The retention of metallic mercury vapor by soils*

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Abstract—Five surface soils from southeastern Montana were exposed to air containing elemental mercury vapor. The majority of the sorbed Hg was found to volatilize at 100–200°C. The sorbed Hg was resistant to extraction by water, neutral salts, methanol or DTPA. Cysteine, acetylacetone and cupferron showed limited extraction of sorbed Hg, while benzene and to a greater extent, hydrochloric acid and sodium hydroxide demonstrated high removals of sorbed Hg. The observed behavior suggests that elemental Hg may be retained by soils as an organo-complex.

INTRODUCTION

THE SORPTION of metallic mercury vapor (Hg^0) by soils is of interest to geochemists concerned with the genesis of mercury ore bodies and with the environmental fate of atmospheric pollutants. Mercury may be introduced into the atmosphere from natural sources including zones of active volcanism and mercury mineralization, and by a range of human activities including ore refining and coal combustion.

The metallic mercury vapor concentration measured by the U.S. Geological Survey in the air over unmineralized, non-industrial areas of the western United States ranged from 0.003 to 0.009 μg Hg^0/m^3 (McCARTHY et al., 1970). A survey by JEPSON (1973) of elemental mercury vapor concentrations in the air of selected U.S. urban areas showed levels up to a 4 μg/m^3. The mercury vapor concentration of the air above fumaroles in Hawaii has been reported to be about 22 μg/m^3 (ESHELMAN et al., 1971), while concentrations as high as 2000 μg/m^3 have been reported for the air in mercury mines (McCARTHY et al., 1970). Mercury vapor concentrations of 2–31 μg/m^3 have been measured in flue-gas resulting from the combustion of coals containing 0.15 to 0.3 ppm Hg (BILLINGS and MATSON, 1972; DIEHL et al., 1972). The threshold limit values for occupational exposure to mercury vapor in air has been set at 10 and 100 μg/m^3 in the U.S.S.R. and the U.S.A. respectively (SCHROEDER, 1970).

Metallic mercury vapor was reported as the dominant Hg species in the near-ground atmosphere of the Tampa Bay, Florida area (JOHNSON and BRAMAN, 1974), and in the incoming steam and gaseous effluents at two geothermal power plants in California

and Mexico (ROBERTSON et al., 1977). PIPERNO (1975) reported mercury to occur principally in the elemental form in coal combustion emissions.

The retention of Hg^0 vapor by clays and organic matter (KOKSOY and BRADSHAW, 1969) has been postulated to explain the occurrence of mercury anomalies ('haloes') surrounding ore bodies. TROST and BISQUE (1972) and FANG (1978) examined the sorption of Hg^0 by soil components, and found much greater sorption (per unit weight) by organic materials as compared to clay minerals. The objective of the work reported here was to examine the extent of sorption of Hg^0 by a range of surface soils, and to investigate the nature of the retained mercury.

MATERIALS AND METHODS

Five surface soils (0–20 cm depth) were collected from uncultivated sites in southeastern Montana (Table 1), air-dried, and ground to pass a 2 mm sieve. The soil pH (1:2 soil:water), organic carbon (Walkley–Black titration), total soluble salts (saturation extract electrical conductivity), and cation exchange capacity (1N ammonium acetate, pH 7) were determined.‡ Calcium carbonate equivalent was determined by the titrimetric method of BUNDY and BREMNER (1972). Native soil mercury levels were determined by flameless atomic absorption spectrometry following digestion of the soil with aqua regia. Particle size was determined by the pipette method (DAY, 1965).

