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Biomethylation of Thallium by Bacteria and First Determination of Biogenic Dimethylthallium in the Ocean

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To investigate a possible biomethylation of thallium, incubation experiments were carried out under aerobic conditions with a sewage sludge and with a mixed bacterial culture isolated from a sewage sludge, as well as under anaerobic conditions with a fresh-water lake sediment, by adding Tl(I) nitrate to these systems. Only in the case of the anaerobic sediment was a significant production of dimethylthallium observed (after three-weeks). Analysing different surface seawater samples and those from a single depth profile down to 4000 m, dimethylthallium was determined above the detection limit of 0.4 ng L^{-1} in about 20% of all samples, ranging from 0.5 to 3.2 ng l^{-1}. The proportion of dimethylthallium in these samples, compared with the total thallium concentration, varied from 3 to 48%. The determination of such low dimethylthallium content was possible by applying a new sensitive analytical method of positive thermal-ionization isotope-dilution mass spectrometry connected with a species-unspecific thallium enrichment by anion-exchange chromatography and a species-specific extraction step. This is the first time that dimethylthallium could be detected in environmental samples. In surface seawater samples the occurrence of dimethylthallium correlated well with relatively high concentrations of chlorophyll-a, used as an indicator for bioactivity. Mostly, other biomethylated compounds such as trimethyl-lead, monomethylcadmium and dimethyl sulphide were also found with peak concentrations at these locations. The depth profile of dimethylthallium shows a maximum in concentration between 40 and 200 m, which corresponds with the highest level of bioactivity normally found in the water column of the ocean. However, even at depths of 1000 and 4000 m significant amounts of dimethylthallium could be analysed, which suggest bacteria as the biogenic source in the deep sea. **Copyright © 2000 John Wiley & Sons, Ltd.**

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INTRODUCTION

Biomethylation is an important chemical process in the environment for many elements. In 1951 Challenger found that biomethylation of arsenic compounds is possible.[1] In the following years biomethylation was also established for many other elements, e.g for the halogens iodine and bromine, for sulphur as well as for selenium.[2–8] Even if biomethylation also takes place in fresh-water systems and soil, the marine environment was found to be the major source for the production of methylated elements. In the case of heavy metals, biomethylation was discovered for mercury, lead and cadmium, forming Me_2Hg, $MeHg^+$, Me_3Pb^+, Me_2Pb^{2+}, and $MeCd^+$, respectively (Me = methyl).[9–12] Possible mechanisms for the biogenic formation of methylated heavy metals are described in the literature.[13,14]

The chemical synthesis of the methylated thallium compounds $MeTl^{2+}$, Me_2Tl^+, and Me_3Tl has been known for a long time.[15] However, only dimethylthallium is a stable compound, so this is the only methylated thallium species which can be

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expected to be found in the environment. In ocean water dimethylthallium should mainly exist as the chloride salt. Diorganothallium halides are among the least reactive organometallic compounds known and they are, for example, unaffected by water, oxygen, light and acids.[16] Biogenic production of dimethylthallium was observed in laboratory experiments by Huber and Kirchmann when thallium(I) was in contact with an anaerobic river sediment.[17] On the other hand, it was not possible in the past to analyse Me_2Tl^+ in the environment. This may have been due to the extremely low concentration level of thallium in the environment, for example in the range of about 10–20 ng l^{-1} in ocean water.[18] Recently, a sensitive and highly selective method for the analysis of dimethylthallium was developed by Schedlbauer and Heumann, which allows the determination of Me_2Tl^+ traces, e.g. in ocean water down to the sub-nanogram per litre level.[19] This technique of positive thermal-ionisation isotope-dilution mass spectrometry (PTI-IDMS) in connection with species-unspecific enrichment of thallium by an anion exchanger and a species-specific extraction step was applied in this work for the determination of dimethylthallium in incubation experiments using bacteria of different origins but also for analysing seawater samples from the Atlantic Ocean.

MATERIALS AND METHODS

Incubation experiments with bacteria

To test a possible biomethylation of thallium, incubation experiments were carried out with a sewage sludge and a mixed bacterial culture isolated from a sewage sludge (both under aerobic conditions), as well as with a fresh-water lake sediment under anaerobic conditions. In all cases a nutritive solution, as described in the literature (containing 0.25 g K_2HPO_4, 0.05 g $MgCl_2$, 0.5 g NH_4Cl, 3 g $Ca(CH_3COO)_2$ and 0.1 g glucose in 100 ml water; all chemicals were of pro analysis purification grade),[17] and a 10^{-2} mol l^{-1} HNO_3 solution, containing different amounts of thallium (I) (0.5, 10 or 300 μg), were added. Two parallel experiments were always carried out under identical conditions. All samples were filtered, using a 0.45 μm pore-size Teflon filter, prior to their Me_2Tl^+ and total thallium determinations.

