Speciation of Volatile Mercury Species Present in Digester and Deposit Gases

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Volatile mercury compounds have been speciated in gases evolved from fermentation of sewage sludge as well as municipal waste. The species were trapped by sequential sampling, using a noble-metal trap in series with an activated-carbon trap. Thermally desorbed Hg^0 and $(CH_3)_2Hg$ were separated by GC at 70 °C and detected by cold vapour atomic fluorescence spectroscopy after thermal reduction. The amounts of mercury detected in the sewage gas correspond to concentrations in the range 50–110 ng m^{-3} for both species whereas the deposit gases were found to contain only elemental mercury. Monomethylmercury species could not be positively identified in any of the gas samples. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Being toxic in all forms, the use of mercury in Sweden is projected to be banned by 2003.[1] The abandonment of mercury-based processes has minor domestic environmental effects, however, since most of the mercury deposition is carried across boundaries in the air. Total gaseous mercury (TGM) is present at sub-parts per trillion (ppt) levels (~0.2 ppt) in clean ambient air.[2] Although divalent mercury, comprising both inorganic and organic species, is only a small fraction of the TGM, it may govern the overall deposition of mercury.[3,4]

The comparative importance of atmospheric input to the pool of organic mercury in the environment has become more evident in recent years.[5] Monomethylmercury (MMHg) species are bioaccumulated through the food chain to reach elevated levels in fish. The sources of atmospheric local- or regional-scale organomercury cycles are not well known, however. Highly toxic dimethylmercury (DMHg) is by far the most volatile mercury compound present in the environment. DMHg has been found to contribute regionally to the exchange of mercury species between the sea and the atmosphere.[6,7] As for many other organometallic compounds, DMHg has low stability under normal environmental aerobic conditions and in the atmosphere it is apt to undergo rapid chemical gas-phase degradation.[8] The expected lifetime due to such processes is about one day.[8] The products reported to form comprise both divalent inorganic and MMHg species as well as elemental Hg.[8]

Evidence has been presented for biotic and abiotic production of dimethylmercury in sediments,[9–12] i.e. from microbiological transformation of MMHg as well as from dismutation of MMHg in the presence of sulphide. Some environments are assumed to promote methylation of mercury, e.g. areas with high organic inputs and anaerobic conditions. Landfills of biodegradable waste and facilities for sewage sludge fermentation are possible sources of such processes. In these environments, methane and carbon dioxide are produced which also may facilitate volatilization of trace-element compounds such as organometallics.[13] In sewage treatment facilities the partitioning of mercury between sludge and the effluent water is very high. More than 95% of the mercury is found in the sludge phase.[14] Storage of sewage sludge on soil may influence the regional atmospheric MMHg concentrations by ~5%.[15]

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Soldano *et al.*[16] and Bzezinska *et al.*[17] have positively identified methylated mercury species in air in the vicinity of sewage plants. However, in the former study the method of Braman and Jackson[18] was used, based on a train of chemically selective absorption traps. The latter study, as well as those to follow, apply GC separation. Sunlight-mediated daily fluxes of MMHg species in the range 10–30 $pg\,m^{-2}\,h^{-1}$ have been observed over soil-improved by sewage sludge.[15] Feldmann and Hirner[19] found two mercury species, besides other metalloids present in sewage and landfill gases, but were not able to quantify them separately. One of the mercury species was identified as DMHg. Hence, there is a clear objective to speciate and quantify the mercury derivative present in digester and landfill gases. We have accomplished this in facilities in the vicinity of Göteborg, Sweden.

EXPERIMENTAL

Sampling sites and methods

A municipal purification control plant, obtaining about 10% sewage from industrial sources and linked to the region of Göteborg (population 700 000), Sweden, was examined. At this location, sludge containing 5% dry material (1–2 $\mu g\,Hg\,g^{-1}$) was treated in a mesophilic anaerobic fermentation step for 15 days at $37\,°C$ in two 1.1-m^3 digester tanks. Samples (0.2–5.0 dm^3) of the slightly pressurized digester gas (60–65% CH_4 and 35–40% CO_2) were taken from the top of the tank by opening a vent.