Forty gram (oven-dry basis) portions of air-dried soil were placed in 100 mm diameter polystyrene Petri dishes and stacked in a 23 liter glass bell jar (Fig. 1). There were three exposure runs and ten plates of each of the five soils per run (2000 g of soil per run). Mercury vapor was generated from a ^{203}Hg-labelled metallic mercury source having an initial specific activity of 60 mCi/g which was contained in a thermoregulated water bath to control vapor concentration. Air was passed over this metallic mercury and down a glass inlet tube to the bottom of the bell jar which contained the soil samples. The Petri dishes of each soil were arranged randomly in a 13-tier support rack within the bell jar. The air exited near the top of the bell jar with the flow rate maintained at 200 ml/min. A magnetically-driven fan at the base inside the bell jar mixed the air within the jar such that the outlet vapor concentration of Hg was assumed to be the ambient concentration (SLATYER, 1971). The internal surfaces of the bell jar and the Petri dish support rack were lightly coated with petroleum

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‡ M. D. KAUFFMAN and E. H. GARDNER (1976) Methods of soil analysis used in the Soil Testing Laboratory at Oregon State University. Special Report 321. Oregon Agr. Sta.

Table 1. Chemical and physical properties of selected eastern Montana soils

Soil Series	Classification	pH	CaCO$_3$ equiv. %	Organic Carbon %	Total Native Hg, ug/kg	Total Soluble Salts mmhos/cm	Cation Exchange Capacity meq/100g	Sand %	Silt %	Clay %
Arvada	Ustollic Natrargid, fine, montmoril-lonitic, mesic	8.1	0.08	1.6	< 60	0.43	22.2	35	25	40
Campspass	Typic Eutroboralf, fine, montmoril-lonitic	6.6	–	6.7	130	0.35	25.5	19	56	25
Heldt	Usteric Camborthid, fine, montmoril-lonitic, mesic	8.3	3.92	1.7	183	0.35	11.4	27	48	25
Bainville	Ustic Torriorthent, fine, silty, mixed (calcareous), mesic	7.5	0.04	1.0	73	0.28	15.8	29	42	29
Terry	Ustollic Haplargid, coarse-loamy, mixed, mesic	8.3	0.20	0.9	< 60	0.31	8.4	74	14	12

jelly to minimize the sorption of mercury vapor (BROWNE and FANG, to be published).

Air exiting the bell jar passed through a series of traps containing Hopcalite, a granular copper-manganese oxide material (MAGOS, 1966), to trap the mercury vapor. The traps were radioassayed on alternate days using a NaI γ-scintillation detector. The soils were exposed to air containing an average outlet concentration of 14.3 μg Hg/m^3 for 10 days and then purged for 2 days with room air. During the exposure and purging periods, the soils were at room temperature (22–34°C).

At the end of each purge period, the plates of each of the five soils were radioassayed using a small animal, whole-body, liquid scintillation spectrometer system (Armac model 446, Packard Instrument Co.) and then the individual soils were bulked and mixed.

To assess the volatile loss of the retained mercury vapor from these soils, 60 g (oven-dry basis) samples of soil covered with 40 g of coarse quartz sand and maintained at room temperature either air-dry or at the $\frac{1}{3}$-bar moisture content (by alternate day additions of distilled water) in small plastic cups kept in a forced draft fume hood, were monitored for 16 days using the Armac system.

To assess the heat lability of the retained mercury, 1.5 g samples of soil contained in 2 ml shell vials were heated in an oven for 2 days to temperatures ranging from 80 to 450°C. A fresh sample was used for each temperature, and there were 3 replicates per soil per temperature. The fraction of the initially retained mercury remaining following the heat treatment was determined by radioassay of the vials using a NaI γ-scintillation spectrometer (Packard Auto-Gamma Spectrometer Model 5230).

To assess the extractability of the mercury by various chemical agents, 10 g (oven dry basis) each soil in triplicate were extracted by overnight shaking at room temperature with 20 ml of the following solutions:

(a) distilled water
(b) 1 N KCl
(c) 1 N CaCl$_2$
(d) 1 N HCl
(e) 1 N NaOH
(f) 0.5 M acetylacetone (2,4-pentanedione)
(g) 0.5 M cupferron (the NH$_4$-salt of N-nitrosophenyl-hydroxylamine)
(h) 0.5 N Cu (C$_2$H$_3$O$_2$)$_2$
(i) 0.005 M DTPA (diethylenetriamine pentaacetic acid): 0.01 M triethanolamine: 0.1 M CaCl$_2$: pH 7.3 solution
(j) 0.1 M cysteine (extraction run at 4°C to inhibit microbial activity)
(k) benzene
(l) methanol.

