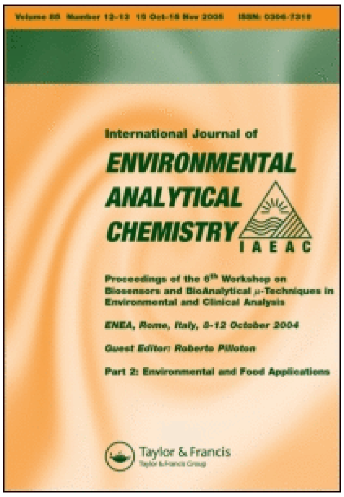

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OCCURRENCE OF VOLATILE METAL AND METALLOID SPECIES IN LANDFILL AND SEWAGE GASES

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Speciation of volatile metals and metalloids in the environment is extensively described in literature. In order to investigate unstable volatile organometallics, on-line coupling of GC with ICP-MS was used. Preliminary results for gases of sewage sludge fermentation at thermophilic and mesophilic conditions are compared with the metal and metalloid speciation in landfill gases. In each case 20 L gas were sampled by cryogenic trapping. The species were identified by element-specific detection either by retention time of standards or by calculation of the boiling point correlation. Characteristic of the separation is the linear correlation of boiling point (bp/°C) versus retention time (rt/min) (bp = 6.39*rt –109.2, r^2 = 0.9926). The amounts of total volatile elements are estimated by semi-quantification. Cd, Sn, Hg, Pb (sewage gas) and Se, Te, Hg, Pb (landfill gas) were determined in the range of ng m^{-3} level; As, Sb, Te and Bi (sewage gas) and As, Sn, Sb and Bi (landfill gas) in the μg m^{-3} level range.

KEY WORDS: Volatile organometallics, GC-ICP-MS, landfill gas, sewage gas, speciation.

INTRODUCTION

The story of volatile organometallics was started in 1893 by B. Gosio. Because of the unreliable analytical methods for identification, more than 50 years were necessary to determine "Gosio gas" as trimethyl arsine[1]. This gas was formed within a micro environment of molds on a wallpaper, which was colored with arsenic-containing pigments. Cullen and Reimer[2] commented in a review how easy an identification can be: "...the garlic-like odor of the arsines is intense and unforgettable and is a good indicator...". But not only the odor can be used as the qualitative analysis: Challenger[1] identified trimethyl arsine as a mercuric chloride adduct. The first instrumental identification was reported by Cox and Alexander[3], who used gas chromatographic and mass spectroscopic methods.

Low-temperature volatilization of organometallics was observed under anaerobic conditions. In cell experiments with *Methanobacterium* strain the presence of carbon dioxide was necessary for volatilization of dimethylarsine hydride[4]. Methane and carbon dioxide production is characteristic for dumping of biodegradable waste and for sewage sludge fermentation. Because of the low stability of organometallics, which are all thermodynamically unstable under normal environmental aerobic conditions, the genesis of these compounds is possible under anaerobic conditions, only. However, due to kinetic stabilization effects the presence of dimethyl mercury and trimethyl arsine in the atmosphere could be verified. Less than 0.1 ng m^{-3} dimethyl arsine can be found within indoor and outdoor environments[2].

Besides the observed volatile metal and metalloid species already described, other species may also exist. One criterion is the affinity, i.e. bond energy of the element-carbon bond. Antimony and bismuth are distinguished by chemistries similar to arsenic and lead. Preliminary studies reported the occurrence of species of antimony and bismuth[5].

Only compounds with high vapour pressures at moderate environmental temperatures lead to low-temperature volatilization of metals and metalloids (e.g. hydrides, alkylated compounds, or halides). Methylation by many organisms (clinically important bacteria and residents of anaerobic sediments and sludge) will be common in model experiments[6] as well as in the anthroposphere[7]. Sewage gas and gases from domestic waste deposits may be prospective media to look for these organometallic species, because they provide suitable conditions for their generation. Biodegradable material produces a gas phase composed of carbon dioxide, methane and hydrogen within waste deposit and fermentation tanks; consequently the partial pressure of oxygen will be reduced. After the initial phase, the contents of carbon dioxide and methane exceed more than 95 Vol.% of the gas, and are accompanied by many gaseous trace compounds as identified in domestic and industrial waste deposits (e.g. benzene, hydrocarbons, halogenated hydrocarbons, hydrogensulfide, ...).

Some industrial products (e.g. insecticides, fungicides, stabilizers) contain organometallics and other element-organic compounds like siloxanes[8], however usually methylated compounds are formed within natural systems in the presence or absence of microbiological activity.

With respect to chemical speciation analysis of volatile organometallics in the atmosphere, either sequential sampling procedures or chromatographic methods are useful techniques. For speciation of mercury in the atmosphere, Schroeder and Jackson[9] fractionated mercury species by sequential sampling, using a sampling train consisting of four different traps in series. Another procedure is the one stage sampling of all compounds by cryogenic trapping including preconcentration and kinetic stabilization simultaneously at very low temperatures (<–80°C). By increasing the temperature a gentle desorption of the compounds can be attained for a non-destructive transportation to the detector. According to the multitude of compounds, an element-specific detector will be necessary. Our recent studies[5] by using an inductively-coupled plasma mass spectrometer as a multielement detector showed that thermodesorption of the sample only was not sufficient for separation of the different species. Gentle thermodesorption in combination with a very short non-polar column with *Supelcoport* (10% SP-2100) showed a sufficient separation for eight different tin species[10]. Förstner *et al.*[11] determined the metal content in landfill gas by absorption of the gases in $KMnO_4$. Neither the detection limits nor the ability of speciation analysis were sufficient.

The aim of our investigation was the identification of volatile metal and metalloid species in landfill and sewage gas by chromatographic separation without derivatization. A multielement detector was used for screening unexpected volatile organometallic compounds.

EXPERIMENTAL METHOD

Sampling procedure

Kinetic stabilization as well as preconcentration of the gas sample was achieved by cryogenic trapping at low-temperature (<–80°C).

The sample collection system consisted of a drying tube, two cryogenic glass traps, a vacuum pump and a gas meter, connected in series. The drying tube (2.2 cm o.d., 9.2 cm length) was filled anhydrous $CaCl_2$ (Merck) or with $Mg(ClO_4)_2$ (Merck) to avoid water condensation into the glass trap and to remove aerosol particles.

The traps (6 mm i.d., 22 cm length) were cooled with acetone/liquid nitrogen (about −80°C); this relatively high trapping temperature was used in order to avoid condensation of methane during sampling. More than 95% of tetramethyl tin was collected in the first trap; for very volatile species like stannane (SnH_4) the sampling efficiency was much lower. Only liquid nitrogen trapped these gases completely.

The trap was packed with *Supelcoport* (10% SP-2100 60/80 mesh, Supelco), which was secured with glass wool plugs. All connections between components were made with teflon tubing (PFA 0.64 cm o.d., 0.32 cm i.d.) and teflon or nylon Swagelok units. The tubing was as short as possible to avoid analyte condensation and loss. Operational blanks were also analysed with each batch of samples. The trap was closed with swagelok stoppers and stored in liquid nitrogen.

Sampling locations

Landfill: A domestic waste deposit, which is located in central Germany was examined. In the deposit gas wells were installed. Evolving gas was pumped to the power station. The contents of methane and oxygen were 45.3% and 0.5%, respectively. The examined gases were sampled from different gas wells of this domestic waste deposit.

Sewage putrification plant: Within the putrification, a fermentation of sewage sludge can be driven under anaerobic conditions at different temperatures. The first stage deals with acetogenic metabolism. The following metabolism of carbon acids (low molecular mass) during methanobacterium treatment results in methane production. Thermophilic and mesophilic strains of methanobacterium are involved. The sewage sludge from a municipal putrification plant (average of domestic and industrial sewage (40/60), 850,000 inhabitants connected, Germany) is treated first at 56°C (thermophilic) and afterwards at moderate temperature of 35°C. From both sites sewage gas was sampled. The average of heavy metal concentration in the sewage sludge was not extraordinarily high (e.g. medium concentration in 1993 3.1 mg kg^{-1} (Hg), 5.0 mg kg^{-1} (Cd), 410 mg kg^{-1} (Pb)).

For determination of volatile metal/metalloid compounds in the environment, preliminary studies of domestic waste deposits and digestion tanks from municipal sewage treatment plants have been performed. The gases were sampled from different gas wells of the deposit, and were usually pumped to power stations. The sewage gas was sampled from thermophilic and mesophilic digestion. In both emissions the contents of methane and carbon dioxide were 61% and 35.2%, respectively; the oxygen content was less than 1%.

Volumes of 20 L of gas were sampled seven times from each location.

Analytical method

The separation technique employed was the combination of thermodesorption of the cryotrapped sample with a chromatographic column (*Supelcoport*, 10% SP-2100), and has been described thoroughly elsewhere[10].

