APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 8, 65–69 (1994)

# Volatile Metal and Metalloid Species in Gases from Municipal Waste Deposits

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**We have detected volatile species of silicon, vanadium, arsenic, bromine, tin, antimony, tellurium, iodine, mercury, lead and bismuth in gases released from domestic waste deposits, using inductively coupled argon plasma mass spectrometry (ICP MS). By concurrent aspiration of a multielement standard solution for calibration, the element concentrations in deposit gas are found to be in the range from 0.1 ng $m^{-3}$ to 10 μg $m^{-3}$ gas. The global amount of some metal species emitted by this process may be of the order of several tons per year. These results suggest a biogeochemical pathway for the transfer of metals into the atmosphere via volatile species. This process may have significant influence on atmospheric cycling of metals as well as on metal toxicity within ecosystems.**

**Keywords: Waste deposit, environmental gas, analysis, volatile metals, biogeochemical transfer**

## INTRODUCTION

The formation of organometallic compounds by biologically or chemically mediated methylation has been extensively described for sulphur, germanium, arsenic, selenium, cadmium, tin, antimony, tellurium, mercury and lead in natural systems,[1,2] and for chromium, palladium, platinum, gold and thallium under laboratory conditions.[2] Transfer of methyl groups to metals and metalloids does not take place only under anaerobic conditions, or within freshly deposited sediments, but also within aerobic environments,[3] and in fossil substances such as gas or oil.[4] Methylation to fully alkylated species may lead to volatilization of the organometallic compounds. Another possible volatilization pathway is the formation of hydrides.[5] As a result, volatile metal compounds may occur in the environment. However, studies have largely been restricted to reports on environmental accidents,[6] to workplace air,[7] and to models of the global geochemical cycle of one particular element.[1,2] Much attention has been paid to environmental systems on the local scale where conditions for biologically (biomethylation) or chemically (transmethylation) mediated methylation may combine favourably (in the presence of metals and organic carbon, bioactivity and anoxic conditions). Biomethylation and/or transmethylation may also occur in domestic waste deposits, especially those which are several years old and in their methane-generating phase.

## EXPERIMENTAL

### Instrumentation and methods

Screening for metal and metalloid compounds in gases from waste deposits requires an extremely sensitive multielement detection method such as inductively coupled argon plasma mass spectrometry (ICP MS).[8] Because of its high cost, ICP MS has not often been used as a detector in gas chromatography.[9,10] Previous ICP MS studies on organometallic compounds were performed on hydrides generated from particular methylated elements (e.g. germanium or mercury) in liquid and solid samples only.[11,12]

The experimental apparatus used in this study was similar to the one described by Jin *et al.*[12] with the exception that we included a nebulization system. Together with the gas sample desorbed from a cryogenic trap, an aqueous solution was introduced, making possible calibration and ensuring stable plasma conditions. Before nebulization, the nebulizer gas was diverted to flow through the cryogenic trap containing the deposit

CCC 0268–2605/94/010065–05

*Received 10 September 1993*
*Accepted 27 October 1993*

gas sample. Concurrently, the aqueous standard solution was nebulized pneumatically and transferred to the plasma with the analyte gas.

Liquid standards could be used for calibration of the gas sample provided the efficiency of the nebulizer was known and similar ionisation yields for standards and analytes were assumed. In contrast to Moenke-Blankenburg *et al.*,[13] who calibrated a vaporized solid with a liquid standard sequentially, here the standard solution and the desorbed sample gas were subjected to simultaneous measurement. The isotopes of the elements in the standard calibration solution (internal standard technique) were not detected in preliminary analysis of the gas samples. A 10 ppb solution of these elements was used. The nebulization efficiency was 4%. Depending on the proximity of the analyte isotopic mass to the mass of any of the three liquid standard isotopes, the integrated counts over time were calibrated with respect to the counts of $^{59}$Co, $^{103}$Rh and $^{203}$Tl.

## Sampling procedure

The sample collection system consisted of a particle filter, a drying tube, a cryogenic glass trap, a vacuum pump and a gas meter, connected in series. A 2.5 cm-diameter Teflon filter with a nominal pore size of 2 μm, housed in a polypropylene filter holder, was used to remove aerosol particles. Sample collection flow rates were 1 l/min; total volume per sample was 20 l.

