hydrochemistry of landlocked basins and fjords. In *Chemical oceanography* (eds. J. P. Riley and G. Skirrow). New York: Academic, 2nd edition. Vol. 2, chapter 15.
- Hallberg, R. O. 1979. Heavy metals in the sediments of the Gulf of Bothnia. *Ambio* **8**, 265–269.
- Hambrick, G. A., Froelich, P. N., Andreae, M. O. and Lewis, B. L. 1984. Determination of methylgermanium species in natural waters by graphite furnace atomic absorption spectrometry with hydride generation. *Anal. Chem.* **56**, in press.
- Kantin, R. 1983. Chemical speciation of antimony in marine algae. *Limnol. Oceanogr.* **28**, 165–168.
- Kremling, K. 1983. The behaviour of Zn, Cd, Cu, Ni, Co, Fe and Mn in anoxic Baltic waters. *Mar. Chem.* **13**, 87–108.
- Kullenberg, G. 1981. The Baltic: a regional sea marine pollution case study. *Mar. Pollut. Bull.* **12**, 179–182.
- Kullenberg, G. and Jacobsen, T. S. 1981. The Baltic Sea: an outline of its physical oceanography. *Mar. Pollut. Bull.* **12**, 183–186.

- McBride, B. C., Merilees, H., Cullen, W. R. and Pickett, W. 1978. Anaerobic and aerobic alkylation of arsenic. *ACS Symp. Ser.* 82, 94–115.
- National Academy of Sciences. 1981. *Atmosphere-biosphere interactions: toward a better understanding of the ecological consequences of fossil fuel combustion*. Washington, D.C.: National Academy Press.
- Nehring, D. and Francke, E. 1983. Die hydrographisch-chemischen Bedingungen in der Ostsee im Jahre 1980. *Fisch.-Forsch.* 22, in press.
- Pacyna, J. M. 1982. *Trace element emission from anthropogenic sources in Europe*. Lillestrøm/Norway: Norwegian Institute for Air Research, NILU 24781.
- Peterson, M. L. and Carpenter, R. 1983. Biogeochemical processes affecting total arsenic and arsenic species distributions in an intermittently anoxic fjord. *Mar. Chem.* 12, 295–321.
- Rahn, K. A. 1976. *The chemical composition of the atmospheric aerosol*. Technical Report, Graduate School of Oceanography, University of Rhode Island, Kingston.
- Rodhe, H., Söderlund, R. and Ekstedt, J. 1980. Deposition of airborne pollutants on the Baltic. *Ambio* 9, 168–173.
- Sanders, J. G. 1979. Microbial rôle in the demethylation and oxidation of methylated arsenicals in seawater. *Chemosphere* 8, 135–137.
- Sanders, J. G. and Windom, H. L. 1980. The uptake and reduction of arsenic by marine algae. *Estuarine Coastal Mar. Sci.* 10, 555–567.
- Slinn, W. G. N., Hasse, L., Hicks, B. B., Hogan, A. W., Lal, D., Liss, P. S., Munnich, K. O., Sehmel, G. A. and Vittori, O. 1978. Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. *Atmos. Environ.* 12, 2055–2087.
- Smith, R. D., Campbell, J. A. and Nielson, K. K. 1979. Concentration dependence upon particle size of volatilized elements in fly ash. *Environ. Sci. Technol.* 13, 553–558.
- van der Sloot, H. A., Massee, R. and Wals, G. D. 1977. Methods for the determination of selenium, arsenic and antimony species in natural waters and their application in an environmental study. In: *Nuclear methods in environmental and energy research*. Washington, D.C.: U.S. Dept. of Energy, CONF-771072, 560–575.
- Walsenchuk, D. G. 1978. The budget and geochemistry of arsenic in a continental shelf environment. *Mar. Chem.* 7, 39–52.
- Wilson, C. L. 1980. *Coal: bridge to the future. Report of the World Coal Study*. Cambridge/Mass.: Ballinger.
- Wong, P. T. S., Chau, Y. K., Luxon, L. and Bengert, G. A. 1977. Methylation of arsenic in the aquatic environment. In *Trace substances in environmental health-XI* (ed. D. D. Hemphill). Columbia: University of Missouri, 100–106.