Inductively-coupled plasma mass spectrometry (ICP-MS) is a reliable detector for volatile organometallics. According to Hutton and coworkers[12], who carried out direct analysis of organometallics (e.g. in SiH_4), reduction of signal intensity with the presence of refractory elements by deposition of e.g. SiO_2 on the sampler and skimmer cones may occur. Hill *et al.*[13] and Jakubowski *et al.*[14] described the different behaviour of dry aerosols (e.g. organometallic gases) in comparison to wet aerosols like nebulized metal solutions. As desorption of water and deposition of SiO_2 on the interface during a chromatographic run will influence the sensitivity of the ICP-MS, an internal standard is required. Furthermore, the content of hydrogen in the plasma is influencing the sensitivity.

Besides the injection of the separated organometallics, nebulized solutions containing the internal standard (10 ng mL^{-1} rhodium) were added to the plasma. The simultaneous detection enables a continuous internal standardization for controlling the sensitivity of the ICP-MS.

A gas chromatograph (*Shimadzu 9A*) with cryogenic option was coupled with a *VG Plasmaquad PQ2+* (Fisons Inst., Winsford, England). For introduction of the dry aerosol a high solid torch was used. The instrumental parameters are shown on Table 1. For measurement of environmental samples a multispecies and multielement determination was used. $^{46}SiOH$, $^{47}SiOH/PO$, ^{48}SO, ^{73}Ge, ^{75}As, ^{77}Se, ^{81}Br, ^{82}Se, ^{113}Cd, ^{119}Sn, ^{120}Sn, ^{121}Sb, ^{123}Sb, ^{125}Te, ^{126}Te, ^{127}I, ^{129}Xe, ^{202}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi, and ^{103}Rh were measured. The masses of Si and P were not chosen, because of the high background of the masses 28 (N_2), 29(N_2H), 30 (NO) and 31 (NOH). The gas chromatographic temperature was linearly increased to 150°C by a rate of 5°C min^{-1} after an isothermal phase at -100°C for 3 minutes.

Reagents and standards

In contrast to the normal analysis of nebulized liquids, no gas standards or reference materials exist for quantification of the trace element content. However, it is possible to prepare some organometallics, but most of these species are difficult to handle.

The following tin standards were used: Sn^{4+} (Merck, Sn as $SnCl_4$ in 5 mol/L HCl, 1000 mg/L), $Sn(CH_3)Cl_3$ (Aldrich, 97%), $Sn(CH_3)_2Cl_2$ (Aldrich, 97%), $Sn(CH_3)_3Cl$ (Merck-Schuchardt, 98%). A stock solution was made of $Sn(n\text{-}C_4H_9)Cl_3$ (Aldrich, 95%), $Sn(n\text{-}C_4H_9)_2Cl_2$ (Fluka, 97%) and $Sn(CH_3)_4$ (Strem, 98%) in methanol (Baker, > 99.5%). Beside the hydrides of tin, a mixture of alkylated hydrides (SbH_3, $Sb(CH_3)H_2$,

Table 1 Operating parameters for GC-ICP-MS.

GC-ICP-MS parameters	
ICP-MS parameters	
Generator (crystal stabilized 27 MHz), power	1350 W
Gasflow (Coolant/Auxilary)	13/1.3 L/min
Nebulizer (Meinhard C-Typ), Sample uptake	1.28 mL/min
Nebulizer gas flow (Ar)	0.900 L/min
Sampler/Skimmer cones (Ni), orifice	1.0/0.7 mm
Detector mode (Channeltron)	pulse counting
Acquiring data (peak jump mode)	10.24 ms per amu
GC parameters	
Column (glass, *Supelcoport*, 10% SP-2100)	22 cm (l), 6 mm (id)
Carrier gas flow (Ar)	20 mL/min
Temperature range	-100°C to + 180°C

$Sb(CH_3)_2H$) and $Sb(CH_3)_3$ were synthesized by Müller[15]. $Hg(CH_3)_2$ (Strem), $As(CH_3)_3$ (Strem) were used for identification as well.

An aqueous solution (4 mL) was acidified with 1.5 mL hydrochloric acid (1 mol L^{-1}) to reach pH 2, and poured into a 50 mL two neck flask. The volatile compounds were purged by helium flow of 500 mL min^{-1} for 10 minutes, and condensed after a drying tube ($Mg(ClO_4)_2$, Merck) into a cryogenic trap filled with Supelcoport (10% SP-2100). After 10 minutes 1 mL alkaline $NaBH_4$ (5%) solution was introduced over a period of 15 s from a dropping-funnel into the solution, and the hydrides were purged by He-flow of 100 mL/min into the trap. The trap was cooled by liquid nitrogen.

RESULTS AND DISCUSSION

Identification

The matrix of CO_2/CH_4 may influence the argon plasma, which can be observed by the internal standard (Rh). Figure 2 shows the stability of the plasma monitored by the Rh signal. However, matrix separation techniques before thermodesorption are not necessary, because the argon plasma is stable during the determination.

Using an ICP, any molecular information will be lost before reaching the detector. But the identification of the metal and metalloid can be determined exactly by ICP-MS, because no isobaric interferences were observed (with some exception, e.g. arsenic, mass 75). If volatile chlorines are generated within the argon plasma, mass 75 $ArCl^+$ can be detected. The intensity of mass 77 can be used for interference correction (Figure 1), according to the isotope ration of Cl (^{35}Cl, 75.8%; ^{37}Cl, 24.2%), while selenium will be detected simultaneously at masses 82 and 77.

According to the analytical method, using direct determination of the sample including the matrix gases (e.g. CO_2), a comparision of the retention time of the standard is usually sufficient for identification, because only a few volatile species for each element are possible. Figure 2 shows a chromatogram of three standards (trimethyl arsine, dimethyl mercury and tetramethyl tin), which are simultaneously detected by multielement detection.

The boiling points (bp) of the standard species and the retention times (rt) show a linear positive correlation ($r^2 = 0.9926$) (Figure 3) in contrast to Donard *et al.*[16], who found an exponential relationship.

The linear equation of the non-polar column for all standards is:

$$bp = 6.39 * rt - 109.2. \qquad (1)$$

The same analytical system showed a similar relationship ($bp = 6.05*rt - 101.6$, $r^2 = 0.9988$) for tin standards[10].

These equations can be used for extrapolation of the boiling point of unknown peaks. By knowing the metal or metalloid and the calculated boiling point, the spectrum of the volatile species will be reduced. In Table 2, a comparison of landfill gas and sewage fermentation gas is shown for volatile species.

Many volatile compounds were detected in landfill gases as well as in sewage fermentation gases. No volatile product was detected for Ge and Tl. Due to low quantities of possible volatile compounds of Se, I, Br, Si, S, P, no species could be identified. Capillary-GC/MS methods would be more reliable for these compounds, because of a relatively bad spectral resolution of the method used here.

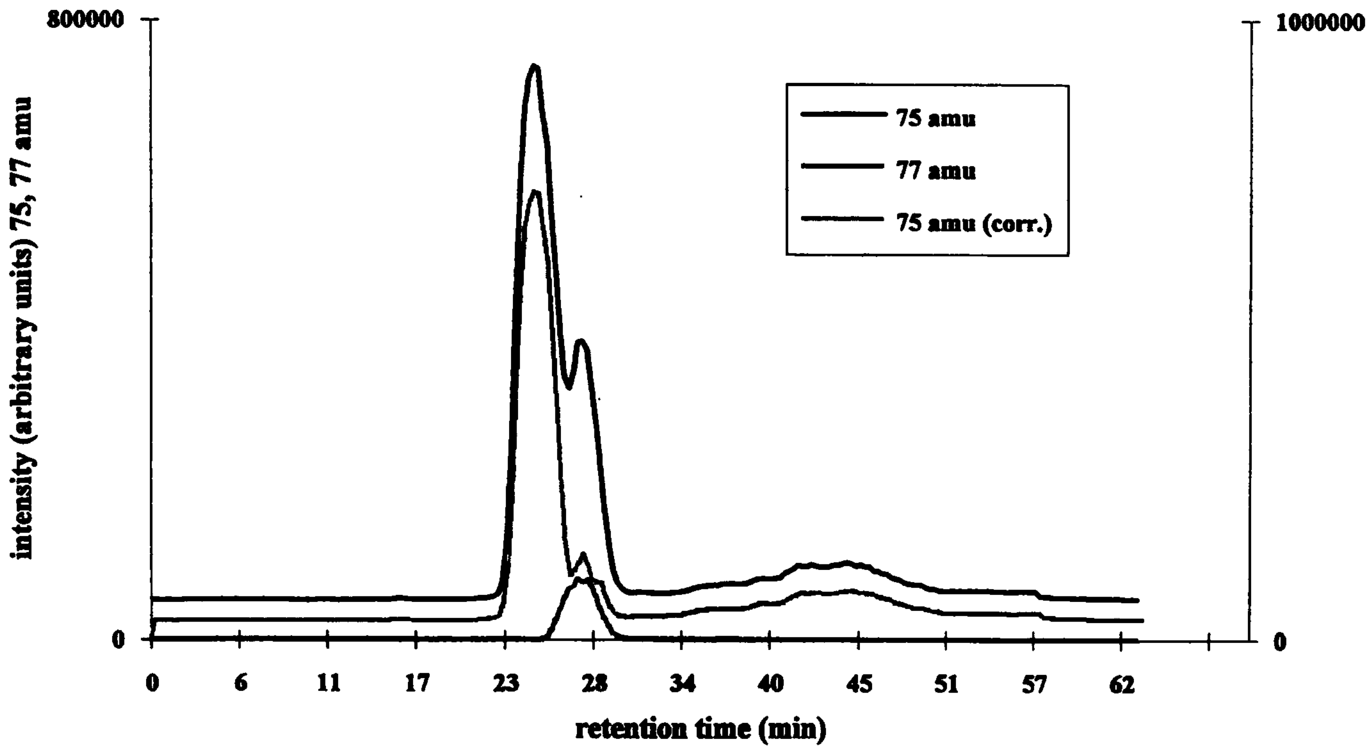

Figure 1 Isobaric interference on 75 amu. $^{40}Ar^{35}Cl$ is subtracted by the intensity of 77 amu, due to the isotopic ratio of $^{35}Cl/^{37}Cl$[52]. The occurrence of ^{77}Se is related to the amounts of ^{82}Se.