Waste water (450 ml) in which sludge was suspended, from a sewage disposal plant, was placed in a 1-litre polyethylene (PE) flask and then mixed with 100 ml of the nutritive solution and with 1 ml of the nitric acid/thallium solution containing 300 μg of thallium. The sample was then stored for three weeks at 30 °C in the dark. The mixed bacterial culture from a sewage sludge was prepared by Mrs R. Grassl and Dr H. Huber (Institute of Biochemistry, Genetics and Microbiology of the University of Regensburg, Germany) under the usual culture techniques for bacteria. The mixed bacterial cultures were suspended in a mixture of 20 ml of the nutritive solution and 1 ml of a nitric acid/thallium solution containing 0.5 and 10 μg thallium(I), respectively. Storage in 30 ml glass tubes then took place under the same conditions as described for the sewage sludge. An anaerobic fresh water sediment was suspended in 20 ml of oxygen-free nutritive solution and 1 ml of an oxygen-free acidic thallium solution, containing 0.5 and 10 μg thallium, respectively, was added. These samples were also stored for three weeks in the dark at 30 °C but exposure to any air was excluded.

Sampling of ocean water

Atlantic seawater samples were taken during two different expeditions of the German research vessel *Polarstern*. Samples at a depth of 10 m and those from a depth profile down to 4000 m were collected during the ANT XIII/2 expedition leg (December 1995 to January 1996) from Cape Town to the German Antarctic Station ‘Neumayer’ at about 70 °S, 8 °W and back to Cape Town (Fig. 1). Other surface seawater samples at 10 m depth were collected during ANT XIV/1 (October to November 1996) from Bremerhaven, Germany, northward to about 65 °N (north of Iceland) and then, at a latitude of about 30 °W, southward to 45 °S (Fig. 2). The final station of this expedition was Punta Quilla in South Argentina.

The surface ocean water samples were obtained from a snorkel system, which continuously pumped seawater under clean conditions from the front of the ship’s bow at a depth of 10 m into a laboratory, where pre-cleaned PE bottles were filled with the samples. To avoid any change in the samples they were frozen immediately and stored at a temperature of less than −10 °C until they were analysed in the home laboratory. Deep-sea samples were collected by special flasks (GOFLO-Niskin) of 12 l volume, whereby heavy-metal contamination was minimized. These flasks were fixed in their opened

