

Methylated Bismuth in the Environment

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Biomethylation of metals and metalloids of Group 14 and 15 metals such as tin, lead and arsenic takes place in the environment, but information about methylated bismuth compounds is rather limited, although bismuth compounds are used widely in alloys, cosmetics and pharmaceutical products.

Cryotrapping gas chromatography and hydride generation gas chromatography coupled with an ICP–MS as a bismuth-selective detector were used to determine volatile bismuth compounds in landfill and in sewage gas, as well as non-volatile methylated compounds in water and sediment samples.

One volatile bismuth compound could be determined in gaseous samples; it was identified as Me₃Bi (TMB) by element-specific detection (ICP–MS, *m/z* 209), matching the retention time with a TMB standard. The molecular structure was recently confirmed by gas-chromatographic fractionation with MS–ion trap detection (electron impact). Among other volatile metal compounds, TMB is a major component in the gases of sewage sludge digesters: concentrations of up to 25 µg m⁻³ have been measured at eight sewage treatment plants. The concentration in landfill gas was approximately one order of magnitude lower.

In laboratory experiments, fermentors containing an anaerobic culture from a clean pond sludge were mixed with contaminated soil from four different industrial areas. After an incubation time of two weeks at 30 °C in the dark, TMB was detected in the headspace of all the samples. The volatilization rate of bismuth did not correlate with the total amount of bismuth in the sediments or with the available fraction after

acid digestion following hydride generation. Some evidence was obtained for the occurrence of methylated bismuth compounds in water samples and in sediments. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Bismuth is a mono-isotopic element (²⁰⁹Bi) and occurs in the Earth's crust of a concentration between 0.1 and 0.2 mg kg⁻¹,¹ which is comparable with the concentration of cadmium and antimony. Bismuth is the heaviest element in Group 15 of the Periodic Table and shows similar chemical behavior to the lighter elements arsenic and antimony. Similarities in the chemistry can also be seen from the heavier elements in the neighboring Groups 14 (germanium, tin and lead) and 16 (selenium, tellurium). All these elements are able to form rather stable methylated compounds.² In addition to the anthropogenic species tetraethyllead and its mixed methylated counterparts, as well as butylated tin species,³ many methylated arsenic,⁴ antimony,⁵ germanium⁶ and selenium⁷ species can be identified in sediments, freshwater, seawater, and in biota, and as volatile species in different gases.^{8–11} It has therefore been speculated that methylated bismuth compounds occur in the environment as well.¹²

BISMUTH COMPOUNDS IN THE ENVIRONMENT

Bismuth occurs in the environment in the form of

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the minerals bismuth ochre (Bi_2S_3), bismuth oxide (Bi_2O_3) and as native bismuth [$\text{Bi}(0)$]. Modeling showed that the major species in seawater ($0.54 \text{ mol Cl}^- \text{ l}^{-1}$) is $[\text{BiCl}_4]^-$ whereas in fresh water ($<10^{-4} \text{ mol Cl}^- \text{ l}^{-1}$) pH-dependent Bi^{3+} , BiOH^{2+} or BiO^+ is predominant.¹³ The concentration in seawater is 20 ng l^{-1} , which is two orders of magnitude lower than for arsenic.¹⁴ In addition to the natural occurrence, different bismuth compounds are introduced from the chemical industry, where it is used as a catalyst for acrylonitrile production as bismuth molybdophosphate.¹⁵ The major applications are in cosmetic products as pigments in eye shadow and lipsticks (BOCl) and as bismuth citrate in hair dye.¹⁶ The pharmaceutical industry produces bismuth subgallate for infectious diseases, bismuth germanium oxide as a contrast substance and bismuth subcitrate for ulcer therapy.¹⁷ All these substances end up in waste water and increase the amount of bismuth in sewage sludge. Only limited information is available for bismuth concentration in sewage. However, some data demonstrate a fairly high value in the range of 5 mg Bi kg^{-1} dry weight of sewage sludge, which is even higher than the amounts of antimony and arsenic.¹⁸ Bismuth is also used in fusible alloys and as a dopant in semiconductors, and TMB is used for the growth of Bi_2Te_3 thin films by MOCVD (metal organic chemical vapor deposition).¹⁹ These products are discarded in municipal and industrial waste. Of the world production of bismuth, 50% — about 5000 t per year — was used in 1990 for pharmaceutical products. These short-life products flow quickly back into the waste streams.²⁰ However, the amount of bismuth used is expected to increase because of some progress in the substitution of lead for gun bullets and of organotin compounds as antifouling paints, and the use of bismuth vanadate for high-performance lead-free pigments.²¹

The aim of this paper is to summarize the results from our groups, which show that methylated bismuth compounds can be found in various anaerobic environments. The paper also explains the particular problems in the speciation analysis for bismuth and its compounds.