The gases drained from a methane-generating waste deposit were investigated as well. The deposit received ~0.022 km^3 of municipial waste from Göteborg during a period of half a century until filling was prohibited in 1978. The gas produced in the landfill, which contained methane, was flared. Examined samples were taken of the gas pumped from gas wells located in the landfill.

DMHg was collected on columns filled with carbotrap[™] sorbent (Supelco, 20/40-mesh) secured with silanized quartz wool plugs. The construction of the traps has been described elsewhere.[20] These traps collect only a small amount of elemental mercury.[21] The remainder of the mercury fraction was instead amalgamated either on a silver-coated denuder[22] upstream or on a gold trap downstream in series. The digester tank gas was passed through an impinger to remove water droplets, and then further

to the sampling train. Connections used were all Teflon. Flow rates of 10–600 $cm^3\,min^{-1}$ were obtained through the absorbents by a slight over-pressure from the digester tank. The variation in flow rates obtained depended on differences in resistance in the sampling trains, besides the pressure related to the phase in the fermentation cycle.

Analytical method

In order to separate DMHg from Hg^0, the method of Bloom and Fitzgerald[21] was employed using a purge and trap method followed by thermodesorption and isothermal GC separation interfaced with CVAFS detection. The GC column in the form of a Pyrex U-tube 40 cm long was packed with 80-mesh OV-3 on Chromasorb WAW-DMSC and sealed with plugs of silanized quartz wool. Exposed adsorbents were analysed within a few hours. The absorbents were stripped of moisture by a warm stream of mercury-free air before analysis. Field blanks were analysed with each batch of samples exposed. The traps were heated to ~200 °C in a stream of high-purity helium (>99.9999%) kept at 60 $cm^3\,min^{-1}$ by applying 10 VDC through a NiCr wire. The resolution between Hg^0 and DMHg peaks eluated was found satisfactory when the GC
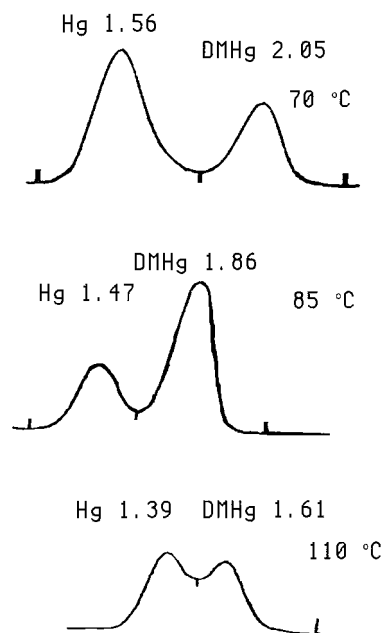
Figure 1 Chromatogram obtained after elution of gas-phase samples at different temperatures.
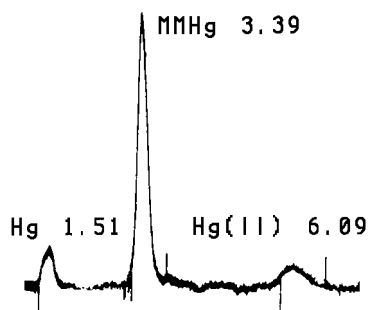
Figure 2 Chromatogram obtained after ethylation of a solution spiked with 100 pg MMHgCl.

column was kept isothermally in a cylindrical oven at 70 °C (Fig. 1). After separation, DMHg was completely reduced thermally at 800 °C and detected as well as quantified as Hg^0. The instrument was calibrated by injection of saturated Hg^0 vapour.