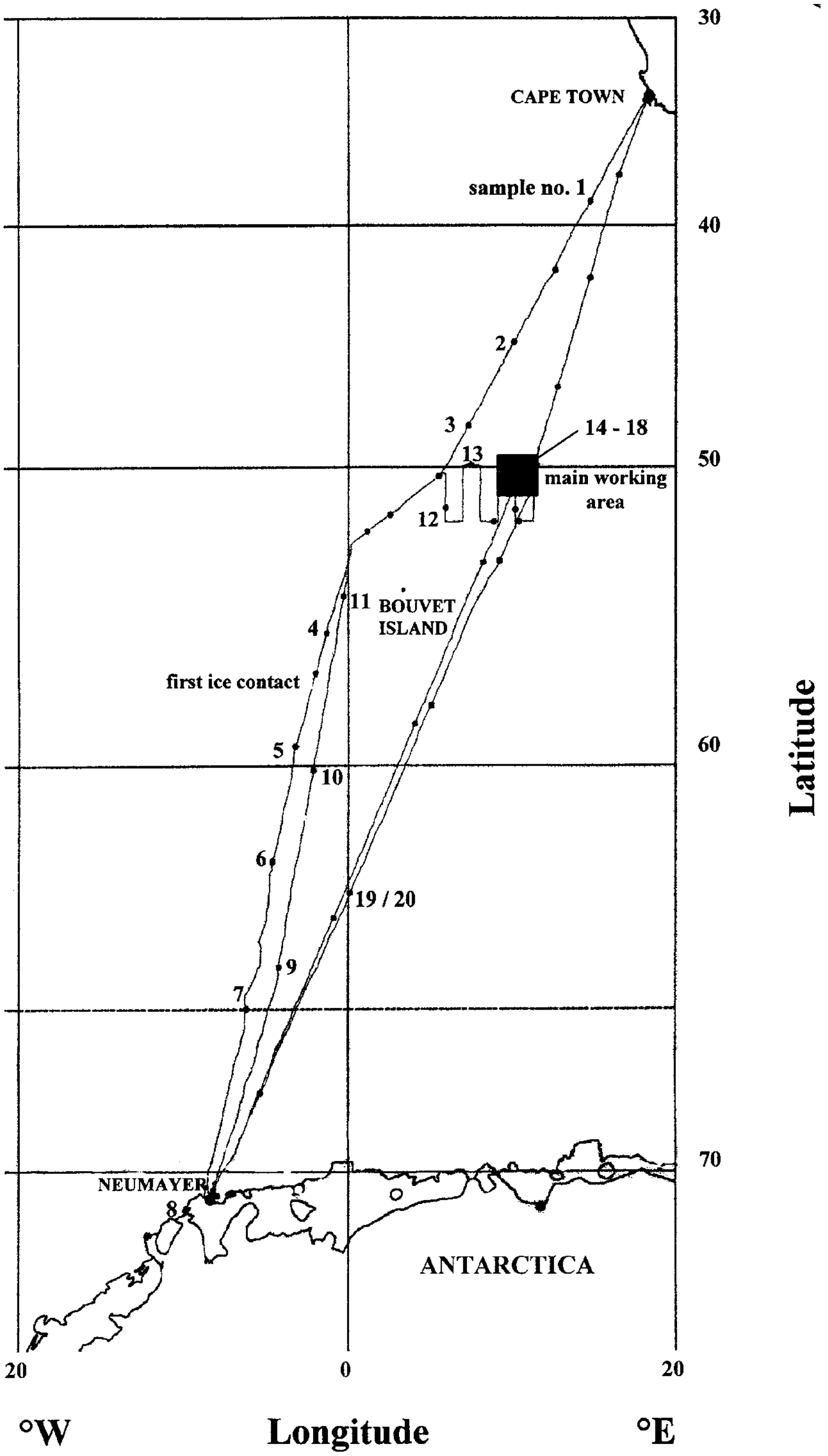

Figure 1 Cruise track of the research vessel *Polarstern* during expedition ANT XIII/2 from Cape Town to the German Antarctic station 'Neumayer' (sample numbers on the cruise track correspond to those listed in Table 2; unnumbered points mark locations for additional Me_3Pb^+, $MeCd^+$ and chlorophyll-a determinations).

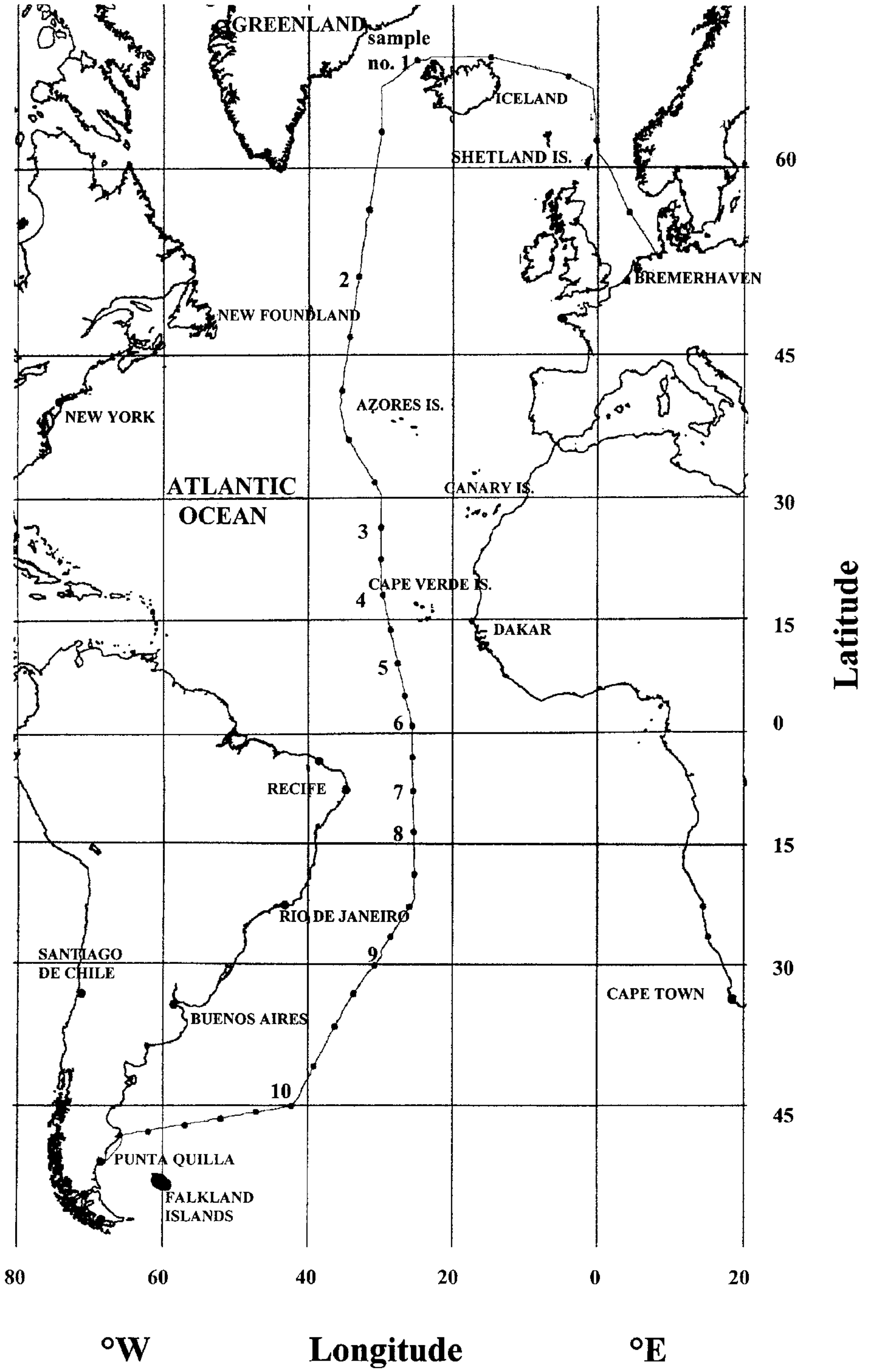

Figure 2 Cruise track of the research vessel *Polarstern* during expedition ANT XIV/1 from Bremerhaven, Germany, to Punta Quilla, Argentina (sample numbers on the cruise track correspond to those listed in Table 3; unnumbered points mark locations for additional Me_3Pb^+, $MeCd^+$, and DMS determinations).

position, together with a CTD (conductivity and temperature with depth) sensing probe, at a rosette on board the ship. After the rosette reached the desired depth, the flask was closed electronically and the rosette was returned on board, where 1-litre samples in pre-cleaned PE bottles were stored under the same low-temperature conditions as described for surface-water samples.