EXPERIMENTAL

Reagents and standards

Trimethylbismuth (TMB) was synthesized by

Grignard reaction from methyl iodine and bismuth trichloride.²² This standard was stored in diethyl ether solution. It was checked by GC-MS, which gave only one bismuth-containing compound. All characteristic mass fragments (m/z 254, 239, 224, 209) were determined. Bismuth trichloride stock solution with a concentration of $1.000 \text{ g Bi l}^{-1}$ (Merck) was used for the semiquantification methodology, which is explained elsewhere.²⁴ Sodium tetrahydroborate (Aldrich) and hydrochloric acid (Merck, suprapur) were used for the off-line hydride generation technique.

Analytical procedure

GC-ICP-MS

Two different systems were used. The system in Essen (method 1) coupled a commercially available gas chromatograph (Shimadzu 9A) equipped with a packed glass column (Table 1) directly via a heated transfer line and a T-piece to the torch of an ICP-MS (VG Elemental PQ2+). The GC could be cooled to -100°C . The Vancouver system (method 2) consisted of a purge-and-trap system coupled to an ICP-MS (PQ2) analogous to the system in Essen (Fig. 1). These analytical systems have been described thoroughly elsewhere.^{23,24} In both systems, the gaseous species were preconcentrated by cryotrapping at -78°C in a U-shaped glass column filled with absorption material (10% SP2100 on either Chromosorb or Supelcoport). In method 1, the trap was installed into the GC, whereas in method 2 a second cryofocusing step was performed. In a refocusing step, the trapped species were volatilized by increasing the temperature of the trap from -78°C to 150°C , and the released gas was purged with a helium flow to a second U-shaped trap (6 mm o.d., 31 cm length), packed with Chromosorb (10% SP-2100 45/60 mesh, Supelco) and frozen out at -196°C . The major difference between the two methods was the heating procedure. In method 1 the trap was cooled to -100°C only, and a gentle heating ramp of 5°C min^{-1} (or $10^\circ\text{C min}^{-1}$, respectively) was applied, whereas in method 2 the trap was cooled to -196°C and an extra cryofocusing step and a non-uniform but fast heating via a variac and a Nichrome wire, which was wrapped around the trap (350°C increase in 5 min), were performed. The difference between methods 1a and b is the small difference in the heating ramp (Table 1). All methods show a similar separation characteristic; the volatile compounds were separated according to their boiling points. Good correlation was achieved between the boiling

Table 1 Instrumental parameters for methods 1 and 2 using GC–ICP–MS, shown schematically in Figure 1^a

Parameter	Method 1a	Method 1b	Method 2
<i>Hydride generation</i>			
Trapping temperature	−196 °C	−196 °C	−196 °C
<i>Cryotrapping GC</i>			
Trapping temperature	−80 °C	−80 °C	−78 °C followed by cryofocusing at −196 °C
Column temperature	−100 to +165 °C	−100 to +165 °C	−196 to +150 °C
Temperature ramp	5 °C min ^{−1}	10 °C min ^{−1}	Exponential, reaches 150 °C in 3 min
Carrier gas	Argon	Argon	Helium
Flow rate	20 ml min ^{−1}	61 ml min ^{−1}	133 ml min ^{−1}
Column	22 cm × 6 mm o.d. Supelcoport 10% SP2100	50 cm × 3 mm i.d. Supelcoport 10% SP2100	22 cm × 6 mm o.d. Chromosorb 10% SP2100
Transfer line	PTFE tube, 100 cm × 0.7 mm i.d., 100 °C	PTFE tube, 100 cm × 0.7 mm i.d., 100 °C	PTFE tube, 100 cm × 0.3 mm i.d., 120 °C

^a Slight modification of method 1 leads to methods 1a and 1b.

point of the methylated volatile species and the retention times.²⁵ Therefore, the retention times for the simple purge-and-trap system (method 2) are much shorter than for methods 1a and 1b.

Method 1a B. pt = $6.39T_r - 109$

Method 1b B. pt = $11.87T_r - 87.1$

Method 2 B. pt = $96T_r - 125$

where T_r is retention temperature (all temperatures in °C), and B.pt is the boiling point.

