

EVAPORATION OF MERCURY FROM DOMESTIC WASTE LEACHATE

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Summary

An experimental study has been made of the rate at which dissolved mercury is lost from domestic waste leachate by evaporation from the air leachate interface. Under ambient conditions an absolute rate of ca 10^{-7} g cm⁻² h⁻¹ was found for the mercury loss. This is in good agreement with values determined previously for pure solutions of mercury. An investigation was also made of mercury losses during the handling of solutions for analysis. The evaporation of mercury into the ullage of partially filled containers can result in significant losses of mercury from solutions containing sub-part per million concentrations. Erroneously low analytical results may thus be obtained if samples of solution are stored in only partially filled containers prior to analysis.

As part of a continuing investigation into the fate of potentially hazardous wastes in landfill sites we have recently examined the release of mercury from primary cell batteries arising in domestic waste [1]. Since other workers have established that mercury may evaporate from aqueous solutions at rates which depend on prevailing Eh and pH conditions [2-7], it was felt necessary to determine the likely loss of mercury during the handling of solutions. The rate of evaporation of mercury from domestic waste leachate under aerobic and anaerobic conditions was also measured for comparison with results obtained with pure solutions and soils.

The loss of mercury from pure dilute solutions of Hg^{II} labelled with ²⁰³Hg has been monitored [2] and attributed to evaporation of Hg. The rate at which the ²⁰³Hg concentration decreased was accelerated at high pH and in the presence of reducing agents such as SnCl₂. Low pH or the presence of I⁻, CN⁻, ClO⁻, MnO₄⁻ or other oxidants reduced the rate of evaporation. These observations have been supported by other experimental work using ²⁰³Hg [3, 4] which also indicates that Hg evaporates from dilute aqueous solutions. At ionic mercury concentrations of less than 0.1 ppm, very rapid loss by evaporation was observed. Since the Hg^{II}/Hg^I couple has a high oxidation potential, facile reduction of Hg^{II} to Hg^I might be expected under environmental conditions and the disproportionation of the Hg₂²⁺ so formed to

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$\text{Hg} + \text{Hg}^{2+}$ is suggested as the major source of Hg in solutions of ionic mercury [4]. The rate of evaporation of mercury from aqueous sodium hydroxide solutions found in the chloralkali industry was found to be 10^{-9} to 10^{-7} $\text{g cm}^{-2} \text{h}^{-1}$ which may be compared to the figure of 10^{-7} $\text{g cm}^{-2} \text{h}^{-1}$ found in Toribara's experiments [4].

The effect of pH and Eh on the rate of mercury evaporation can be estimated from the Eh -pH diagrams of solid and solution species in equilibrium with water containing 10^{-3} mol l^{-1} of chloride and total sulphur at 25°C [6]. Under conditions which might be encountered in the environment (viz. pH in the range 5-9 and Eh in the range -0.4 to +0.4) Hg is the predominant species. Thus, under these conditions, loss of Hg by evaporation should occur and the lost Hg will be replaced in solution at the expense of HgCl_2 , $\text{Hg}(\text{OH})_2$ and HgS until the mercury content of the solution is reduced to zero. The field of Hg extends into the region of high pH and reducing Eh and these conditions will promote the loss of mercury by evaporation. In contrast low pH conditions or, more effectively, Eh conditions more oxidizing than +0.4 will result in the conversion of Hg to HgCl_2 , $\text{Hg}(\text{OH})_2$ or HgS and thus retard or eliminate the evaporation process. These observations are in accord with the experimental work described above and the use of acid permanganate solutions to trap Hg from gas streams provides a practical demonstration of pH- Eh effects.

A study of the transfer of $(\text{CH}_3)\text{HgCl}$ from aqueous media to nitrogen [7] found less than 1% transfer under the experimental conditions. Using the same gas flow rate and time, ca. 50% of the mercury was volatilized after digestion with $\text{KMnO}_4/\text{H}_2\text{SO}_4$ followed by reduction with $\text{H}_2\text{NOH}/\text{SnCl}_2$ to convert $(\text{CH}_3)\text{HgCl}$ to Hg. More forcing conditions gave better than 95% transfer of mercury to the gas stream. Thus, it would appear that $(\text{CH}_3)\text{HgCl}$ volatilizes from water about 100 times slower than Hg. No information on $(\text{CH}_3)_2\text{Hg}$ was provided. However, since this compound is extremely volatile and insoluble in water, very rapid evaporation might be expected.

Some experimental work [8-14] has been carried out on the evaporation of organomercury compounds from soils, probably stimulated by the agricultural utilisation of these materials. For the purposes of this paper the most significant findings of this work are that adsorption processes reduce the rate of mercury evaporation [8, 9] and that microbial activity may increase the evaporation rate by an order of magnitude [10]. Domestic waste supports considerable microbial activity and also contains quantities of suspended material which may adsorb dissolved mercury. The following experiments were thus carried out to investigate the effects of these leachate components on the evaporation of mercury as compared to a 'model' leachate consisting of a 5,000 vpm acetic acid solution buffered to pH 9 to promote mercury evaporation.