Analytical methods

Positive thermal-ionisation isotope-dilution mass spectrometry (PTI–IDMS) in connection with a species-unspecific thallium enrichment at the strongly basic anion exchanger Dowex AG1-X8, followed by a species-specific extraction step with methyl isobutyl ketone (MIBK), was applied for the determination of dimethylthallium in seawater samples as well as in solutions from the incubation experiments. Seawater 400–500 ml or the filtered solution from the bacterial experiments (10–20 ml) was mixed with a ^{203}Tl-enriched Me_2Tl^+ spike solution for the isotope-dilution step. Synthesis of the isotopically labelled dimethylthallium compound and its characterization with respect to the isotopic composition and concentration are described elesewhere.[19] Complexation of dimethylthallium and of inorganic thallium was then carried out by sodium diethyldithiocarbamate (NaDDTC) in ammoniacal solution. The negatively charged complexes were fixed on the anion exchanger column. Afterwards, thallium could be eluted by 6 ml of 2 mol l^{-1} nitric acid. After selective oxidation of inorganic thallium(I) to thallium(III) by an aqueous solution saturated with bromine, inorganic thallium was extracted by MIBK whereas Me_2Tl^+ remained in the aqueous phase. Me_2Tl^+ was not decomposed during this oxidation process, which was demonstrated by adding known amounts of a dimethylthallium standard to ocean water samples and treating them in the same way as other samples.[19] After a couple of clean-up steps for the mass-spectrometric measurement, the isotope ratio $^{203}Tl/^{205}Tl$ of the isotope-diluted sample was determined by PTI-MS. By analysis of aliquots of the same ocean water sample the reproducibility of Me_2Tl^+ determinations was found to be in the range 3–8%. A more detailed description of the whole analytical procedure and the validation of this analytical method was published recently.[19] The detection limit for Me_2Tl^+ speciation in seawater samples is 0.4–0.5 ng Tl l^{-1} using 500–400 ml of sample. The detection limit for the incubation experiments is much higher because of the smaller sample volume, on the one hand, and the limitation by the high excess of inorganic thallium, on the other. The species-selectivity coefficient between dimethylthallium and inorganic thallium is about 500, which means that Me_2Tl^+ can be analysed in the presence of a five-hundredfold excess of inorganic thallium.

A simplified sample treatment procedure was applied for total thallium determinations by PTI-IDMS. In the case of seawater samples, a sample volume of only 50 ml was used and a ^{203}Tl-enriched spike solution of thallium(I) nitrate was applied instead of the dimethylthallium spike. To convert all the different thallium species into inorganic thallium(III), the isotope-diluted sample was first treated with aqua regia and then evaporated to dryness before applying the same clean-up steps for the isotope ratio measurement by PTI-MS as were applied for the Me_2Tl^+ species analysis. The detection limit for total thallium determinations in ocean water is 1.4 ng l^{-1}.

The methylated lead and cadmium compounds Me_3Pb^+ and $MeCd^+$, respectively, were also determined in surface seawater samples during the two different expeditions. A differential-pulse anodic-stripping voltammetric (DPASV) method, using a mercury film electrode, was applied to analyse both methylated heavy-metal compounds in 50-ml sample aliquots of seawater.[20] The DPASV method used for Me_3Pb^+ analysis was adapted from a procedure developed by Mikac and Branica.[21] Inorganic Pb^{2+} had to be eliminated before the determination of trimethyllead took place, which was carried out by co-precipitation of inorganic lead with barium sulphate. In contrast to the Me_3Pb^+ analysis, the determination of $MeCd^+$ did not need any separation from Cd^{2+} ions because the electroanalytical detection of the methylated cadmium compound was not disturbed by inorganic cadmium. The stripping potential for the different cadmium species differed by 112 mV. A more detailed description of the $MeCd^+$ determination by DPASV is given elsewhere.[12] Using 50-ml seawater samples the detection limits for Me_3Pb^+ and $MeCd^+$ are 0.5 ng Pb or Cd per litre.

RESULTS AND DISCUSSION

Incubation experiments

The results of the incubation experiments with

Table 1 Production of Me_2Tl^+ by incubation experiments with bacterial cultures of different origins after three weeks of storage at 30 °C

Source of bacterial culture	Inorganic thallium added (μg)	Volume of solution (ml)	Concentration in solution after storage (ng Tl ml^{-1})[a] Total Tl	Me_2Tl^+
Sewage sludge (aerobic)	300	551	530 ± 15	< 0.4
Mixed culture isolated	10	21	502 ± 33	< 1.1
from sewage sludge (aerobic)	0.5	21	24 ± 1	< 0.06
Fresh-water sediment	10	21	477 ± 20	< 1.2
(anaerobic)	0.5	21	22.6 ± 0.4	2.6 ± 0.3

[a] Means, with deviations calculated from the results of two independent experiments under identical conditions.

bacterial cultures of different origins are summarized in Table 1. Except for the experiment with a fresh-water sediment under anaerobic conditions, containing only an added amount of 0.5 μg of inorganic thallium, all other experiments resulted in dimethylthallium concentrations below the detection limit. This detection limit varied with the amount of sample used for analysis and with the amount of added thallium(I). In the case of the fresh-water sediment, where 0.5 μg of inorganic thallium was added, 11.5% of the total thallium was found to be biomethylated after an incubation time of three weeks.