The drying tube (2.2 cm o.d., 9.2 cm long) was filled with anhydrous calcium chloride (Merck) to avoid water condensation into the glass trap. The trap (12 mm o.d., 22 cm long) was cooled with acetone/liquid nitrogen (at about −80 °C); this relatively high trapping temperature was used in order to avoid condensation of methane during sampling and of argon during analysis. The trap was packed with glass beads (DMCS treated 60/80 mesh, Alltech), which were secured with silanized glass wool plugs. A Nichrome resistance wire (0.5 mm o.d., 5.5 ohm $m^{-1}$) was wound around the trap for heating during analysis. All connections between components are 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.

Samples were taken from two domestic waste sites. These locations were 60 km apart and received waste from different cities in Germany.

## RESULTS AND DISCUSSION

The gas samples were desorbed into the argon plasma of the ICP MS. The mass scan mode of ICP MS was used for the identification of the volatile elements in gas samples, in consideration of possible isobaric interferences. Figure 1 illustrates the relative abundances of naturally occurring isotopes compared with the gas sample. The isotope ratios of tin and antimony confirm the qualitative identification of these metals. Eleven elements (silicon, vanadium, arsenic, bromine, tin, antimony, tellurium, iodine, mercury, lead and bismuth) were detectable above blank levels in the waste deposit gas samples.

Figure 2 shows typical transient measurements and variation of the tellurium and bismuth intensities with temperature. As a result of the gradually increasing trap temperature during chromatographic analysis, different metal species were separated according to their volatility. All elements showed a similar bimodal release pattern: one peak occurred at a very early stage immediately after removing the liquid nitrogen from the trap, and the second desorption peak appeared just after external heating of the trap was initiated.

Comparable results were obtained from both sites (metal concentrations in the same order of magnitude), and we believe that generalization from these results is appropriate. The integrated intensities (sample minus blank) of the detected isotypes are presented in Fig. 3.

Based on the internal standard calibration method as described above, the estimated concentrations of metals and metalloids arsenic, selenium, tin, antimony, tellurium, mercury, lead, bismuth plus iodine in gases from two different waste deposits were in the range of 0.1–1000 ng $m^{-3}$; silicon was found at high microgram/metre$^3$ levels. The concentrations of the elements tin and antimony were determined (eight gas samples from two deposits) to be 120–4400 ng $m^{-3}$ (tin) and 40–2400 ng $m^{-3}$ (antimony). Concentration range of arsenic (3–32 ng $m^{-3}$) and lead (5–18 ng $m^{-3}$) were also determined in the gas samples. The following elements were found at low concentrations, although these were significantly higher than the blank: selenium (<0.5 ng $m^{-3}$), tellurium (1.2–5.5 ng $m^{-3}$), iodine (0.1–2.7 ng $m^{-3}$), mercury (0.1–11 ng $m^{-3}$) and bismuth (0.2–6.5 ng $m^{-3}$).

It should be noted, however, that these values represent lower limits to the real metal and metal-