To start the analysis, both systems were heated and a carrier gas flow was applied. The separated species were transported through a heated Teflon transfer line to the torch of the ICP–MS. Additionally, an aqueous solution was introduced as a wet aerosol into the plasma by means of a nebulizer. Both gas flows were mixed together in a T piece (o.d. 6 mm) inserted between the spray chamber and the torch, replacing the quartz elbow usually in this position. Time-resolved analysis and multi-isotope determination were applied to check for

ANALYTICAL SET-UP

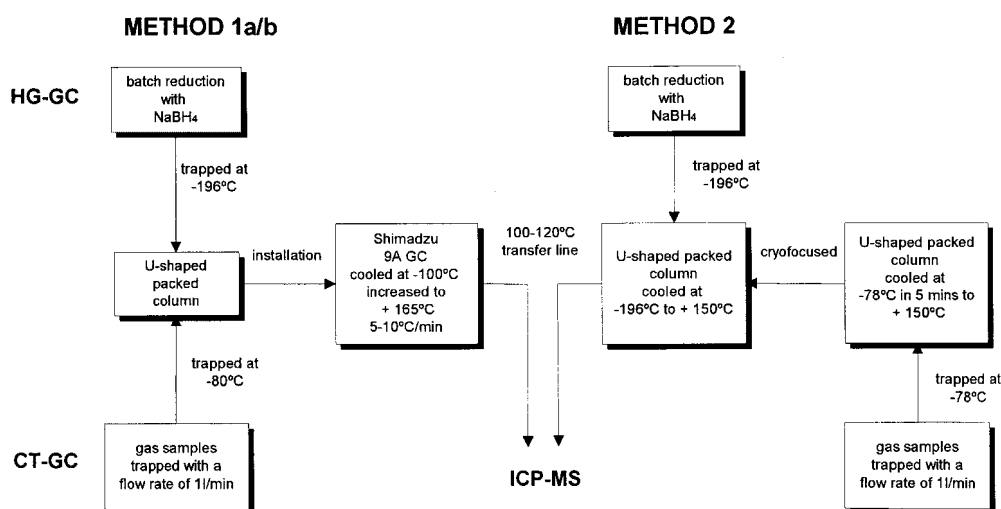


Figure 1 Schematic of the two different analytical systems for cryotrapping GC–ICP–MS and the two different methods for hydride-generation GC–ICP–MS.

other elements and intermolecular interferences. Bismuth was monitored on m/z 209.

HG–GC–ICP–MS

In order to investigate water samples for the occurrence of methylated bismuth species, hydride-generation methodology followed by GC–ICP–MS analysis was chosen. Aqueous samples (10 ml) were treated with 1 ml HCl (0.1 mol l^{-1}) to reach pH 2. Subsequently, 1 ml of 5% NaBH_4 solution was added in 15 s. The volatile hydrides were purged into a cooled trap (-196°C) by means of a 400 ml min^{-1} He flow. The traps were analyzed by the same procedure as was used for the traps containing cryofocused gas samples.

Environmental sampling

Gas and water samples from municipal landfills

The gases from the six municipal waste deposits investigated (locations I to N) are collected in gas wells and pumped in pipelines either to a furnace or to a power station. Landfill I is in the Palatinate (Germany); J in Hessen (Germany); K N in Northrhine-Westfalia (Germany); L in Bavaria and M. in Delta, B. C. (Canada).

The gases in the gas wells were sampled directly by means of a cryogenic sampling unit consisting of a U-shaped glass tube (22 cm i.d., 6 mm o.d.) and filled with non-polar chromatographic material (10% SP2100 on Supelcoport). The trap was cooled at -78°C to -80°C with an acetone/liquid nitrogen slush or an acetone/dry ice mixture.

On one waste deposit (location M) the gas percolating through a rainwater puddle 20 cm deep was sampled by a floating open-bottom gas-collecting device in the form of a cylinder (Plexiglas). A Teflon tube (o.d. 6 mm) was attached to the valve on the very top of this cylinder (i.d. 30 cm, height 10 cm). A Styrofoam ring on the outside of the cylinder was used to float this device and ropes held it in place on the water surface. The gas which bubbled through the water was collected under this device and pumped directly into a Tedlar bag. The flow rate of the membrane pump was adjusted to the same flow rate as the gases being generated under the sampling device by keeping a constant water level in the Plexiglas cylinder during the sampling time. The sampling bags were covered in black plastic bags to avoid the influence of UV light on the samples. Within 48 h the gas was cryotrapped under the same conditions as for the gas samples from the other waste deposits.