It is interesting that the only other biomethylation of thallium in laboratory experiments (reported by Huber and Kirchmann.[17]), was also observed under anaerobic conditions. These authors used an anaerobic river sediment, whereas in this work an anaerobic sediment from a lake was applied. However, it is not quite clear why dimethylthallium was not found in the incubation experiment with the same lake sediment when 10 μg instead of 0.5 μg thallium(I) was added. One explanation may be that too high a concentration of thallium can reduce the activity of microorganisms,[18] which possibly hinders significant formation of Me_2Tl^+.

Table 2 Determination of Me_2Tl^+ and total thallium in surface seawater samples from the South Atlantic[a]

Sample no.	Date	Location	Me_2Tl^+ (ng Tl l^{-1})	Total Tl (ng l^{-1})
1	5 Dec. 1995	39°23′S, 14°29′E	< 0.49	5.0
2	7 Dec. 1995	46°05′S, 09°22′E	< 0.50	5.8
3	8 Dec. 1995	49°14′S, 06°42′E	< 0.52	9.4
4	11 Dec. 1995	56°48′S, 01°45′W	< 0.51	7.8
5	12 Dec. 1995	60°03′S, 03°23′W	< 0.49	7.4
6	13 Dec. 1995	64°04′S, 04°55′W	< 0.45	11.3
7	14 Dec. 1995	67°49′S, 06°55′W	< 0.49	12.8
8	19 Dec. 1995	70°09′S, 07°55′W	< 0.50	14.0
9	20 Dec. 1995	63°32′S, 03°28′W	1.10	9.9
10	21 Dec. 1995	58°13′S, 01°25′W	< 0.48	7.4
11	22 Dec. 1995	54°00′S, 00°04′W	< 0.49	8.0
12	24 Dec. 1995	52°00′S, 06°28′E	0.87	7.3
13	25 Dec. 1995	50°28′S, 08°09′E	3.20	6.6
14	27 Dec. 1995	49°41′S, 10°21′E	< 0.48	8.5
15	29 Dec. 1995	49°51′S, 11°32′E	< 0.44	8.9
16	30 Dec. 1995	51°09′S, 10°19′E	< 0.49	9.4
17/1	5 Jan. 1996	50°43′S, 09°32′E	0.59	11.1
18	7 Jan. 1996	50°41′S, 10°15′E	< 0.46	10.5
19	16 Jan. 1996	65°33′S, 02°03′W	< 0.49	11.8
20	16 Jan. 1996	63°38′S, 00°01′E	< 0.45	11.5

[a] Expedition ANT XIII/2; sample numbers are identical to those in Fig. 1.

Table 3 Determination of Me_2Tl^+ and total thallium in surface seawater samples from the Atlantic Ocean from Bremerhaven, Germany, to Punta Quilla, Argentina[a]

Sample no.	Date	Location	Me_2Tl^+ (ng Tl l^{-1})	Total Tl (ng l^{-1})
1	10 Oct. 1996	65°34′ N, 27°50′ W	<0.45	20.1
2	13 Oct. 1996	50°02′ N, 33°34′ W	0.51	19.0
3	18 Oct. 1996	25°24′ N, 30°00′ W	0.87	17.1
4	20 Oct. 1996	18°36′ N, 29°52′ W	<0.46	12.4
5	22 Oct. 1996	08°49′ N, 27°30′ E	<0.44	8.3
6	24 Oct. 1996	00°37′ S, 25°39′ W	0.67	1.6
7	26 Oct. 1996	08°51′ S, 25°31′ W	<0.48	3.5
8	27 Oct. 1996	14°07′ S, 25°26′ W	<0.47	8.3
9	31 Oct. 1996	30°21′ S, 31°06′ W	<0.45	9.0
10	4 Nov. 1996	45°17′ S, 46°33′ W	0.57	9.1

[a] Expedition ANT XIV/1; sample numbers are identical to those in Fig. 2.

Surface seawater concentrations in the Atlantic Ocean

During two different expeditions of the German research vessel *Polarstern* (ANT XIII/2 and ANT XIV/1), different surface seawater samples at a depth of 10 m were analysed for dimethyl thallium. The two cruise tracks across the Atlantic Ocean are represented by Figs 1 and 2. Points on the ship's route mark locations where sampling for the determination of methylated lead and cadmium took place. All sampling locations, where Me_2Tl^+ also was analysed, are numbered. These numbers are identical with those in Tables 2 and 3, respectively, where the exact position and date of sampling as well as the results of the dimethylthallium and total thallium determinations are presented. A total of only 30 surface seawater samples from both expeditions were analysed for Me_2Tl^+, because of the limiting storage space on board the ship for the 500-ml samples at -10 °C and analysis of the samples by PTI-IDMS was very time-consuming.