The sewage sludge subjected to alkaline digestion was speciated for MMHg using the GC–CVAFS technique described above, including derivatization to volatile, fully alkylated mercury compound $CH_3HgC_2H_5$ by aqueous-phase ethylation and venting to a carbotrap[TM]. This method has been described elsewhere[20,23,24] and only a short description will be given here. Samples (1–2 g) were placed in Teflon vials, digested at 75 °C for 3 h in 10 cm³ of 25% methanolic KOH and diluted to 18 cm³ with methanol. Aliquots of 0.2 cm³ were added to aqueous solutions buffered to pH 4.9 with an ethylation reagent concentration of $\sim$5 mg dm⁻³. The derivatization time at 20 °C was generally 12–15 min followed by purging of the fully alkylated compounds to a carbotrap. Attention was paid to the purity of the ethylating reagent, which was frozen in 2-cm³ portions until used. Each portion containing $Na[B(C_2H_5)_4]$, kept at 0 °C during utilization, was subject to performance testing including standard additions and calibrations during sample analysis. In Fig. 2, a typical chromatogram obtained from a spike of MMHg is shown. As can be seen, only carbotrap[TM]

sorbents which insignificantly decompose the ethylation derivatives of MMHg to Hg^0 during thermal desorption were used. These traps were also used exclusively for sampling gas-phase DMHg.

RESULTS AND DISCUSSION

The detection limit (three standard deviations of the field blank) was $\sim$10 pg for DMHg (8 ± 3 pg, $n = 7$) and Hg^0 (11 ± 3 pg, $n = 10$, gold trap). Monomethylmercury and other divalent species, if present, would also be collected by this method but were not detected in any of the gas samples collected.

Silver denuders at our laboratory have been shown to remove Hg^0 selectively ($98.1 \pm 4.5\%$, $n = 10$) from $(CH_3)_2Hg$ whereas the gold traps retain both mercury compounds.[25] Constellations of a silver denuder and a carbotrap[TM] as well as a carbotrap[TM] and a gold trap in series were exposed to the digester gas. The two different categories of carbotraps[TM] exposed were found to give similar DMHg concentrations ($P < 0.10$, $n = 10$). The amount of Hg^0 collected by the carbotrap[TM] was generally less than 1% of the total amount of Hg^0 passed. On four occasions, 20 samples were taken of the digester gas. Normally, a sampling train of a carbotrap[TM] in series with a gold trap was used.

DMHg and Hg^0 were detected in all digester gas samples. The TGM concentrations, summarized in Table 1, are in the range reported for gases evolved from thermophilic as well as mesophilic fermentation of sewage sludge.[26] Our speciation data indicate dimethylation of mercury to occur to a certain extent in the anaerobic digestion process. Biomethylation is probably the cause of DMHg production in the fermentation process, since formation of DMHg by transmethylation has not been reported yet to occur in environmental systems. Methylation to fully methylated neutral mercury species as well as reduction to elemental

Table 1. Statistical summary of concentration of Hg and DMHg in digester gas

Sampling date	DMHg (ng m⁻³), $\bar{x} \pm \sigma$	Hg^0 (ng m⁻³), $\bar{x} \pm \sigma$	TGM[a] (ng m⁻³), $\bar{x} \pm \sigma$
12 May 1997	54.5 ± 6.6 ($n = 4$)	64.5 ± 7.5 ($n = 4$)	119.0 ± 10.0 ($n = 4$)
16 May 1997	92.5 ± 7.8 ($n = 10$)	69.7 ± 9.9 ($n = 5$)	162.2 ± 12.6 ($n = 5$)
11 June 1997	55.7 ± 7.6 ($n = 3$)	70.6 ± 10.5 ($n = 3$)	126.3 ± 13.0 ($n = 3$)
13 June 1997	63.4 ± 10.7 ($n = 3$)	87.5 ± 9.5 ($n = 3$)	150.3 ± 14.2 ($n = 3$)

[a] TGM = Hg^0 + DMHg.