All these waste deposits were used to dump

industrial and domestic wastes in Germany and Canada. The volume of the samples varied from 4 to 20 l.

Additionally to the gas samples, condensed water from the gas wells and the rainwater from the puddle on the landfill were sampled. The water, which was in contact with the landfill gas, was sampled into polyethylene (PE) bottles, which were filled to the top to avoid oxidation. The samples were stored at 4°C in the dark.

Sewage gas

In addition to the gases from landfills, the gases produced by the fermentation of sewage sludge from eight different sewage treatment plants were also sampled (locations A to H). These are municipal plants, so the waste water was mainly of domestic origin with small amounts of industrial effluents. A–G are in Northrhine-Westfalia (Germany); H is in Vancouver, BC (Canada).

Fermentation experiments

Each of three sediments from contaminated sites in Germany (Klein Dalzig, sediments from the river Weisse-Elster; Planena, sediments from the river Saale; Jessnitz, sediments from a small creek near Bitterfeld) and one waste deposit from a copper mine near Eisleben (Theissen) were mixed 1:1 with pond sludge from an uncontaminated village pond. The pond sludge was used for the inoculation of the sediments to achieve uniform conditions for methanogenesis. Approximately 500 g of this mixture was placed in a 2-liter glass bottle, 500 ml of a nutrient solution containing acetate and some essential metal salts (all amounts in g l^{-1} : NaCl , 0.9; $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.2; NH_4Cl , 1.0; CH_3COONa , 0.82; KH_2PO_4 , 0.75; $\text{KH}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, 1.45; $\text{Na}_2\text{S}_x \cdot 7-9\text{H}_2\text{O}$, 0.25; EDTA-Na , 0.1; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.1; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.17; $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1; ZnCl_2 , 0.1; $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$, 0.02; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.03; H_3BO_3 , 0.01; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.01; H_2SeO_3 , 0.001; HCl , 0.01) were added, and the bottles were sealed airtight with gum septa. The experiments were set up in duplicate. After storage for two weeks at 30°C , the headspace gas was sampled by purging the headspace with helium and trapping the gas. Method 1b was performed in order to determine the volatile metal and metalloid compounds generated from these cultures. Additionally, total bismuth in the sediments was measured with ICP–AES following a digestion of the sediment with aqua regia (DEV, S7). In order to speciate the available bismuth in the sediments, about 50–200 mg of each sediment was placed in a

batch reactor and suspended with 10 ml water (Seralpur), 1 ml of 6% HCl was added and HG-GC-ICP-MS was performed to determine the available bismuth as bismuthine (BiH_3) and possible denvolized non-volatile methylbismuth compounds. Here, we focus on the bismuth compounds, but a more thoroughly description will be published elsewhere (D. Glindemann, A. Bergmann, A. V. Hirner, E. M. Krupp, P. Kuschik in preparation 1999).

RESULTS AND DISCUSSION

Standards

The headspace of the TMB standard dissolved in diethyl ether was analyzed by method 1a and CT-GC-ICP-MS and gave only one peak at a retention time of 33 min (method 1a) (Fig. 2b). After hydride generation of the same solution, four distinctive peaks were recorded on the m/z 209 trace of the ICP-MS (Fig. 2a). In addition to TMB, other methylated bismuth species were generated: Fig. 2(a) shows that BiH_3 , MeBiH_2 , Me_2BiH and TMB can be separated easily according to their boiling points (17, 72, 103 and 109 °C).²⁶ It is not clear, however, why all four different bismuthines were generated. Whether dimethylbismuth, methylbismuth and inorganic bismuth were already in solution, or whether demethylation of TMB took place during the derivatization, cannot be answered yet. It is likely that a demethylation process is responsible for this occurrence of partially methylated bismuth compounds, because the weak Bi-C bond (143 kJ mol^{-1})²⁷ can be cleaved easily by acid. A similar demethylation process can be observed for antimony at pH 2.²⁸

Despite the similarities to arsenic and antimony, there are major differences for bismuth. Bismuth occurs as a trivalent cation or as a bismuth oxide cation, whereas arsenic and also antimony are metalloids and occur mostly as the pentavalent anions arsenate and antimonate, respectively. Thermodynamic data on organometallic compounds show that the standard formation enthalpy for TMB ($+192 \text{ kJ mol}^{-1}$) is very high compared with $+13 \text{ kJ mol}^{-1}$ for trimethylarsine (TMA), and $+33 \text{ kJ mol}^{-1}$ for trimethylstibine (TMS).²⁹ Bismuth is more electropositive and is a metal, so the average dissociation energy of the metal-carbon bond is very low for TMB ($+143 \text{ kJ mol}^{-1}$) compared with $+229 \text{ kJ mol}^{-1}$ for TMA and