As can be seen from the results in Tables 2 and 3, in four samples from each of both expeditions significant concentrations of dimethylthallium were determined. In all other samples the Me_2Tl^+ concentration did not exceed the detection limit. Concentrations ranged from <0.44 to 3.2 ng l^{-1}, which is at the same level as was found for trimethyl-lead and monomethylcadmium (see Figs 3 and 4, and Ref. 12). On the other hand, concentrations of monomethyl- and dimethylmercury, $MeHg^+$ and Me_2Hg, in the Atlantic Ocean normally do not exceed 0.1 ng l^{-1}.[10] The dimethylthallium concentration seems to be independent of the total thallium content, which can be followed by a comparison of the results listed in the last two columns of Tables 2 and 3. In the case of positive Me_2Tl^+ detection, the portion of methylated thallium varied in the range of 3–48%.

Positive detections of Me_2Tl^+ correlated well with relatively high concentrations of chlorophyll-a in surface water. In Fig. 3 the biomass indicator chlorophyll-a, determined by Bathmann and Smetacek from the Alfred-Wegener-Institute (AWI) of Polar and Marine Research, Bremerhaven, Germany, is therefore presented also. High chlorophyll-a concentrations were observed in the area of the sub-Antarctic and polar front as well as in the pack-ice region, where algae bloomed during this time. These are the same locations in which Me_2Tl^+ could also be detected and where peak concentrations of Me_3Pb^+ and $MeCd^+$ were found. However, there is no exact correlation between the concentration of the three different methylated heavy-metal compounds for all the samples analysed. This may be due to the fact that the various marine organisms produce specific fingerprints of methylated heavy metals. For example, it was found that not all different types of macroalgae are able to methylate lead and not a single macroalga had been found, until now, which produces $MeCd^+$.[11] Methylation of lead and cadmium was also found to be different for different marine bacterial cultures.[20]

Figure 4 represents the north–south concentration profiles of the three methylated heavy-metal compounds from about 65 °N to 45 °S, which were determined during expedition ANT XIV/1. The concentration of dimethyl sulphide (DMS), a biomethylation product always found in the ocean, is also plotted for comparison. The DMS measurements were carried out by Belviso, CNRS, Gif-sur-