Hg (II) 5.56

Hg 1.19 MMHg 2.78
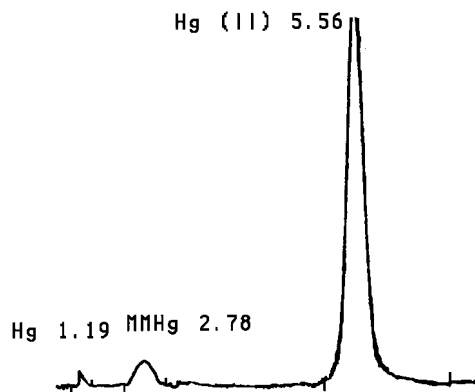
Figure 3 Chromatogram from a digested sewage sludge sample.

mercury are potential mechanisms of microbiological mercury tolerance. The vapour pressure of DMHg (~7 kPa) is at least three orders of magnitude higher than that of MMHg species. MMHg species are in turn about one order of magnitude as volatile as Hg^0 (~0.1 Pa). The MMHg species are much more hydrophilic than Hg^0 and DMHg and are therefore retained in substrate. The rate-determining step of DMHg volatilization during sludge fermentation is the methylation of MMHg.[26] The dimethylation is promoted in cultures with H_2S production according to the schematic reaction shown in Eqn 1.

$$2\ CH_3Hg^+ + S^{2-} \longrightarrow [(CH_3Hg)_2S] \longrightarrow (CH_3)_2Hg$$

$$+\beta\text{-}HgS \qquad [1]$$
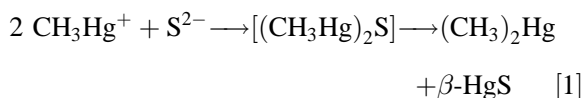
The production of DMHg from MMHg has been reported to occur in sediments from the rivers Elbe and Po.[11,12] At the pH values existing during fermentation, DMHg would certainly not be affected by acidolysis.[27]

In the landfill gas, the only detectable mercury species was elemental mercury. The Hg^0 concentration was determined on two occasions as 8.7 ± 2.9 ng m^{-3} ($n = 6$). The ambient air TGM concentration at this site (1.7 ± 0.2 ng m^{-3}, $n = 23$) was not found to be significantly higher than the background concentration. The measurements were accomplished in a semicontinuous way by a portable AAS analyser, GARDIS-1A.[28] The estimated TGM concentrations are in accordance with those reported for landfill gases by Hirner *et al.*[13] but lower than those of Feldmann and Hirner.[19] In the latter gases, apart from DMHg, Hg^0 or CH_3HgCl was proposed to be present also. The

landfills have been found to produce condensation water with high MMHg concentrations (S.E. Lindberg, personal communication).

Samples of sewage sludge present in the digester during the sampling period were subjected to analysis. Dissolved gaseous mercury in liquefied sludge was vented by bubbling. The MMHg content in the samples leaving the digester was 0.01 μg g^{-1} as dry weight. With the figures supplied by the manufacturer on total mercury, MMHg comprises <1%, which is in agreement with the content reported in the literature.[15] Figure 3 shows a chromatogram from a corresponding sample.

Recently, artificial formation of MMHg in samples rich in organic matter and high in divalent mercury has been reported to occur during analysis.[29,30] The gas samples exposed are not biased by this kind of artefact formation, however. Bubbling of liquefied sludge samples in the laboratory does not show any detectable volatilization of organomercurials. Emission of MMHg from sewage sludge has however only been found to occur if mediated by UV radiation.[15]

The global fluxes of TGM from deposits of sewage sludge have been estimated to be of the order of 10 Mg yr^{-1}.[15] Although, the fractional contribution from land amended by waste and sewage sludge to the total atmospheric mercury cycle is limited, it may certainly influence local and regional cycling of MMHg. Based on the sparse number of data and the diversity of the results reported, further observations are needed to assess the occurrence of DMHg in gases from methane-generating sources and the contribution to the atmospheric organomercury cycle.

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