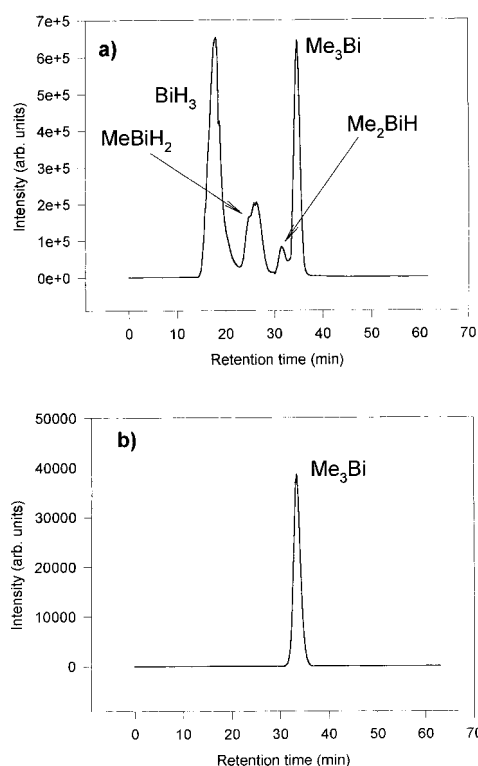


Figure 2 Chromatograms using method 1a and GC-ICP-MS (m/z 209 detection). A standard of trimethylbismuth (TMB) in diethyl ether was derivatized with NaBH_4 at pH 2 to produce volatile BiH_3 , MeBiH_2 , Me_2BiH and TMB (a), while only TMB was detected when purged with helium (b).

$+216 \text{ kJ mol}^{-1}$ for TMS.²⁷ This means that much energy is involved (i.e. taken up) in the formation of TMB (endothermic) and that the bismuth-carbon bond is very weak and can be cleaved easily (e.g. by oxygen). Therefore the stability of TMB in air would be expected to be very limited and is certainly lower than for TMA and TMS.

Furthermore, the hydride-generation process has to be studied more thoroughly with methylbismuth standards to clarify whether hydride generation can be used as a derivatization method to identify monomethyl- and dimethyl-bismuth compounds in water samples.

Environmental studies

In each gas sample from the different municipal waste deposits and from sewage sludge fermentation tanks only one bismuth peak was recorded on the m/z 209 trace. No interference from possible

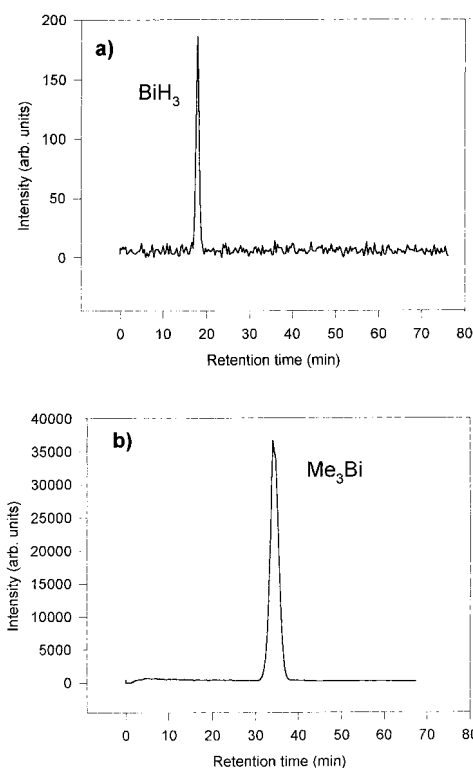


Figure 3 Chromatograms using method 1a and GC-ICP-MS (m/z 209 detection). (a) Hydride generation of 0.1 ml condensed water from the gas pipeline containing landfill gas gives only BiH_3 . (b) TMB in landfill gas.