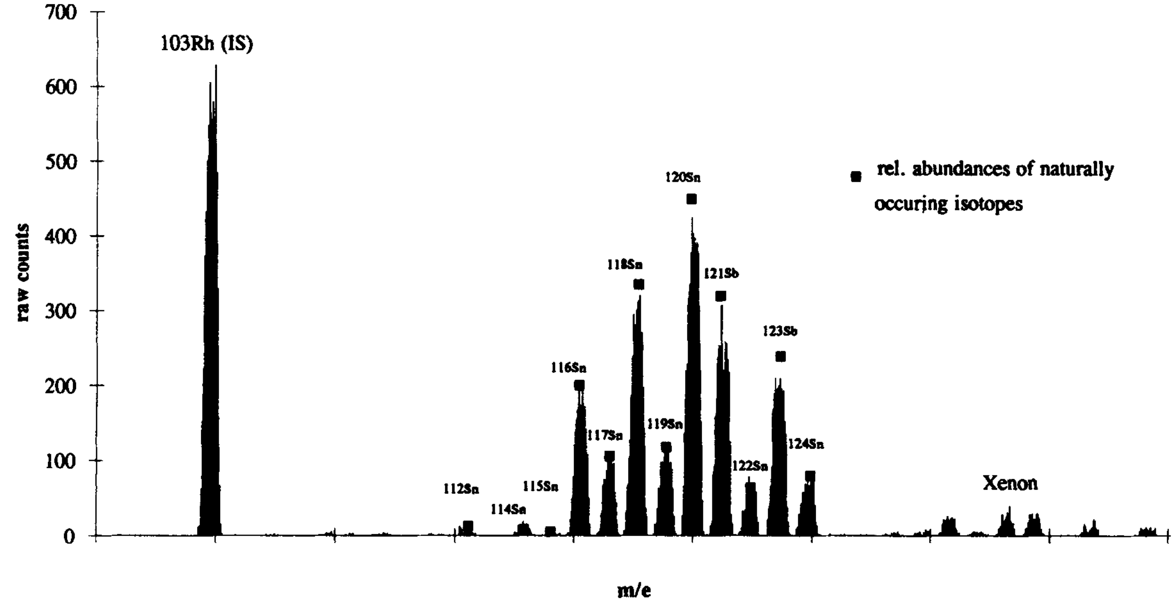

**Figure 1** Mass spectrum of a domestic wastge deposit gas sample compared with the relative abundances of naturally occurring isotopes.

loid concentrations in the deposit gases as we cannot preclude incomplete trapping of more volatile compounds, given that the samples were collected at −80 °C. Furthermore, we have assumed that no loss of analyte occurred between sample collection and analysis.

The concentrations of volatile metal and metalloid species in gases from waste deposits thus typically range from $10^{-8}$ to $10^{-5}\,\mathrm{g\,m^{-3}}$. Combined with a calculated global methane emission of $(30\text{–}70) \times 10^6$ tons per year [approx. $(1\text{–}2) \times 10^{11}\,\mathrm{m^3}$ methane per year] from solid wastes[14] and a methane content of 40% in landfill gases, this would lead to typical global metal and metalloid emissions of several kilograms per year (for example, in the case of mercury and arsenic)

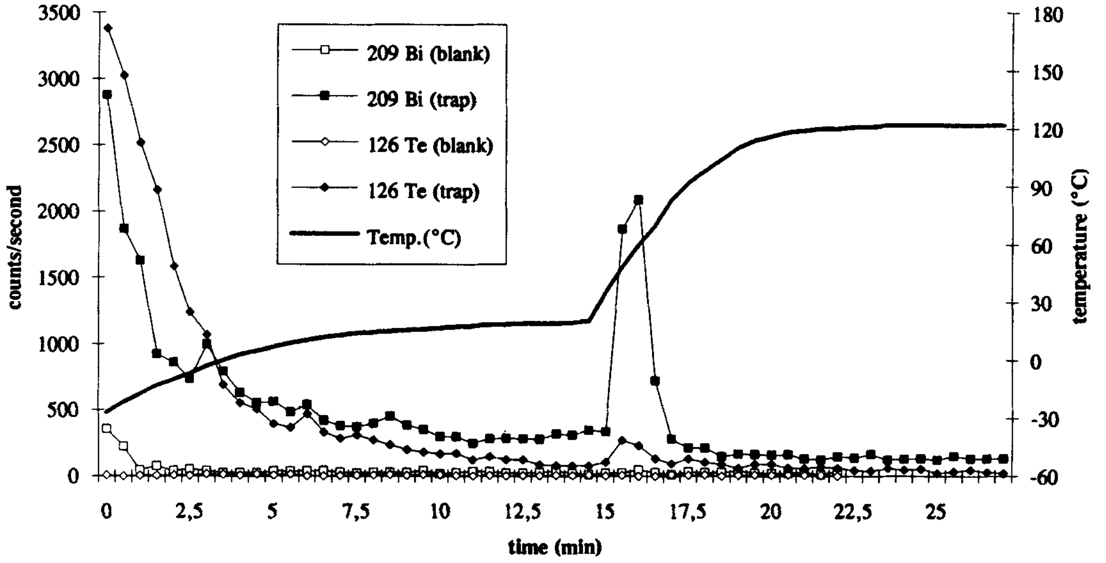

**Figure 2** Time-resolved analysis of masses 126 and 209 during temperature-controlled desorption of sample-loaded traps, and of blank traps.