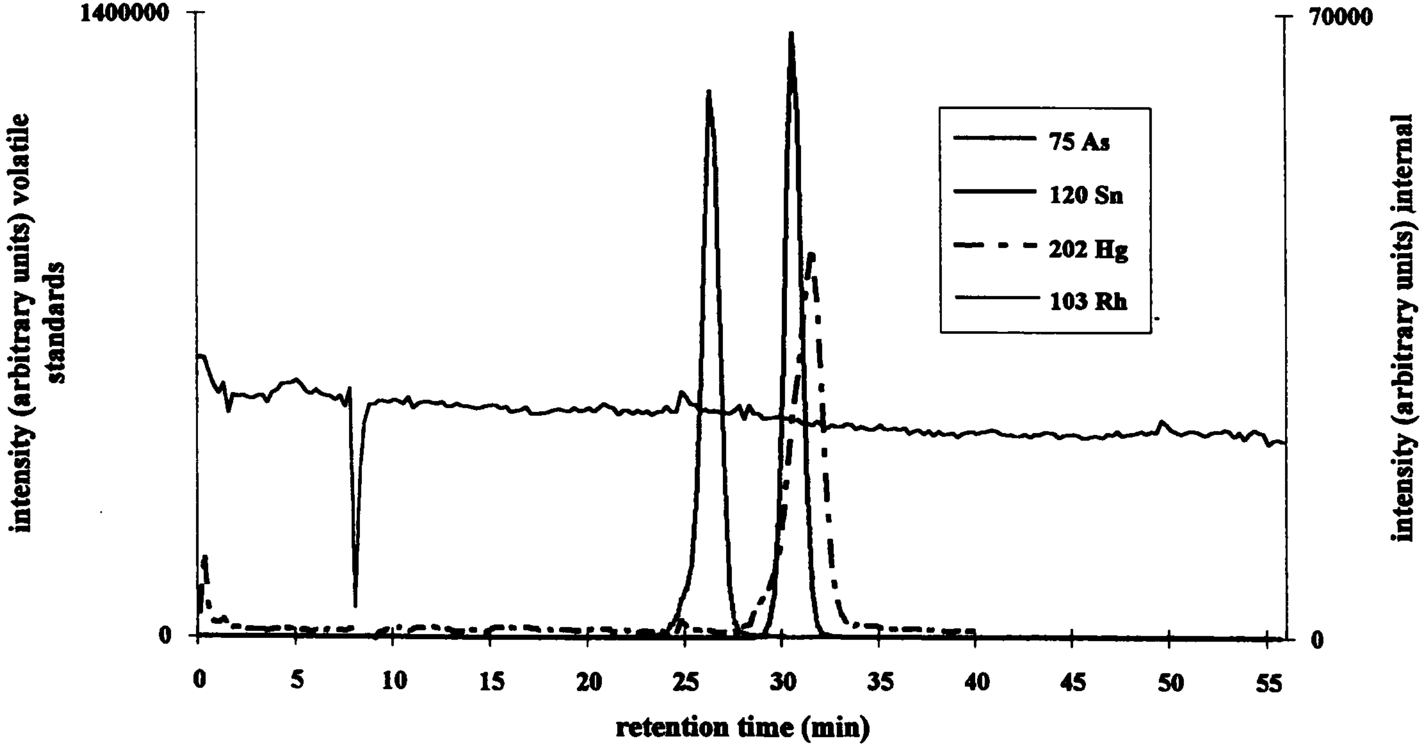

Figure 2 Trimethyl arsine, dimethyl mercury and tetramethyl tin measured simultaneously by GC-ICP-MS in a multielement detection mode. Rhodium as internal standard run simultaneously.

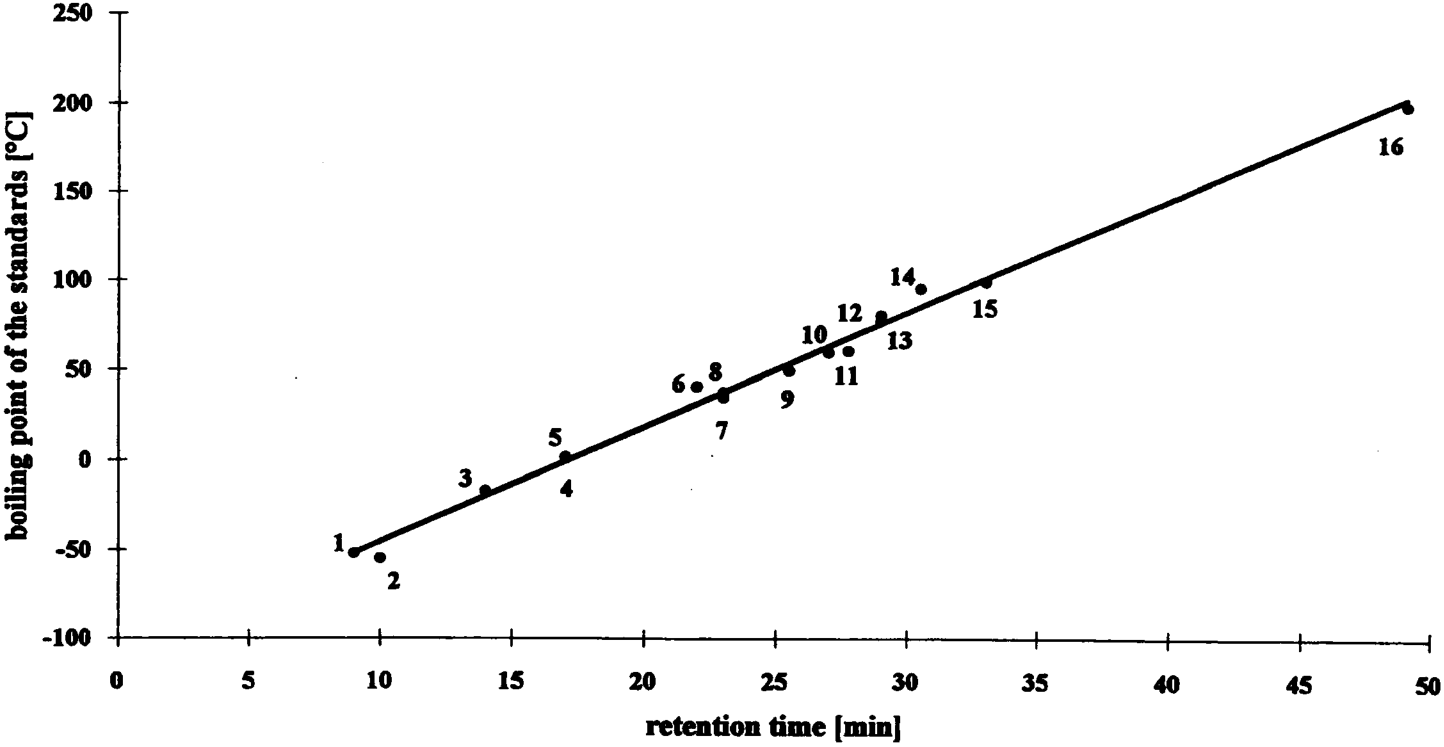

Figure 3 Correlation of the boiling point of 16 standard species to the retention time of the used analytical method. **1** (SnH_4), **2** (AsH_3), **3** (SbH_3), **4** ($As(CH_3)H_2$, **5** $Sn(CH_3)H_3$)), **6** ($Sb(CH_3)H_2$), **7** ($Sn(CH_3)_2H_2$), **8** ($As(CH_3)_2H$), **9** ($As(CH_3)_3$), **10** ($Sn(CH_3)_3H$), **11** ($Sb(CH_3)_2H$), **12** ($Sn(CH_3)_4$), **13** ($Sb(CH_3)_3$), **14** ($Hg(CH_3)_2$), **15** ($Sn(n\text{-}C_4H_9)H_3$), **16** ($Sn(n\text{-}C_4H_9)_2H_2$). bp = −109.16 + 6.39 * rt.