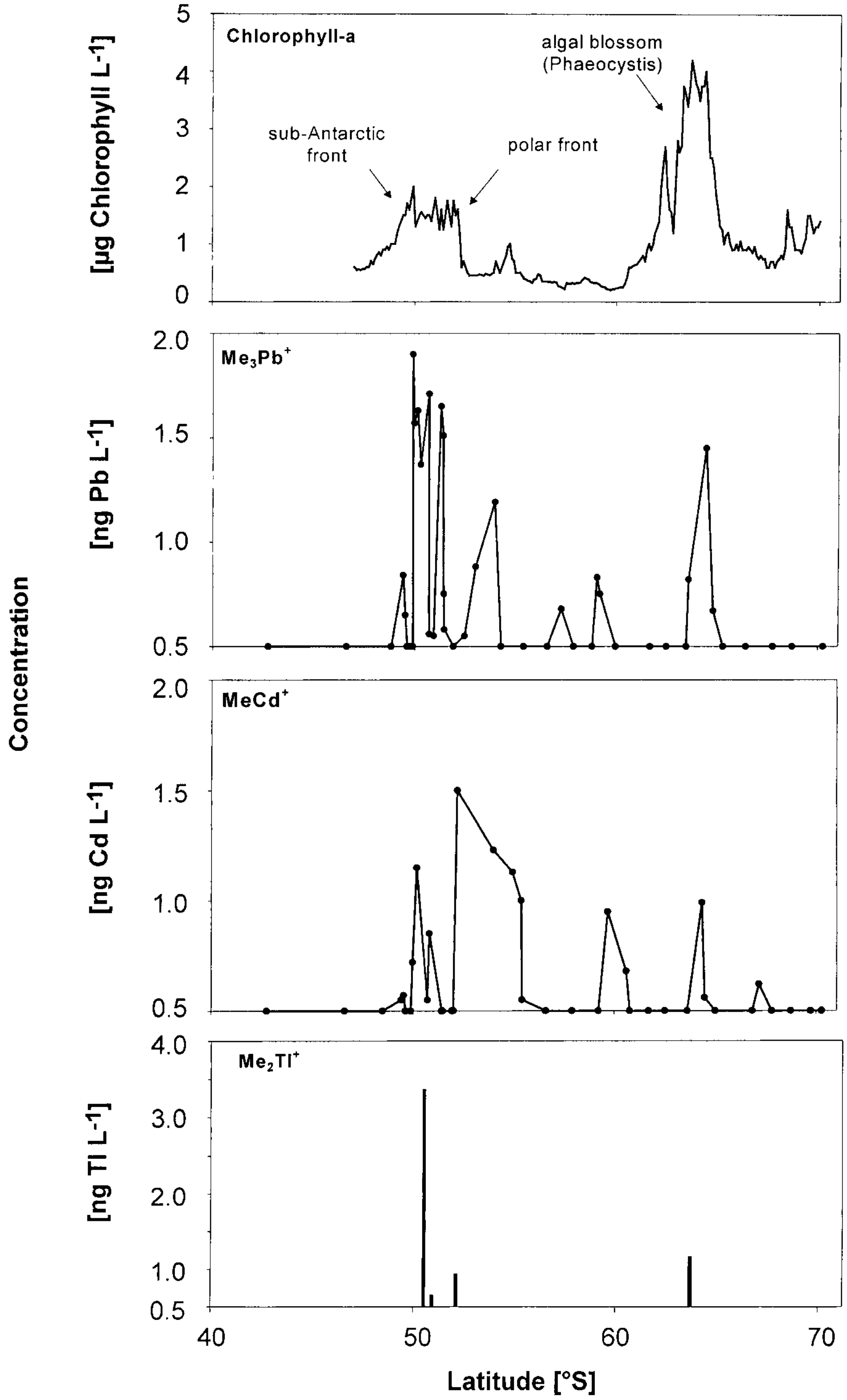

Figure 3 Concentration profiles of methylated thallium, cadmium, lead and chlorophyll-a in surface seawater samples of the South Atlantic determined during expedition ANT XIII/2 sampling (for locations see Fig. 1). Chlorophyll-a data are from Dr U. Bathmann and Professor V. Smetacek, AWI, Bremerhaven, Germany.

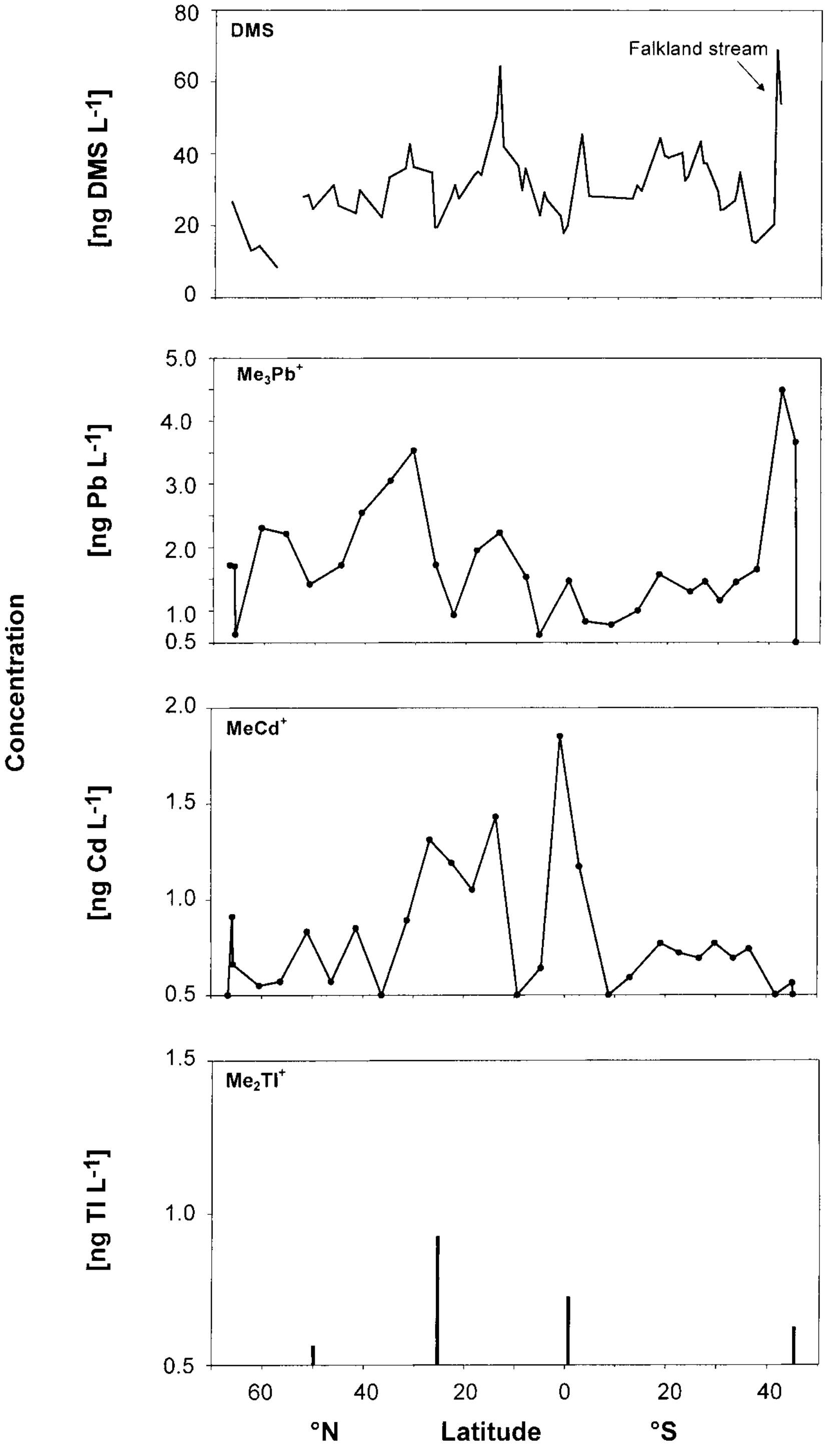

Figure 4 Concentration profiles of methylated thallium, cadmium, lead and DMS in surface seawater samples of the Atlantic Ocean from 65 °N to 45 °S determined during expedition ANT XIV/1 sampling (for locations see Fig. 2). DMS data are from Dr S. Belviso, CNRS, Gif-sur-Yvette, France.