Solutions of mercury, as mercuric nitrate, were prepared in leachate from domestic waste and in 5,000 vpm acetic acid solution buffered to pH 9 with sodium hydroxide. A 1 litre aliquot of solution was then placed in a 1 litre

culture vessel fitted with a lid and gas purge. A flow of 300 ml/min of nitrogen or air was used to flush the ullage above the solutions in the culture vessels and to give a change of the gas in the vessel every 30 to 45 seconds. Three vessels were set up, one containing leachate under nitrogen, one containing leachate under air and one containing 5,000 vpm acetic acid solution at pH 9 under air. The liquid was stirred with a glass coated magnet to prevent the formation of concentration gradients in the solutions. Samples of the culture vessel contents were removed at intervals and diluted in concentrated nitric acid before being submitted for analysis.

The initial experiments were carried out using ca. 100 ppm w/v mercury solutions. However, over a 10 day period rather erratic results were obtained and no clear evidence was found that evaporation of mercury was occurring. The 5,000 vpm aqueous acetic acid solution buffered to pH 9 deposited a droplet of mercury over the experimental period and this was found to constitute ca. 20% of the added mercury. It would seem that, in this case, the formation of Hg is far more rapid than its loss by evaporation. A second set of experiments was carried out using a nominal initial mercury concentration of 10 ppm. More consistent results were obtained at this concentration level although they were still subject to some scatter. The analytical error was estimated at $\pm 5\%$ and these results were corrected for the evaporation of water assuming a constant rate. The analytical data and corrected figures are given in Table 1 and presented graphically in Figs. 1 and 2.

The data obtained from the 5,000 vpm acetic acid solution buffered to pH 9 were fairly consistent showing an average decrease in mercury concentration of 3.8 ppb/h (Fig. 1). The results from the leachate solutions were somewhat scattered but, on average, there seemed little difference between

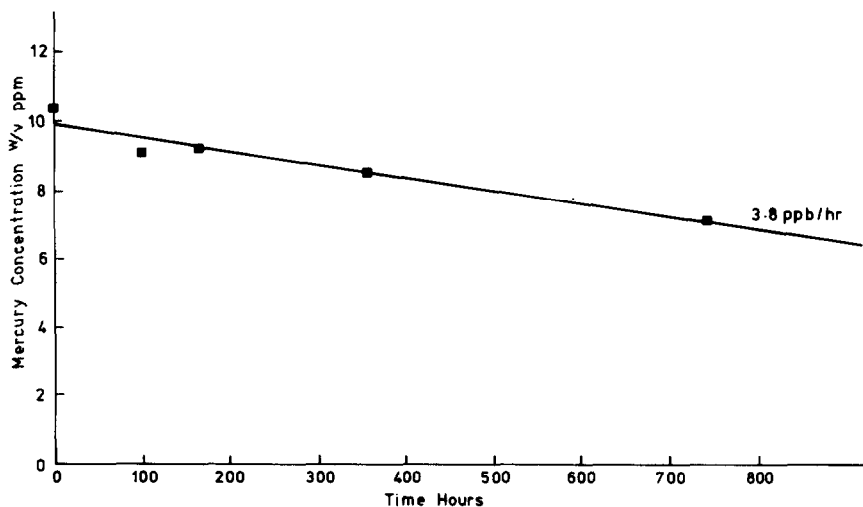


Fig. 1. Evaporation of mercury from 5,000 vpm acetic acid at pH 9, $23 \pm 3^\circ\text{C}$.

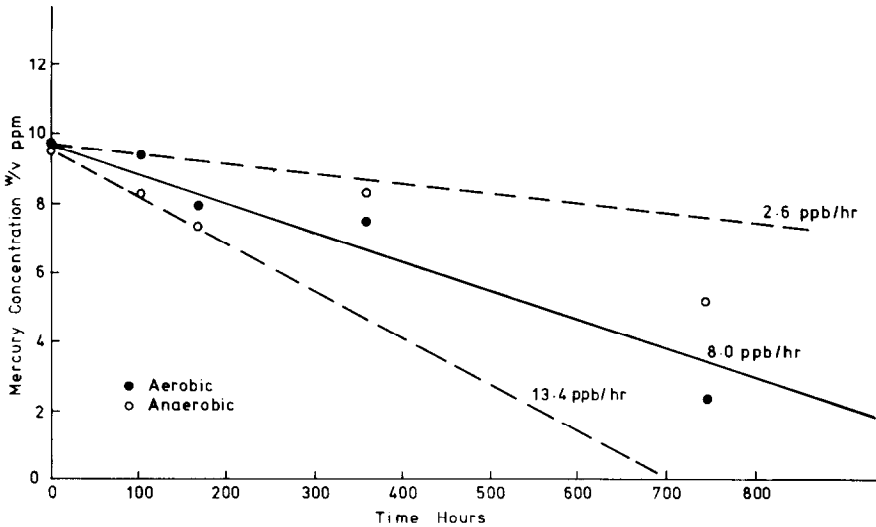


Fig. 2. Evaporation of mercury from leachate at $23 \pm 3^\circ\text{C}$.