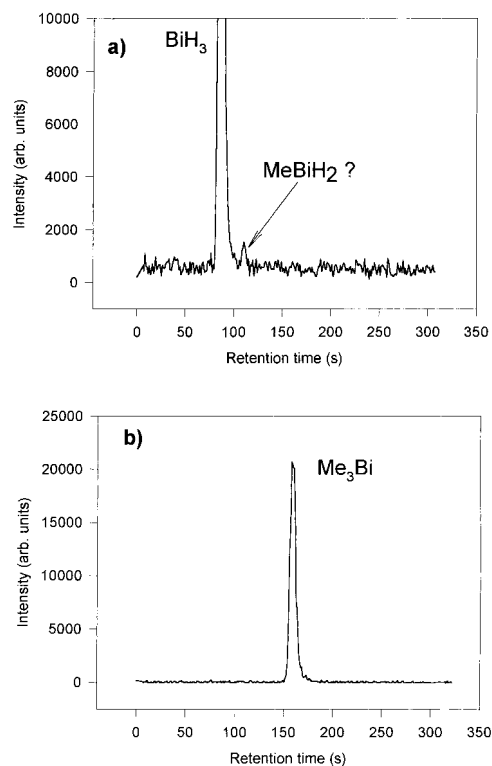


Figure 4 Chromatograms using method 2 and GC-ICP-MS (m/z 209 detection). (a) Rainwater (1 ml) from the puddle through which landfill gas percolated was derivatized with NaBH_4 at pH 2 to give BiH_3 and possibly MeBiH_2 . (b) The landfill gas contained TMB only.

$^{208}\text{Pb}^1\text{H}^+$ was encountered because m/z 208 was simultaneously monitored but no peak was recorded at the same time as the peak at m/z 209 appeared. To confirm that TMB occurs in these gases from anaerobic systems, electron-impact mass spectrometry (EI-MS) following cryotrapping, gas-chromatographic separation and fractionation was performed, which is described elsewhere.³⁰ The structure of TMB was confirmed by the major fragments (m/z 254, Me_3Bi^+ ; m/z 239, Me_2Bi^+ ; m/z 224, MeBi^+ ; m/z 210, BiH^+). The BiH^+ was derived from an H-migration from the CH_3 group. Only TMB, and no other volatile bismuth compound, could be detected in the gas samples.

The gases from the gas pipelines on the landfills showed the same concentration as the gases sampled on the top of the rainwater puddle through which landfill gas was percolating. This suggests that TMB is stable enough to percolate through water which is exposed to air. Hydride generation

was performed for these water samples and one major peak of BiH_3 was recorded (Fig. 3a). Only a small peak, which is considered to be MeBiH_2 according to the retention time, was found in the rainwater sample, (Fig. 4a) but not in any of the analyzed water samples from the pipeline (Fig. 3a). This indicates that non-volatile methylated bismuth compounds might exist in the aquatic environment. However, these findings have to be confirmed by the evaluation of hydride generation for methylbismuth compounds. Besides other volatile organometallic compounds, trimethylstibine (TMS) can be found in landfill and sewage gases.³⁰ In contrast to the absence of methylated bismuth compounds in the water system, methylated antimony compounds [i.e. monomethyl-, dimethyl-, and trimethyl-antimony(V) compounds] could be determined as the major antimony species in the rainwater samples²⁸ and in the condensed water from the gas pipeline.³¹ A reason for the absence of TMB in water could be

Table 2 TMB concentrations in sewage and landfill gases and in migration and soil gas close to landfill site N

Location	Gas source	No. of samples	TMB conc. ($\mu\text{g m}^{-3}$)	Published reference
A (1997)	Sewage gas	5	5.00 ± 1.29	
A (1998)	Sewage gas	6	5.53 ± 1.59	
B	Sewage gas	3	1.67 ± 0.16	
C	Sewage gas	3	24.2 ± 1.58	
D	Sewage gas	5	6.24 ± 1.37	
E	Sewage gas	3	4.29 ± 0.65	
F	Sewage gas	5	$0.003\text{--}0.016$	
G	Sewage gas ^a	5	$0.17\text{--}1.06$	9
H	Sewage gas ^b	4	$1\text{--}5$	
I	Landfill gas	4	$0.0002\text{--}0.0065$	8
J (1993)	Landfill gas	11	$0.312\text{--}0.892$	31
J (1998)	Landfill gas		0.168	
K	Landfill gas	4	$0.088\text{--}0.335$	41
L	Landfill gas	3	$0.378\text{--}0.610$	41
L	Gas from the leachate pipeline	3	$0.624\text{--}0.927$	41
M	Landfill gas ^b	6	$0.01\text{--}0.03$	
N	Gas wells on landfill	9	$0.01\text{--}0.403$	
N	Soil gas 100 m from landfill N	6	$0\text{--}0.034$	

^a Thermophilic digestion.^b Sampled into Tedlar bags.

that TMB in general is not very soluble and, unlike TMS, cannot easily be oxidized to form a water-soluble compound such as trimethylbismuth oxide (compared with trimethylantimony oxide). Therefore, the accumulation of TMB in water is unlikely;