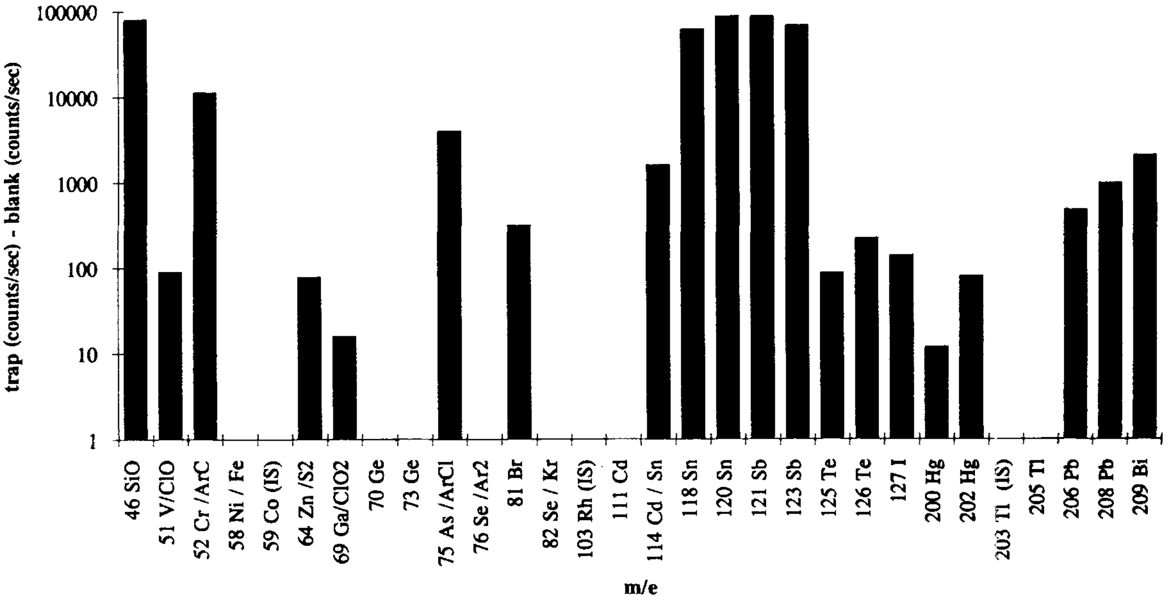

**Figure 3** Schematic mass spectrum reconstructed on basis of data stored during time-resolved analysis of a typical deposit gas sample. As the blank intensities have already been subtracted, only net intensities for masses 46 to 209 are shown.

to several tonnes per year (for example, in the case of tin and antimony). However, these numbers must be regarded as very rough estimates, and will progressively be improved with increasing knowledge about the majority of other methane emission processes (e.g. natural gas leaks, coal mining, rice fields, domestic animals, sewage treatment plants), and about the role biomethylation and transmethylation are playing therein. Since the total production of methane from all processes is an order of magnitude greater than the methane production from landfills, total volatile metal emissions connected with methane release may be considerable.

## CONCLUSIONS

These results may necesitate changes to biogeochemical models of global cycling[15, 16] as well as a re-evaluation of the toxic threat posed by emissions from landfills and other methanogenic environments. In the form of organometallic compounds and/or hydrides, a substantial amount of metals and metalloids may be volatized. These species are significantly more toxic than the inorganic species of the cations.[16, 17] For example, the biovolatilization of arsenic has led to notorious poisoning incidents.[18] The stability of many volatile metal species under atmospheric conditions is sufficient (up to a day) to permit their transport to human populations in the regions surrounding landfills. By chemical reactions in the atmosphere, the volatile species are transformed into inorganic forms, eventually forming atmospheric aerosols, which add to the toxic metal burden of the atmosphere in populated regions.

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