Table 2 Identified species of the elements in sewage and landfill gas; *the identification is confirmed by the retention time of a gas standard, the other species are identified by calculation of the boiling point (1013 mbar) by the equation (bp = 6.394 * rt –109.2).

Element	*Sewage gas*	*Landfill gas*	*Calc. bp/°C*	*Ref.bp/°C*
As	AsH_3^*	AsH_3^*	–45	-55^{63}
	$As(CH_3)H_2^*$	–	3	2^{64}
	$As(CH_3)_2H^*$	$As(CH_3)_2H^*$	38	$35–37^{64}$
	$As(CH_3)_3^*$	$As(CH_3)_3^*$	57	$50–51^{64}$
	$As(C_2H_5)(CH_3)_2$	$As(C_2H_5)(CH_3)_2$	89	87^{64}
		$As(C_2H_5)_3$	147	140^{63}
Bi	$Bi(CH_3)_3$	$Bi(CH_3)_3$	108	110^{43}
Cd	$Cd(CH_3)_2$ (?)	–	73	106^{63}
Hg	$Hg(CH_3)_2^*$	$Hg(CH_3)_2^*$	92	96^{63}
Pb	$Pb(CH_3)_4$	$Pb(CH_3)_4$	115	$110^{\sim 35}–110^{57}$
	$Pb(C_2H_5)(CH_3)_3$	–	140	$135^{\sim 35}$
	$Pb(C_2H_5)_2(CH_3)_2$	–	166	$155^{\sim 35}$
	$Pb(C_2H_5)_3(CH_3)$	–	191	$171^{\sim 35}$
	$Pb(C_2H_5)_4$	$Pb(C_2H_5)_4$	210	$184^{\sim 35}–200^{\sim 57}$
Sb		SbH_3^*	–16	-17^{63}
	$Sb(CH_3)_3^*$	$Sb(CH_3)_3^*$	82	81^{65}
Sn		SnH_4^*	–39	-52^{66}
	$Sn(CH_3)_4^*$	$Sn(CH_3)_4^*$	82	78^{67}
	$Sn(n\text{–}C_4H_9)H_3^*$	$Sn(n\text{-}C_4H_9)H_3^*$	98	$98–100^{68}$
	$Sn(n\text{-}C_4H_9)_2H_2^*$	$Sn(n\text{-}C_4H_9)_2H_2^*$	204	$200^{\sim 69}$
Te	$(CH_3)_2Te$	$(CH_3)_2Te$	82	83^{63}

~ extrapolated boiling point.

Tin

In both gas systems tin species were detected (Figure 4). Besides the concentration, the number of species was smaller in sewage gas. Only tetramethyl tin, *n*-butyltin hydride and di(*n*-butyl)tin hydride were detected in both systems. Butylated tin hydride may be a product of degradation of e.g. anti-fouling paints. In landfill gas, SnH_4 was detected. In contrast to the well separated peaks in sewage gas, the landfill gas contained many peaks, which were not adequately separated. The retention times of these species are similar to the retention time of the degradation products of the tin standard cocktail reported earlier[10]. Potential candidates are the mixed alkylated hydrides (e.g. n-butylmethyltin hydride, *n*-butyldimethyltin hydride). Maguire[17] determined tributylmethyl tin and dibutyldimethyl tin in a Canadian harbour sediment.

Nevertheless, volatile organotin compounds are rarely described in literature. The major product was tetramethyl tin which is produced from trimethyltin hydroxides in sterile sediments[6]. A conversion from trimethyltin chloride to tetramethyl tin is recorded by Guard et al. in 1981[18]. Beside alkylated compounds, Jackson *et al.*[19] suggested the occurrence of volatile hydrides (e.g. tributyltin hydride). According to Donard and Weber[20] and our results[21], stannane was produced under environmental anaerobic conditions. Hydride synthesis has been described recently for phosphorus. Volatile phosphorus as phosphine (PH_3) was determined as a biogenetic formation product in sewage plant sludges[22], and in the surface sediment of Hamburg harbour[23].

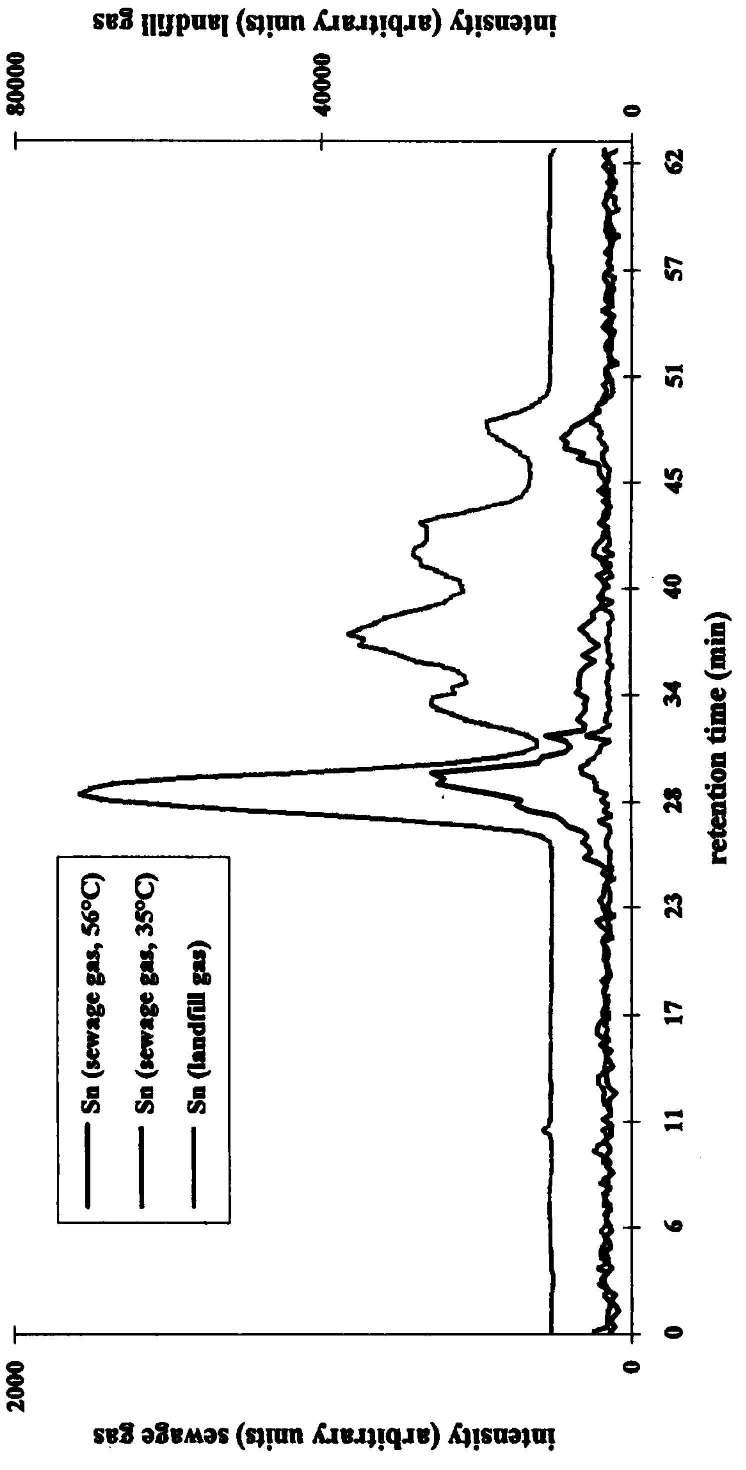

Figure 4 GC-ICP-MS chromatogram of volatile tin (mass 119) compounds and comparison of sewage gas (thermophilic and mesophilic fermentation) to landfill gas.

Tellurium

The natural abundance of tellurium being low, Craig[24] suggested a relatively low impact of the volatile telluride on the environment. Though the unknown peak of Te in the present work could be calculated as dimethyl telluride (Table 2). According to the boiling point correlation, the unknown major peak, which is present in sewage as well as in landfill gas might be dimethyl telluride. This confirms the microbiological experiments of Alexander *et al.*[25], who observed "smelling methylated products" by bacterial reduction of tellurites, and a recording a garlic odor of the breath of workers, who were in contact with tellurium[26]. Microbial methylation for selenium and tellurium was detected very early by Challenger[27]. A strain of *Penicillium* from sewage and *S. brevicaulis* produced dimethyl selenide and dimethyl telluride. Karlson and Frankenberger[28] established that no environmental data on alkylated tellurides exists, although there is one publication dealing with volatile tellurium in the atmosphere (0.24 ng m^{-3} was sampled on gold-coated beads). But no speciation was carried out[29].