TABLE 1

Evaporation of mercury from leachate*

Time (h)	Mercury concentrations in aqueous phase (w/v, ppm)**					
	Anaerobic leachate		Aerobic leachate		pH 9 buffer	
	Observed	Corrected	Observed	Corrected	Observed	Corrected
0	9.5	9.5	9.7	9.7	10.4	10.4
70	8.6	8.24	9.7	9.30	9.5	9.13
166	8.1	8.30	8.8	7.93	10.2	9.26
358	10.6	8.35	9.5	7.48	10.6	8.50
742	8.4	5.26	4.4	2.46	12.0	7.08
Rate of water loss (ml/h)	0.593		0.593		0.553	

*Typical composition of leachate: pH 6.0, total organic carbon 5,000 ppm, total organic acids 8,000 ppm, iron 100 ppm, chloride 1,000 ppm. Measurements $23 \pm 3^\circ\text{C}$.

**Mercury analyses were carried out by Environmental and Medical Sciences Division, Harwell Laboratory, using atomic absorption techniques.

the aerobic and anaerobic evaporation rates. A value of 8.0 ppb/h was estimated for the overall rate at which the concentration of mercury in leachate decreased. The extreme values for the rate of loss of mercury as suggested by the data are indicated by broken lines in Fig. 2. These were 2.6 and 13.4 ppb/h giving the mean value of 8.0 ppb/h.

The evaporation experiments were conducted in containers of 80 cm² cross sectional area and the results in the figure were corrected to concentrations in 1 litre of solution. Thus a rate of mercury loss in the range 2.6 to 13.4 ppb/h from 1 litre of solution through 80 cm² corresponds with an absolute rate of loss in the range 3.25×10^{-8} to 1.675×10^{-7} g cm⁻² h⁻¹. The mean value of 8.0 ppb/h corresponds with an absolute rate of 1.0×10^{-7} g cm⁻² h⁻¹. These figures are in good agreement with the previously determined [4] value of 10^{-7} g cm⁻² h⁻¹ for aqueous solutions and it would appear that mercury evaporates from leachate at much the same rate as from aqueous solution. However, under the conditions used the rate for leachate was about twice that for the acetic acid solution buffered to pH 9.

To assess mercury losses during the handling of solutions additional experiments were carried out on solutions containing less than 1 ppm of mercury. A solution of 5,000 vpm acetic acid in water was allowed to equilibrate for several days with a droplet of mercury metal. After this time aliquots of the solution were decanted into ground glass stoppered bottles. One was completely filled and stoppered immediately, a second was half filled and stoppered immediately and a third was half filled, left unstoppered for 30 minutes and the contents then used to completely fill a smaller bottle which was immediately stoppered. The experiment was duplicated and the solutions submitted for analysis after several days. The results of both tests are presented in Table 2.

The results of both experiments are similar although the mercury concentrations in the first experiment were some 2½ times higher than in the second experiment. Compared to the immediately stoppered and filled bottle, an immediately stoppered but half-filled bottle gave ca. 20% lower mercury concentration values. Exposure of the solutions to air for 30 minutes in an unstoppered bottle produced a 10% lower value. These results suggest that partially filled containers of leachates contaminated with mercury [7] to the extent of 0.1 to 1.0 ppm may result in erroneously low mercury analyses being obtained. However, the exposure of samples to air for a few seconds during transfer from container to container does not seem likely to introduce large

TABLE 2

Loss of mercury in handling

Handling method	Mercury concentration (w/v, ppb)* (23 ± 3° C)	
	First experiment	Second experiment
Filled bottle	430 (100%)	180 (100%)
Half filled bottle	330 (77%)	140 (78%)
Unstoppered bottle	380 (88%)	160 (89%)

*Mercury analyses were carried out by Environmental and Medical Sciences Division, Harwell Laboratory, using atomic absorption techniques.

errors in the analytical data. Prolonged exposure of the solution to air should, of course, be avoided.

In conclusion it should be noted that the conditions used in these evaporation experiments do not attempt to model conditions within a landfill site [15]. The higher temperature (perhaps 50°C), absence of agitation, presence of potential adsorbants and presence of sulphide to precipitate mercury could all substantially change the behaviour of the mercury-leachate system. However, the results do indicate that ppm levels of dissolved mercury in leachate exposed to the atmosphere after leaving a landfill site may evaporate at a rate comparable with that defined by studies of relatively 'clean' mercury solutions.

Acknowledgement

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