Table 3 TMB concentrations in landfill and sewage gases (Table 2) compared with other volatile organometallic compounds detected

Species	Concentration ($\mu\text{g m}^{-3}$)		Reference
	Minimum	Maximum	
Me ₃ Bi	0.0002	24.2	
Me ₃ As	0.001	75.5	
Me ₃ Sb	0.04	83.7	41
Me ₄ Sn	0.07	54.8	41
PbMe ₄ ^a	0.005	0.510	41
Me ₂ Hg	0.0001	0.79	
Me ₂ Te	0.0012	1.76	
MeI	0.0001	0.230	41
Me ₂ Se	bdl ^b	0.550 ^c	41
Ni(CO) ₄	0.5	1.0	42
Mo(CO) ₆	0.2	3.6	24
W(CO) ₆	0.005	0.015	24

^a Total volatile Pb.^b bdl, below detection limit.^c Aerobic vent.

it will either be demethylated or volatilized into the atmosphere. However, it is possible that partially methylated bismuth can be complexed by other substances such as humic acids or form methylbismuth dithiolate and stay in solution.

In contrast to the minor contribution of methylated bismuth compounds in water, volatile TMB occurs in rather high amounts in the sewage and landfill gases (Figs 3b, 4b). The concentrations measured by a semiquantitative technique,²³ which uses a stable bismuth solution to calibrate the ICP-MS, are shown in Table 2. Previously published data are indicated in the table.

The concentrations measured were up to $25 \mu\text{g}$ bismuth as TMB per m^3 . It seems that the concentration of TMB in the sewage gas is a little higher than in landfill gas. If these amounts are compared with the amounts of other volatile organometallic compounds found in these gases, it is surprising that more volatile TMB is generated than other very well-known substances in the environment, e.g. dimethylmercury or dimethylselenide (Table 3).

The global impact of TMB generated from landfill sites on the biogeochemical cycle of bismuth can be calculated, if TMB correlates with methane production from landfills. Between 16 and 281 kg TMB will be generated from landfill

Table 4 Bismuth concentration in the anaerobic cultures

	Total Bi (mg kg ⁻¹)	HG Bi ^a		Volatile Bi: TMB ^d (ng kg ⁻¹)
		As BiH ₃ ^b (μg kg ⁻¹)	As MeBiH ₂ ^c (μg kg ⁻¹)	
A1	<5	0.048	bdl ^e	0.51
A2	<5	0.048	bdl	0.49
B1	<5	130	bdl	0.25
B2	<5	130	bdl	0.23
C1	<5	0.108	0.060	48
C2	<5	0.108	0.060	44
D1	367	5.91	bdl	0.084
D2	367	5.91	bdl	0.076
E1	<5	nm ^f	nm	0.56

^a Available bismuth after hydride generation (HG).^b At pH 2.^c Methylated Bi species as Me BiH₂.^d Volatile TMB (without hydride generation).^e bdl, below detection limit.^f nm, not measured.

sites worldwide, if it is assumed that the TMB produced is in the range of 0.2–1 μg m⁻³ in landfill gas with an average methane concentration of 20–65%,³² and an annual production from landfills of (20–70) × 10¹² g per year.³³ If 0.4 m³ landfill gas is produced per kg of refuse, then approximately 0.4 μg bismuth as TMB is generated from 1 kg of refuse. The annual worldwide generation of TMB from domestic sewage treatment can be calculated to be 30–4980 kg TMB assuming a TMB concentration of 1–25 μg m⁻³, a methane concentration of 62–75%,³² and a methane production of (15–80) × 10¹² g.³³ So these amounts are quite substantial, which is surprising because only a minor amount of the 5000 t bismuth world production is deposited in the sewage system.

Fermentation experiments

The fermentation experiments showed that bi-methylation of bismuth occurs and all the cultures produced TMB. The duplicates showed good agreement in terms of TMB production. The volatilization rates, however, differed by at least three orders of magnitude for the different sediments. No correlation of the total bismuth shown in Table 4 and the volatile TMB can be found. There is the possibility that the high amounts of heavy metals in the sludge from the mixing area (fermentor) minimizes the growth of the methanogens. The amount of bismuth which can be