Antimony

For antimony, one major peak was detected in both systems, which was identified as $Sb(CH_3)_3$ by comparision to the retention time of standards. Similar concentrations of $Sb(CH_3)_3$ have been found in these gases. Stibine (SbH_3) was detected only in landfill gas in a very low concentration. References concerning antimony are very rare, nevertheless the methylation of antimony was reported by Parris and Brinckman[30]. Also mono- and dimethylstibinic acid were found in river and seawater[31]. Benson and Cooney[32] suggested a similar bioalkylation process of antimony by marine algae similar to arsenic.

Lead

The five tetraalkyl lead compounds ($(C_2H_5)_nPb(CH_3)_{n-4}$, n = 0–4) show moderate vapour pressures between 0.35–31.6 mbar at 20°C. Thus the emission of tetraalkyl lead, which was used as an antiknock fluid for commercial gasolines was observed. This has been reviewed by Harrison[33] and van Cleuvenbergen *et al.*[34].

For lead no standards were available. But the calculated boiling points of the unknown peaks, were very similar to those of the mixed alkylated products[35]. The extrapolation of the boiling points are less than the extrapolation of tetraethyl lead by Hewitt[57] (see Table 2). This explains the small shift in boiling points of the mixed alkylated products (Table 2). Thus in landfill gas tetraethyl lead and tetramethyl lead could be detected at a very low level (Figure 5). Tetraalkyl lead decomposes in water to tri- and dialkyllead ions, which are quite soluble and thus may be washed out by rain, ending up in surface water. The salts of these compounds have appreciable vapour pressures, and therefore could be expected in the atmosphere. The concentration of organolead compounds in mesophilic and thermophilic fermentation is even higher. Five species were observed; triethylmethyl lead is the main product. After the emission of tetraethyl lead into the atmosphere, some $Pb(C_2H_5)_3^+$ will be solved into water. Methylation can occur, by either biomethylation or transmethylation during fermentation. In fish the accumulated organolead (mostly in ionic form) in methylated to tetramethyl lead in their organs; the highest level was found in the colon[36].

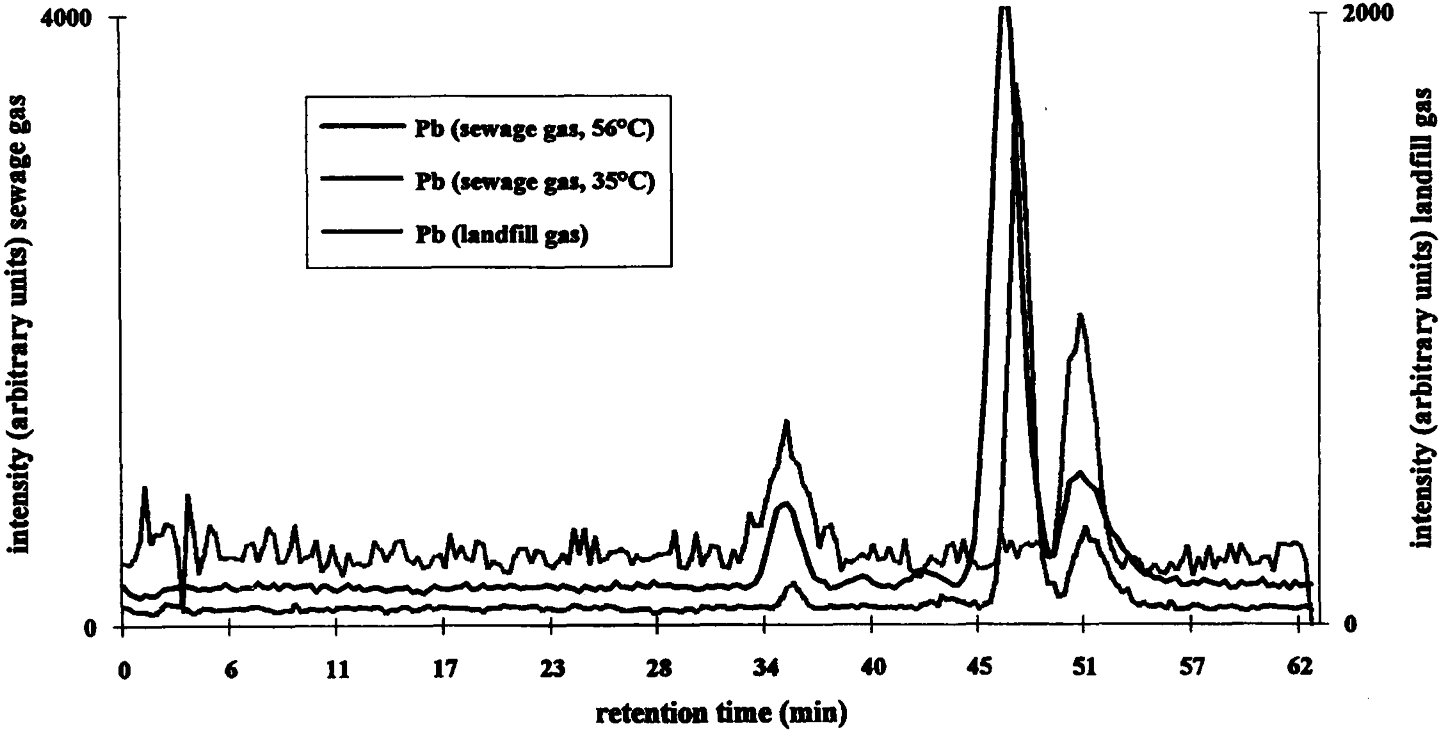

Figure 5 GC-ICP-MS chromatogram of volatile lead (mass 208) compounds and comparison of sewage gas (thermophilic and mesophilic fermentation) to landfill gas. Tetramethyl lead and tetraethyl lead were determined in all samples, but the mixed alkylated products only in sewage gas.

Model studies with *Aeromonas, Alcaligenes, Acinobacter, Flavabacterin,* which were isolated from lake sediments metabolized organic and inorganic lead into volatile tetramethyl lead[37]. Biomethylation of lead or the tri and dialkylated compounds leads to volatilization. However, biomethylation of lead could be only demonstrated, if anthropogenic emissions into the atmosphere could be stopped completely. Although the use of organolead as an additive to gasoline has been steadily decreasing in the last few years in Europe, volatile lead compounds can still be detected in the atmosphere.

Cadmium

Only in sewage gas in thermophilic as well as in mesophilic fermentation, a volatile cadmium species could be detected. The calculated boiling point (73°C) did not correspond very well to dimethyl cadmium (106°C). There are few references in the literature for volatile cadmium compounds. Huey *et al.* (1976)[7] detected a volatile cadmium species during methylation of mercury to methylmercury after exposure of a volatile cadmium product to Hg^{2+}. Robinson and Kiesel[38] treated methylcobalamin with a Cd^{2+} solution; an unknown volatile product was trapped but not specified.

Mercury

Apart from dimethyl mercury, which was recorded in all gas samples, other unknown peaks were observed in sewage gas (Figure 6). Neither methylmercury hydride, as a possible candidate for a more volatile species, nor other alkylated mercury compounds in sewage gas could be identified. The broadened peak at a high oven temperature of 150°C corresponds to semi-volatile species (boiling point > 200°C); elemental mercury as well as methylmercury chloride are possible candidates.

Volatile mercury in the atmosphere was investigated quite intensively due to the presence of mercury from high temperature combustion processes as well as industrial emissions, and because of its toxicity and potential transformation into the more hazardous organomercury species. Low-temperature volatilization of mercury over lake surfaces in Sweden was investigated by Xiao *et al.*[39]. They found a daytime flux during summer in the range of 3–20 ng h^{-1} m^{-2}. During the night the flux was three times lower; in winter no volatile mercury was detected. The flux over forest soil was found to be much lower in magnitude. The amount of volatilized mercury depends on temperature as described by the Arrhenius equation. Volatile species were elemental mercury and smaller amounts of dimethyl mercury[40]. Compared to some studies in urban air elemental mercury was the major species, but dimethyl mercury was also detected in concentrations of 0.2–1.6 ng m^{-3} in Toronto/Canada (1987)[41,42].

Bismuth

One isolated peak was detected in all gas samples (Figure 7). The calculated boiling point, 108°C, is similar to trimethyl bismuth (108.8°C)[43]. Due to the thermodynamic stability of volatile bismuth species, trimethyl bismuth is the most stable methylated compound in this boiling point range. Nevertheless trimethyl bismuth is unstable against oxygen and water[44]. Thayer[45] noticed, that no evidence for biomethylation of bismuth has appeared. Thus further investigations with bismuth standards are necessary for identification.