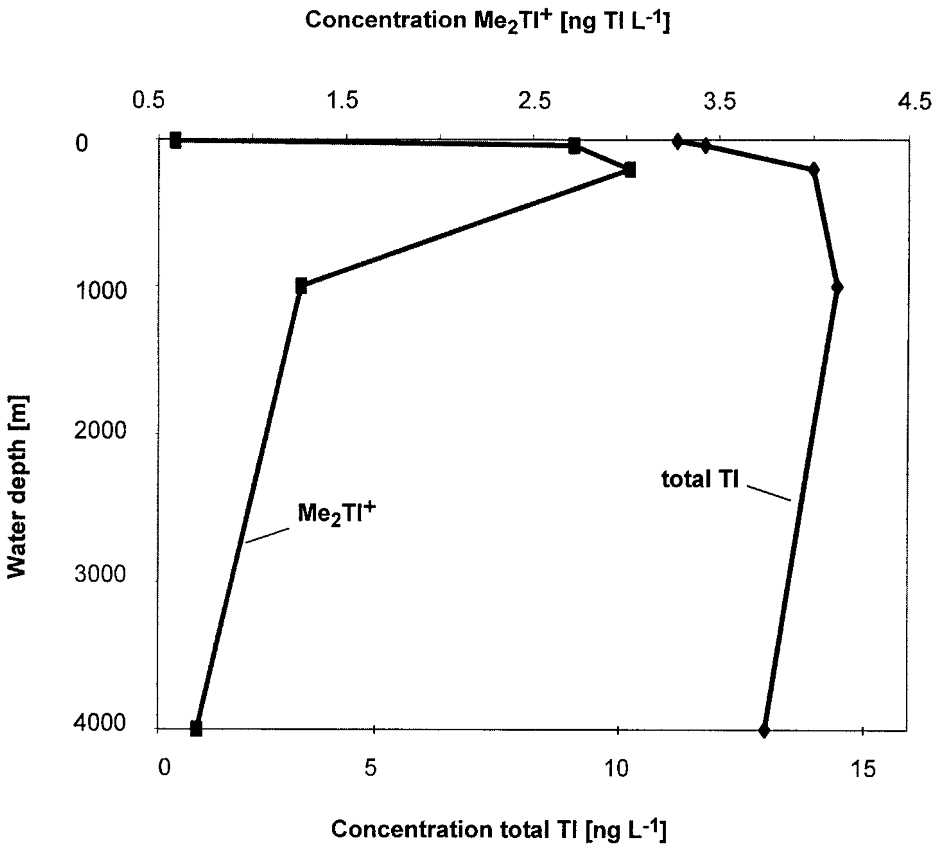

Figure 5 Depth concentration profile of dimethyl thallium and total thallium at 50°43′S, 09°32′E in the South Atlantic (sample no. 17 during expedition ANT XIII/2; see Fig. 1).

Yvette, France. Again, detectable Me_2Tl^+ concentrations correlated well with most of the peak concentrations of the other methylated elements. It is especially remarkable that the highest DMS and Me_3Pb^+ concentrations were found in the Falkland stream with its high bioactivity, where positive Me_2Tl^+ detection was also obtained.

Contrary to surface seawater samples, significant concentrations of dimethylthallium were determined in all the samples collected from a depth profile in the South Atlantic. Figure 5 demonstrates that the Me_2Tl^+ concentration profile did not fit the corresponding profile for total thallium. Whereas total thallium did not vary much with depth, a maximum in concentration was found for dimethylthallium between 40 and 200 m. This correlates well with the known depth for a normally high bioactivity in the water column of the ocean. However, it was especially surprising that even at depths of 1000 and 4000 m, significant Me_2Tl^+ contents were analysed. Because marine algae do not grow at these depths it can be assumed that bacteria have produced dimethylthallium preferentially at this deep-sea level. However, further investigations must confirm this assumption in the future.

CONCLUSION

Incubation experiments with bacterial cultures of different origins only resulted in biomethylation of thallium for a lake sediment under anaerobic conditions. It is interesting in this connection that the only other positive detection of biogenic dimethylthallium by incubation experiments, known until now, was also found under anaerobic conditions using bacteria from a river sediment.[17] Application of the sensitive analytical method of PTI-IDMS in connection with species-unspecific thallium enrichment and species-specific extraction of Me_2Tl^+, recently developed,[19] allowed the first identification and quantification of methylated thallium in the environment at the low nanogram per litre level. With respect to its chemical stability, while Me_2Tl^+ is one of the last biomethylated heavy-metal compounds to be discovered in the environment, it could be expected to exist there. However, it will be an important task for the future to answer questions on alternative mechanisms of biomethylation, to find the optimum conditions for the production of methylated heavy metals in the environment, and to obtain more information on specific fingerprints of biomethylation dependent on the biological species involved.

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