After shaking, the tubes were centrifuged at 27,000 g for 10 min, and 4 ml aliquots of the supernatant were sampled for radioassay using the NaI spectrometer.

RESULTS AND DISCUSSION

Radioassay of the individual Petri dishes of soil removed from the bell jar exposure system showed the coefficients of variation for the measured Hg uptakes of the ten dishes of each soil type to be 4% or less, indicating that well-mixed conditions did indeed exist within the bell jar, and that the assumption of an ambient vapor concentration equal to that measured at the outlet is valid. The relative order of mercury sorption by the soils (Table 2) was Bainvilville > Campspass > Heldt > Arvada > Terry. The
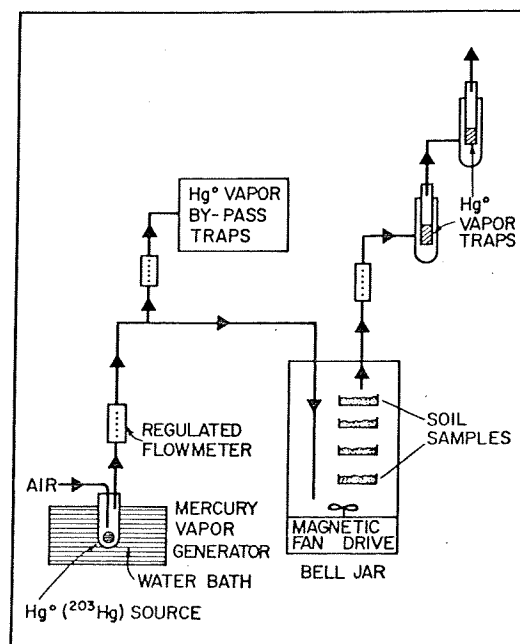

Fig. 1. Schematic representation of system used to expose soils to metallic mercury vapor.

Table 2. Uptake of mercury by five Montana soils following 10 day exposure to air stream containing 14.3 μg Hg^0/m^3 air. Values shown are means of three replicates $\pm$1 standard error

SOIL	μg Hg/kg soil[1]
Arvada	10.5 $\pm$ 1.7
Campspass	40.8 $\pm$ 1.0
Heldt	23.7 $\pm$ 2.4
Bainville	45.6 $\pm$ 2.7
Terry	9.5 $\pm$ 1.0

2000 g of soil contained in the bell jar removed an average of 56% of the entering mercury vapor.

No loss of the sorbed mercury from the soils maintained at air-dryness was observed over the 16 day monitoring period. Soils maintained at the $\frac{1}{3}$-bar moisture tension showed maximal loses of about 5% of the total sorbed mercury.

The majority of the sorbed mercury was liberated at temperatures between 100 and 200°C (Fig. 2). Similar steep, S-shaped Hg-loss vs temperature curves have been reported for several mercury compounds alone (KOKSOY et al., 1967), or mixed with soil (KOKSOY and BRADSHAW, 1969). Elemental mercury showed losses of 30–35% at 70–80°C, while mercurous and mercuric chloride showed losses of only 1–6% in this temperature range. All three compounds showed complete mercury volatilization below 250°C (KOKSOY et al., 1967). In contrast, mercuric sulfide and oxide did not show any Hg-loss until the samples were heated to 210–270°C, with complete Hg-liberation at 340 and 535°C, respectively (KOKSOY et al., 1967). On the basis of this literature evidence, HgS and HgO appear to be unlikely candidates for the sorbed mercury species observed in the studies reported here.

Major volatile losses of Hg from the soils studied here occurred at a somewhat lower temperature range (100–200°C) than demonstrated by KOKSOY and BRADSHAW (1969) for soil samples taken from sites surrounding a cinnabar deposit in Turkey. Based on field evidence, these investigators postulated the gaseous dispersion of metallic mercury vapor away from the zone of mineralization, and its subsequent sorption by soil organic matter as an important mechanism for the observed Hg enrichment patterns observed in the soils of the secondary environment. These soils showed maximal Hg losses in the 200–300°C range.