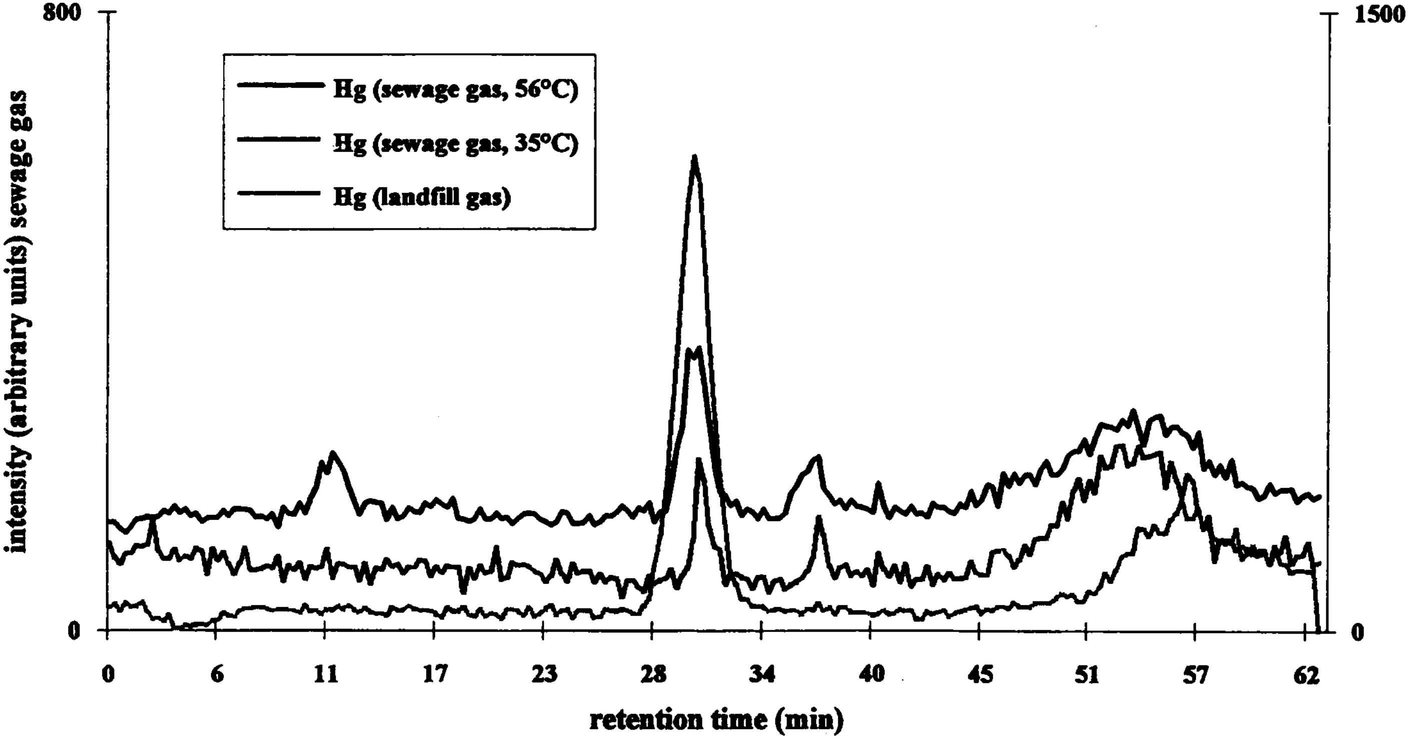

Figure 6 GC-ICP-MS chromatogram of volatile mercury (mass 200) compounds and comparison of sewage gas (thermophilic and mesophilic fermentation) to landfill gas.

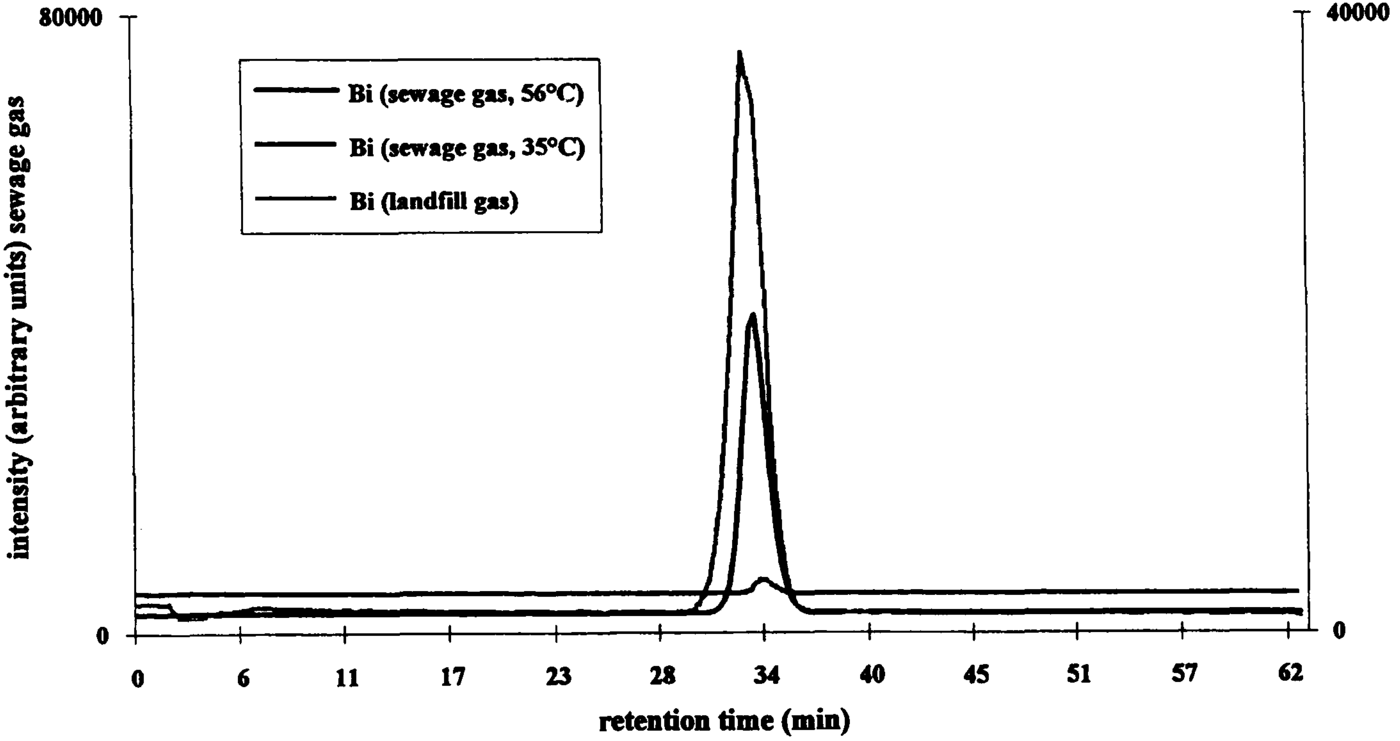

Figure 7 GC-ICP-MS chromatogram of volatile bismuth (mass 209) compounds and comparision of sewage gas (thermophilic and mesophilic fermentation) to landfill gas. Only one peak is observed. The concentration of the species is much less in mesophilic fermentation than in the other ones.

Arsenic

The problem of the element-specific detection of arsenic is discussed above. After correction of isobaric interferences, one major species could be separated in landfill gas (trimethyl arsine). Additionally arsine was detected. Beside trimethyl arsine, dimethyl and monomethyl arsine were detected in sewage gas, which parallel findings of McBride and Edwards[46], who found dimethyl arsine in sewage flora under similar conditions as the methanogenic strain.

The interaction of different arsenic compounds with the fungi *Scopulariopsis brevicaulis* leading to arsine production was investigated by Challenger[1]. Beside trimethyl arsine, other arsines were generated in the course of model studies by interaction with fungi or bacteria. Volatile arsine was produced by rumen bacteria[47]; production of arsenic hydrides was also observed. Arsenic oxide interacted with fungi from sewage (*C. humicola and S. brevicaulis*) by production of trimethyl arsine and a small amount of monomethyl arsine[48]. McBride and Wolfe[4] reported some volatile arsine production from *Methanobacterium.* Trimethyl arsine and dimethyl arsine were evolved by *Methanobacterium thermoautotrophicum*[2]. A mixture of glucose and soils enriched with sodium arsenate released arsine (AsH_3). Cheng and Focht[49] isolated *Pseudomonas and Alcaligenes* as soil bacteria. Also marine plants and algae methylated arsenic, but no certain observation of volatile compounds is reported. Apart from model studies, there are also a few environmental studies: e.g. soil microorganisms produced dimethyl arsine[50].

Trimethyl arsine was confirmed by the retention time of a standard. Dimethyl arsine, monomethyl arsine and arsine could be compared with the degradation product of trimethyl arsine after hydride generation of the standard.

Also mixed alkylated arsines were identified by boiling point calculation. Methylated and ethylated forms of arsenic were determined in natural gas samples by Irgolic *et al.*[51] and Delgado-Morales *et al.*[52]. The synthesis of these products without any microbiological activity was discussed. However, in further studies better separation techniques must be used, and structure information will be necessary for a multitude of semi-volatile compounds.