volatilized by hydride-generation methodology following acid digestion (pH 2) also showed differences of at least two orders of magnitude for the different sediments. The different amounts do not correlate with TMB production in those cultures. In addition to the occurrence of BiH₃, small amounts of MeBiH₂ were recorded, which is an indication that methylated bismuth compounds are present in this anaerobic culture. One possible compound would be MeBi(SR)₂, which was recently investigated for its anti-cancer properties.³⁴ A uniform anaerobic culture was achieved from the procedure to mix the anaerobic pond sludge with the sediments; the duplicates show good agreement for TMB production and in the amount of generated bismuthines. However, it could not be excluded that the mixing of the sediment with the same anaerobic sludge prevents different anaerobic cultures. These might metabolize bismuth in a different way. Furthermore, the bioavailability of bismuth in the cultures, i.e. the bismuth species present in the different cultures, was probably also an important factor in TMB production. Therefore procedures for speciation of water-soluble bismuth species are urgently needed. The ethylation of bismuth, recently shown³⁵, could be used for the development of a bismuth speciation method. However, whether the integrity of the species can be conserved or not has to be proven.

Toxicological aspects

In contrast to compounds of many other heavy metals such as lead and thallium, bismuth compounds such as BiOCl show very low toxicity. However, bismuth has similar physical properties to lead. Bismuth is progressively being substituted for lead in several applications, for example as an additive in glass and ceramics, glazes and lubricating oils, and in lead shot for waterfowl (the last are usually dumped in wetlands and lakes). This reduced toxicity permits the use of bismuth compounds in the cosmetic and pharmaceutical industries and encouraged Palmieri to describe bismuth as an ‘... amazingly “green” environmentally-minded element ...’.³⁶

Bismuth has a strong lone-pair effect and can bind both to Zn(II) sites (e.g., metallothionein) and to Fe(III) sites (e.g. transferrin) in proteins.³⁷ However, the low toxicity of pharmaceutical products such as bismuth subcitrate, subnitrate and subsalicylate as well as bismuth trichloride is probably derived from their low intestinal absorp-

tion rate (<1%).³⁸ Furthermore, the change in the oxidation state from Bi(III) to Bi(V) is rather difficult compared with arsenic and antimony, which might be important for its toxicokinetics. The toxicokinetics can easily be changed if a lipophilic and volatile bismuth compound like TMB is applied. Some toxicological data of TMB are available from the time when TMB was investigated for its antiknock properties in petrol.³⁹ Sollmann and Seifter⁴⁰ examined the toxicological effects on various animals. In addition, toxicological data from accidental exposure were also reported. Two human subjects were exposed. A peculiar garlic or turnip taste was noticed, stronger than the odor. Itching and burning of the eyes were mentioned. If the exposure was prolonged, a feeling of warmth developed in the flush area, accompanied by sweating and followed by headache. Dizziness and faint feelings developed as a first stage of anesthesia. The concentration in the air was unknown, but the 24 h urinary output was measured to be as high as 0.82 mg bismuth. The urine from a second person, who felt symptom-free, contained 0.38 mg bismuth. The urinary output from non-contaminated individuals is about $12.5 \pm 29 \mu\text{g}$ per day.²⁰

Fatal dosages to rabbits and rats were examined, and it appeared that they were not dependent on the kind of mammals that were used. The average fatal dose of an intravenous application of TMB was found to be 10 mg/kg body weight. The animals (rabbits, rats) died after a 10 min exposure to 310 mg Bi as TMB per m^3 or after 45 min of exposure to 186 mg m^{-3} , respectively, of which an unknown proportion was oxidized before inhalation. These concentrations are at least four orders of magnitude higher than the measured concentrations in landfill and in sewage gases. Therefore, no fatal concentration of TMB could be measured in these gases. However, it should be noticed that no recent research has been done on the toxicological effects of TMB, which should be necessary to assess the workplace air in the vicinity of TMB sources such as landfills and sewage treatment plants or in the semiconductor industry, where TMB is used in MOCVD to produce thin films of Bi_2Te_3 .¹⁹

Conclusions

In addition to volatile arsines and stibine, trimethylbismuthine (TMB) was also produced from municipal waste deposits and from sewage sludge fermentation tanks.

Laboratory experiments could confirm the

methylation of bismuth in anaerobic cultures. However, there was only minor evidence that non-volatile methylbismuth compounds exist in sediments and in fresh water, in contrast to methylated arsenic(V) and antimony(V) compounds. Cryotrapping GC-ICP-MS was used successfully for the speciation of volatile compounds; however, no reliable speciation methods for non-volatile bismuth compounds are available. The applications of bismuth in sensitive areas such as pharmaceutical products and cosmetics should motivate environmental analytical chemists to develop better analytical methods for the speciation of bismuth in the environment.

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