Sodium hydroxide, hydrochloric acid and benzene removed the most sorbed mercury (Table 3). Little or no mercury was extractable by water, potassium or calcium chloride, cupric acetate, methanol or DTPA, while cysteine, acetylacetone and cupferron showed limited extraction abilities.

While water soluble mercury compounds such as HgCl$_2$ have been identified in mineralized rock zones

(KOKSOY and BRADSHAW, 1969), the failure of distilled water to extract the sorbed mercury (Table 3) makes such compounds unlikely candidates for the sorbed species observed here. The failure of KCl or CaCl$_2$ to remove the sorbed mercury indicates that no significant amount exists as a species which is readily available to ion exchange.

Hydrochloric acid extracted from 1 to 80% of the total sorbed mercury. The low Hg extraction from the Heldt soil is undoubtedly due to the reduction in the effective H$^+$ concentration resulting from reaction with the free lime present in this soil (Table 1). When the Heldt soil was extracted with 1.4 N HCl, 50% of the sorbed mercury was released. Sodium hydroxide extracted 74–92% of the sorbed mercury from the soils. While both HCl and NaOH are rather non-selective extractants which can solubilize portions of both the mineral- and the organic-soil colloids, the uniformly high yield of sorbed mercury seen with the NaOH extractions suggests the association of the
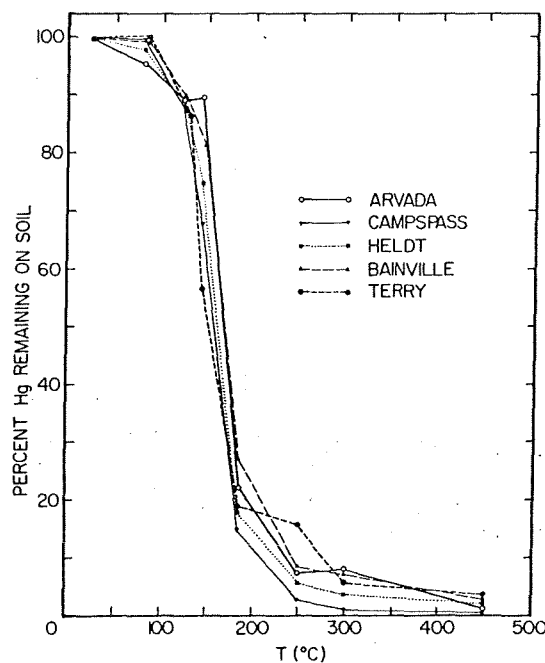

Fig. 2. Volatile loss of sorbed mercury from soils as a function of temperature.

Table 3. Removal of sorbed mercury vapor from soils by various chemical extractants. Values shown are means of three replicates

Extractant	Soil	Arvada	Campspass	Heldt %	Bainville	Terry
(a) distilled water		0.1	0.2	0.4	0.3	0.4
(b) 1 N KCl		0.1	0.0	0.0	0.0	0.2
(c) 1 N CaCl$_2$		0.2	0.1	0.2	0.0	0.2
(d) 1 N HCl		71.1	15.8	1.2*	68.0	79.6
(e) 1 N NaOH		91.7	74.3	89.3	82.7	92.3
(f) 0.5 M acetylacetone		2.6	0.9	2.8	2.5	3.7
(g) 0.5 M cupferron		2.7	8.7	4.7	3.2	2.5
(h) 0.5 N Cu (C$_2$H$_3$O$_2$)$_2$		0.6	0.3	0.0	0.3	1.2
(i) DTPA:TEA:CaCl$_2$		0.2	0.4	0.5	0.5	0.1
(j) 0.1 M cysteine		4.0	3.7	5.3	3.1	2.9
(k) benzene		9.3	5.1	11.9	14.7	12.8
(l) methanol		1.1	0.4	0.3	0.1	0.7