Quantification

As gaseous standards do not exist, only semi-quantifications can be achieved. Because of the lability of some species, alternative calibration techniques are necessary. The interelement calibration technique used relies on the assumption that sensitivities for all species of one element are equal. In the range of 10 to 1000 ng, alkylated tin hydrides show similar sensitivities[10]. The semi-quantification of volatile tin and arsenic was tested by the individual external standardization technique[53]and applied to total metal contents in the range of one order of magnitude. This can be used for acquiring semi-quantitative data about the total desorbable tin species, which was reported earlier[10]. For accurate quantification, the whole analytical system must be calibrated as a complete unit including collector device and GC-ICP-MS. A known volume of air, which is saturated by the volatile species (e.g. dimethyl mercury) at constant temperature can be used as calibration standard[54]. This procedure can only be used for a relatively stable product, otherwise a sufficient calibration is not guaranteed.

For estimation of the importance of the flux of volatile organometallics for the biogeochemical cycle, a semi-quantification technique was used, which was described earlier[5,10].

Liquid solutions can be used as an internal standard, if the transfer rate of the standard into the plasma is known, and similar ionisation yields exist for standards and analytes. A 10 µg L^{-1} solution of ^{103}Rh was used, exhibiting a 2.9% transfer rate into the ICP. The transfer rate of the gas sample into the plasma is nearly 100%[55]. Before analysis, the relative sensitivity of ^{103}Rh in relation to the analyzed isotope (e.g. ^{120}Sn) was determined in a standard liquid solution. The relative sensitivity factor was determined under the identical plasma conditions as for gas sample analysis. The ratio of analyte ion intensity to the continuous flow of nebulized Rh was used for internal standardization. Besides this detector calibration as described, the sampling efficiency was controlled by using a standard gas mixture.

The volatilization of the elements in sewage fermentation gas and landfill gas were in the same range of magnitude, with the exception of tin. The results of seven samples are listed in Table 3. The variation in sewage gas analysis is very high. There exists a tendency, that concentrations in the thermophilic fermentation are one order of magnitude higher than in the mesophilic process. Though the input of metal and metalloids are similar in these processes, the soluble organometalic ions in the sewage sludge were not determined in this study. Further investigations are necessary to determine, if the bacterial strains or the temperature effect was responsible.

Volatile cadmium was detected in sewage gas only, either in thermophilic and in mesophilic fermentation. This preliminary result indicates, that the concentration of volatile organometallics is one order of magnitude higher in thermophilic than in mesophilic fermentation. The flux could be an effect of the temperature, depending on the boiling points of the compounds. This was also observed with the flux rate of mercury over lake surfaces by Xiao *et al.*[39]. On the other hand, the input into the fermentation tank must be analysed with respect to the presence of organometallic ions (e.g. $Hg(CH_3)^+$). The kinetic effect of further methylation not only depends on temperature, but also on the concentration of partially alkylated ions. Microbiological activities could affect the genesis of volatile organometallics.

Discussion about the environmental impact

In general, metallorganics are often substantially more toxic than their inorganic counterparts from which they are derived (e.g. Hg, Pb, Sn, Te), with As and Sb being

Table 3 Comparision of the total volatile metal and metalloid concentration from sewage and landfill gas[10] by semi-quantification technique with interelement calibration.

Element	*Concentration range (µg m^{-3})* *Sewage gas*		*Landfill gas*[10]	
	min	*max*	*min*	*max*
Ge	–	n.d.	–	n.d
As	16.1	30.4	16.2	48.5
Se	–	n.d.	0.003	0.004
Cd	0.004	0.007	–	n.d
Sn	0.007	0.017	8.62	35.0
Sb	0.618	14.72	23.9	71.6
Te	< 0.001	0.887	0.048	0.075
Hg	0.012	0.026	0.049	0.130
Pb	0.023	0.055	0.013	0.033
Bi	0.016	1.056	0.312	0.892

n.d. = not detectable

exceptions. It should be noted that the toxic effects of volatile neutral alkylated metallorganics ($Sn(CH_3)_4$, $Pb(CH_3)_4$, $Hg(CH_3)_2$) usually derive from transformation to $(CH_3)_3M^+$ (M = Sn, Pb) and $Hg(CH_3)^+$ within organisms. Toxicity of alkyl groups varies from organism to organism, but methyl, ethyl, propyl and butyl groups tend to be the most toxic ones[56].

Toxicological potential is caused by good coordination to base atoms (S, O, N) on enzyme sites and penetration of the blood-brain barrier and cell membranes as well as disruption of mitochondrial function and ion transport.

The chemical nature of organometallics (lipophilic and hydrophilic groups) allow for transport in aqueous body fluids as well as subsequent diffusion through fatty tissue and cell walls.

Transfer of methyl groups to metals and metalloids is not restricted to anaerobic conditions, but can also be found within aerobic environments as well as in fossil substances like natural gas or oil. Another possible volatilisation pathway is the formation of hydrides. Degradation of these compounds in the atmosphere depends on the stability of the M-C bond. Degradation procedures are thermal, chemical and biological cleavage as well as γ- and UV irradiation. Atmospheric half-lives of $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$ are estimated to 10 hours and 2 hours in summer months, and about 34 hours and 8 hours for the winter, respectively[57]. Atmospheric stabilities of organometallics could be sufficient for taking into consideration toxicological assessments on a local scale.

An exposure to hazardous gases such as landfill gas was observed e.g. in a school (Oldham, England)[58]. More than 20 Vol. % methane was recorded beneath the floor of the sports block. This indicates that migration of landfill gases from a municipal waste deposit to living locations can occur. Recent preliminary studies[59] investigated the gentoxicity of landfill gas. Gaseous monitoring together with bioassays showed elevated mean mutation rates above the mean control groups.

According to Summers and Silver[60], who assumed that methylation of inorganic arsenic is related to methane production, some sources of volatile metal/metalloid compounds are conceivable, because all processes are generating methane at relatively low temperatures and are characterized by methanobacterium strains: landfill, thermophilic/mesophilic fermentation of sewage sludge, natural gas, swamps, rice fields (marsh gas), seams (mine gas), colon, geothermal sources, industrial emissions (e.g. $Pb(CH_3)_4$).

Little attention has been paid to environmental systems at the local scale, where conditions for biomethylation may combine favourably (presence of metals and organic carbon, bioactivity, reducing conditions). Fungi can produce a reductive atmosphere at microscopical scale and consequently biomethylation can also happen.

CONCLUSION

The described method (GC-ICP-MS) without matrix separation and derivatization, can be useful when searching for hitherto unexpected volatile species, such as trimethyl stibine. The described method is used for identification and semi-quantification of volatile, labile metal and metalloid compounds in gases from domestic waste disposal sites, and in sewage fermentation gas. Both the preconcentrated sampling and the chromatographic separation at a very low temperature in combination with multi-element detection allows non-destructive analysis without derivatisation. Biomethylation and/or transmethylation may occur within waste deposits, especially those which are several years old and are in their methane generating phase. Preliminary studies of sewage gases show the occurrence of volatile species of antimony, arsenic, cadmium, mercury, lead, tellurium, and bismuth. According to their toxicity more investigations towards the genesis of metallorganics in the environment are necessary. Tributyltin derivatives have boiling points higher than 200°C, which cannot be determined with this method, because the transfer lines are consisting of PTFE, not tolerating temperatures above 180°C. If this line is made of metal, an interface, as constructed by Pritzl *et al.*[61] would be more suitable for semi-volatile compounds (bp > 200°C). Because of memory effects, however, the injection of metals in to the chromatographic system is difficult in respect to the determination of many elements like mercury.

For a better separation of the semi-volatile species (e.g. tetrabutyltin) coupling of supercritical fluid chromatography with ICP-MS might be useful analytical system[62]. In general, it could be demonstrated that coupling of a low-temperature gas chromatograph with inductively-coupled argon plasma mass spectrometry (GC-ICP-MS) is a reliable analytical method for volatile organometallics.