* 1.4 N HCl extracted 49.6%.

sorbed mercury species with the soil organic matter. Acidification of the NaOH extract (STEVENSON, 1965) shows a large portion of the Hg thus removed from the soil to be associated (as a sorbed or coprecipitated species) with the insoluble, humic acid (Table 4). Whether the Hg present in the solution phase of the acidified NaOH extract exists as a species soluble in both acid and alkali, as a fulvic acid complex, or as a species which has been acid-leached from the humic acid is not clear. Only a limited portion (0.5–4%) of the Hg extractable by 1 N HCl (or 1.4 N HCl for the Heldt soil) partitioned into benzene upon shaking with the HCl extracts. TROST and BISQUE (1972) and FANG (1978) have shown soil organic matter analogs, e.g. peat, humic acid, pine mull, etc. to have high Hg⁰ sorption capacities.

Due to their ability to chelate metals, aqueous solutions of acetylacetone and cupferron have proven to be good extractants of organic matter from podzolic B horizons (MARTIN and REEVE, 1957). Both of these reagents, in particular the cupferron with the Campspass soil, extracted a small portion of the sorbed mercury, lending further support to the existence of the

mercury as an organo-mercury complex. However no sorbed Hg was extracted with cupric acetate, even though copper forms very stable complexes with organic matter (STEVENSON and ARDAKANI, 1972).

The DTPA solution tested here has been used as a soil extractant for several trace elements including zinc, iron, manganese and copper (FOLLET and LINDSAY, 1971). This chelate however was ineffectual as on extractant for the sorbed mercury. Cysteine, a monothiol amino acid, was selected for use because of the known affinity of mercury to form complexes with sulfhydryl groups. The 0.1 M cysteine solution extracted from 3–5% of the total sorbed mercury indicating that at least a portion of the sorbed mercury is available for complexation.

The selective extraction of organomercurials into organic solvents has long been used as the method for partitioning the total mercury content of biological materials into organic vs inorganic mercury components (e.g. MILLER et al., 1958; GAGE, 1961). The higher removals of sorbed mercury obtained with benzene as compared to methanol suggests the occurrence of at least a portion of the sorbed Hg as, or

Table 4. Gross chemical fractionation of sorbed Hg extracted from soils by 1N NaOH

Soil	% of sorbed Hg in acidified NaOH extract associated with humic acid fraction
Arvada	46
Campspass	86
Heldt	58
Bainville	66
Terry	52

in association with, an organic compound with an affinity for non-polar as compared to polar organic solvents.

FANG (1978) showed the same relative order of Hg^0 sorption for these same five soils. Using a technique developed by CLARKSON and GREENWOOD (1970) for the selective determination of inorganic mercury in the presence of organomercurial compounds in urine, blood, and animal tissues, FANG (1978) ascribed 20–27% of the sorbed mercury in the Arvada, Heldt and Terry soils, and 10 and 2% of the sorbed mercury in the Bainville and Campsspass soils, respectively, to an inorganic species. This evidence further supports the existence of a large portion of the sorbed mercury as an organo-complex.

SUMMARY AND CONCLUSIONS

Soils have a high affinity for elemental mercury. The sorbed mercury is resistant to loss at room temperature, but a large portion is rapidly volatilized at 100–200°C. The solution extraction trials suggest that the sorbed Hg is retained as an organomercury species.

The retention of Hg^0 by soils as demonstrated here offers an explanation for the enrichment in Hg seen in the soils around a coal-fired power plant (KLEIN and RUSSELL, 1973).

In predictions of ground level air concentrations of mercury vapor used in evaluating power plant sitings, the effects of mercury vapor removal mechanisms have generally been neglected (LYONS, 1977). The data presented here indicate that the sorption of Hg^0 by surface soils offers one such significant atmospheric removal mechanism. Such processes diminish the inhalation hazards associated with metallic mercury vapor to organisms downwind from the source. However information is needed regarding the abiotic and biotic cycling of this soil-sorbed mercury in order to fully assess its environmental impact.

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