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Reference

1. F. Challenger, *Chem. Rev.*, **36**, 315–361 (1945).
2. W. R. Cullen and K. J. Reimer, *Chem. Rev.*, **89**, 713–764 (1989).
3. D. P. Cox and M. Alexander, *Bull. Environ. Contam. Toxicol.*, **9**, 84–88 (1973).
4. B. C. McBride and R. S. Wolfe, *Biochemistry*, **10**, 4312–4317 (1971).
5. A. V. Hirner, J. Feldmann, R. Goguel, S. Rapsomanikis, R. Fischer and M. O. Andreae, *Appl. Organomet. Chem.*, **8**, 65–69 (1994).
6. Y. K. Chau, P. T. S. Wong, O. Kramar and G. A. Bengart, In: *Proc. Intern. Conf. Heavy Metals in the Environment (Amsterdam)* (Ernst W.H.O., ed., CEP Consultants, Edinburgh, 1981).
7. C. Huey, F. E. Brinckman, W. P. Iverson and S. O. Grim: *Prog. Water Technol.* (P. A. Krenkel, ed., 1975), p 7.
8. H. Woermann, J. Stuth and J. Schulz, *GIT*, **5**, 400–403 (1993).
9. W. H. Schroeder and R. A. Jackson, *Intern. Jour. Environ. Anal. Chem.*, **22**, 1–18 (1985).
10. J. Feldmann, R. Grümping and A. V. Hirner, *Fresenius J. Anal. Chem.*, **350**, 228–234 (1994).
11. U. Förstner, C. Colombi and R. Kistler, In: *Metals and Their Compounds in the Environment* (E. Merian, ed., VCH, Weinheim, 1983) pp. 333–356.
12. R. C. Hutton, M. Bridenne, E. Coffre, Y. Marot and F. Simondet, *J. Anal. At. Spectrom.*, **5**, 463–466 (1990).
13. S. Hill, J. Hartley and L. Ebdon, *J. Anal. At. Spectrom.*, **7**, 895–898 (1992).
14. N. Jakubowski, I. Feldmann and D. Stuewer, *J. Anal. At. Spectrom.*, **8**, 969–977 (1993).
15. L. M. Müller, *Bestimmung organischer Antimon- und Bismutverbindungen im Deponiegas*, (Diploma Thesis), University of Essen (1994).
16. O. F. X. Donard, S. Rapsomanikis and J. H. Weber, *Anal. Chem.* **58**, 772–777 (1986).
17. R. J. Maguire, *Environ. Sci. Technol.*, **18**, 291–294 (1984).
18. H. E. Guard, A. B. Cobet and W. M. Coleman, *Science*, **213**, 770–771 (1981).
19. J. A. A. Jackson, W. R. Blair, F. E. Brinckman and W. P. Iverson, *Environ. Sci. Technol.*, **16**, 110–119 (1982).
20. O. F. X. Donard and J. H. Weber, *Nature*, **332**, 339–341 (1988).
21. J. Feldmann and A. V. Hirner, In: *Colloquium Analytical Atomspectrometry Symposium (CANAS 93)* (K. Dittrich, B. Welz, eds., Oberhof, Germany, DV21, 1993), pp. 335–339.

22. I. Devai, L. Felföldy, I. Winter and S. Plosz, *Nature,* **333**, 343–345 (1988).
23. G. Gassmann and F. Schorn, *Naturwissenschaften,* **80**, 78–80 (1993).
24. Y. K. Chau, In: *Organometallic compounds in the environment* (P. J. Craig, ed., Logman, Harlow, 1986), 254–278.
25. J. Alexander, Y. Thomassen and J. Assethy, In: *Handbook of Toxicology of Inorganic Compounds* (H. G. Seiler, H. Sigel and A. Sigel, eds., **61**, 1988), p. 669.
26. L. Fishbein, In: *Metals and Their Compounds in the Environment,* (E. Merian, ed., VCH, Weinheim, 1991), 1211-1226.
27. F. Challenger, *Adv. Enzymol.,* **12**, 429–491 (1951).
28. U. Karlson and W. T. Frankenberger, Jr., In: *Metal ions in biological systems,* (H. Sigel and A. Sigel, eds, Marcel Dekker, New York, **29**, 1993), pp. 185–228.
29. S. Muangnoicharoen, *Diss. Abstr. Int. B,* **51**, 176 (1990).
30. G. E. Parris and F. E. Brinckman, *Environ. Sci. Technol.,* **10**, 1128–1134 (1976).
31. M. O. Andreae, J. F. Asmodé, P. Foster and L. Van't dack, *Anal. Chem.,* **53**, 1766–1771 (1981).
32. A. A. Benson and R. V. Cooney, In: *The Biological Alkylation of Heavy Metals* (P. J. Craig and F. Glocking, eds., Royal Chemistry Society, London, 1988, pp. 345.
33. R. M. Harrison, *Advan. Environ. Sci. Technol.,* **17**, 319–333 (1986).
34. R. J. A. van Cleuvenbergen and F. C. Adams, In: *Environmental Chemistry 3E* (O. Hutzinger, ed., Springer, Berlin, 1990, pp. 97–103.
35. G. Calingaert, H. A. Beatty and H. R. Neal, *J. Am. Chem. Soc.,* **61**, 2755–2758 (1939).
36. P. T. S. Wong and Y. K, Chau, *Comm. of Eur. Communities/ET Al Heavy Metals in the Environ. Int. Conf.,* London, **131** (1979).
37. P. T. S. Wong, Y. K. Chau and P. L. Luxon, *Nature,* **253**, 263–264 (1975).
38. J. W. Robinson and E. L. Kiesel, *J. Environ, Sci. Health,* **16**, 341–352 (1981).
39. Z. F. Xiao, J. Munthe, W. H. Schroeder and O. Lindqvist, *Tellus* **43B**, 267–279 (1991).
40. W. Schroeder, O. Lindqvist, J. Munthe and Z. Xiao, *Sci. Tot. Environ.* **125**, 47–66 (1992).
41. W. H. Schroeder and R. A. Jackson, *Chemosphere,* **16**, 183–199 (1987).
42. A. Bzezinska, J. Van Loon, D. Williams, K. Oguma, K. Fuwa and I. H. Haraguchi, *Spectrochim. Acta,* **38B**, 1339–1346 (1983).
43. E. Amberger, *Ber. Deut, Chem. Ges.,* **94**, 1447–1452 (1961).
44. O. J. Scherer, P. Hornig and M. Schmidt, *J. Organomet. Chem.,* **6**, 259–264 (1966).
45. J. S. Thayer, In: *Metal Ions in Biological Systems,* (H. Sigel and A. Sigel, eds., **29**, Marcel Dekker, New York, 1993), pp. 1-36.
46. B. C. McBride and T. L. Edwards, *Biological Implications of Metals in the Environment,* ERDA Symp. Ser. No. 42 (1977).
47. B. C. McBride, H. Merilees, W. R. Cullen and W. A. Pickett,, *ACS Symp. Ser.* **82**, 94–115 (1982).
48. W. R. Cullen, B. C. McBride and A. W. Pickett, *Appl. Organomet. Chem.,* **4**, 119–125 (1990).
49. C. N. Cheng and D. D. Focht, *Appl. Environ. Microbiol.,* **38**, 494–498 (1979).
50. D. L. Johnson and R. S. Braman, *Chemosphere,* **6**, 333 (1975).
51. K. L. Irgolic, D. Spall, B. K. Puri, D. Ilger and R. A. Zingaro, *Appl. Organomet, Chem.,* **5**, 117–124 (1991).
52. W. Delgardo-Morales, M. S. Mohan nd R. A. Zingaro, *Intern. J. Environ. Anal. Chem.,* **54**, 203–220 (1994).
53. J. Feldmann, *Erfassung flüchtiger metallorganischer Verbindungen in der Umwelt mittels GC/ICP-MS* (Ph. D. Thesis), University of Essen (1994).
54. R. S. Braman and D. L. Johnson, *Environ. Sci. Technol.,* **8**, 996–1003 (1974).
55. A. Kim, S. Hill, L. Ebdon and S. Rowland, *J. High. Resolut. Chromatogr.,* **15**, 665–668 (1992).
56. R. M. Harrison and S. Rapsomanikis, *Environmental Analysis Using Chromatography Interfaced With Atomic Spectroscopy* (Wiley, New York, 1989).
57. C. N. Hewitt, In: *Organometallic Compounds in the Environment,* (P. J. Craig, ed., Longman, 1986), pp. 160–197.
58. L. M. Morris and M. G. Staff., *J. IWEM,* **7**, 548–556 (1993).
59. T. H. Ma, *Environmental Mutagen Society, Abstracts,* **40** (1994).
60. A. O. Summers and S. Silver, *Ann. Rev. Microbiol.,* **32**, 637–672 (1978).
61. G. Pritzl, F. Stuer-Lauridsen, L. Carlsen A. K. Jensen and T. K. Thorsen, *24th Intern. Conf. on Environ. Anal. Chem.,* Ottawa, 1P09 (1994).
62. N. P. Vela and J. A. Caruso, *J. Anal. At. Spectrom.,* **8**. 787–794 (1993).
63. *CRC Handbook of Chemistry and Physics,* (R. C. Weast, ed., CRC Press, Boca Raton 1975–1976).
64. S. Saaman, In: *Methoden in der organischen Chemie,* XIII/8 (E. Müller, ed., Thieme, Stuttgart, 1978), pp. 50–53.

65. M. Wieber, In: *Gmelin Handbook of Inorganic Chemistry, Organoantimony Compounds* **2** (Springer, Berlin, 1981), p.1, p.90.
66. F. Paneth, W. Haken and E. Rabinowitsch, *Ber. Deut. Chem. Ges.*, **57**, 1891–1903 (1924).
67. H. Schumann and I. Schumann, In: *Gmelin Handbook of Inorganic Chemistry*, **4** (Springer, Berlin, 1976), pp. 30–57.
68. G. A. Gill and W. F. Fitzgerald, *Mar. Chem.*, **20**, 227–243 (1987).
69. V. F. Hodge, S. L. Seidel and E. D. Goldberg, *Anal. Chem.*, **51**, 1256–1259 (1981).