

# ADSORPTION OF MERCURY COMPOUNDS BY TROPICAL SOILS

(I. Adsorption in Soil Profiles in Relation to Their Physical, Chemical, and Mineralogical Properties)

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**Abstract.** Mercury adsorption of  $\text{HgCl}_2$  and 2-methoxyethylmercury chloride (Aretan) ( $100 \text{ mg Hg L}^{-1}$ ) was measured for three soil profiles from Morogoro, Arusha, and Dar es Salaam in Tanzania. The adsorption was investigated for the physical, chemical, and mineralogical properties of the soils. All soil samples showed greater capacity for adsorption of Aretan than for  $\text{HgCl}_2$ . In the Morogoro profile Hg adsorption decreased with depth but in the other two soils, the minimum adsorption occurred in the third horizon and increased both upwards and downwards. In the Morogoro profile, Aretan adsorption correlated well with pH. Adsorption of both Aretan and  $\text{HgCl}_2$  correlated well with the distribution of organic C and with the cation exchange capacity of the soils. In the Arusha and Dar es Salaam profiles Hg adsorption was not significantly correlated with any of the soil properties tested.

## 1. Introduction

Mercury added to soils from fungicides (Gilmour and Miller, 1973; MacLean *et al.*, 1973; Gowen *et al.*, 1976) or disposal of Hg-containing wastes (Fimreite, 1970; D'Itri, 1972; Lagerwerff, 1972) may be adsorbed and precipitated in the soils, lost to the atmosphere through volatilization, and leached to lower depths in the soil profile (Hogg *et al.*, 1978). Leaching may be expected to take place in sandy soils devoid of organic and inorganic colloids (Aomine and Inoue, 1967; Inoue and Aomine, 1969; Trost and Bisque, 1972).

Hogg *et al.* (1978) stated that adsorption probably is the dominant initial fate, and may determine the amount of Hg remaining in soil solution at equilibrium. Variations in Hg adsorption between soil types may be explained by differences in the nature and quantity of their clays and organic matter. Variations in a soils' physico-chemical and mineralogical properties within the profile may determine the soil's capacity to distribute the adsorbed Hg within the profile. Most of the studies on Hg adsorption reported

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the literature have evaluated the adsorption of surface soils only. In the investigations reported here, Hg adsorption by three profiles belonging to distinct soil orders was studied. An attempt was made to relate the influence of the physico-chemical and mineralogical properties of these soils to Hg adsorption.

## 2. Materials and Methods

### 2.1. SOILS USED AND THEIR LOCATIONS

The soils were collected from three different profiles in Morogoro, Arusha, and Dar es Salaam in Tanzania. The Morogoro profile is located at Mzumbe Secondary School ( $6^{\circ}56' S 37^{\circ}34' E$ ), on a 5% slope. The soil at this location is an Orthic Ferralsol (FAO/UNESCO, 1977) or Oxisol (Soil Survey Staff, 1975) with savanna type of vegetation. The mean annual rainfall is about 700 mm.

The Arusha profile is situated at the Tropical Pesticides Research Institute ( $3^{\circ}20' S 36^{\circ}37' E$ ), on a 5% slope. The vegetation is savanna type. The soil is Mollic Andosol (FAO/UNESCO, 1977) or Andept (Inceptisol) (Soil Survey Staff, 1975). The mean annual rainfall is over 1000 mm.

The Dar es Salaam profile is located on a flat ground at the Central Veterinary Laboratory ( $6^{\circ}59' S 39^{\circ}16' E$ ), Temeke. The soil is Cambic Arenosol (FAO/UNESCO, 1977) or Entisol (Soil Survey Staff, 1975). Vegetation consists of planted coconut trees, with shrub and grass as undergrowth. The mean annual rainfall is over 1000 mm.

Samples were collected from each profile, with the horizons delineated according to their color and structural variations. Soil samples were air-dried, ground, and passed through 2 mm or 0.25 mm sieves. The soil samples passed through 2 mm sieve were used only for pH measurement and particle size analysis. For all chemical analyses, the samples passed through 0.25 mm sieve were used.

### 2.2. PHYSICAL, CHEMICAL, AND MINERALOGICAL ANALYSES

The pH was determined in a 1:2 soil:solution ratio of 0.01 M  $CaCl_2$  solution. The cation exchange capacity (CEC) was determined by the ammonium acetate (pH 7.0) method (Chapman, 1965). Organic C was determined by the wet oxidation method of Walkley and Black (Allison, 1965). Free Fe oxides were extracted by Na citrate-bicarbonate-dithionite (Kunze, 1965) and the Fe content in the extract was measured by atomic absorption spectrophotometry.

The particle size distribution was measured by the hydrometer method (Day, 1965). Samples for mineralogical analysis were prepared according to the procedure developed by Jorgensen (1983). The clay fractions ( $< 2 \mu m$ ) were separated by wet sieving from the soils of the Morogoro and Arusha profiles. Thin layers of the clays were deposited on  $0.45 \mu m$  millipore membrane filters by filtering clay suspensions under vacuum. The layers were transferred to clean glass slides by sandwiching them between the filter papers and the glass slides and rolling a glass rod back and forth over the membrane filters. The filters were carefully detached, leaving the thin clay layers on the glass slides,

which were allowed to dry. For the samples coarser than the clay fraction, the filter membranes bearing the samples were simply glued on glass slides. The mineralogical composition was determined by the Philips 1710 X-Ray diffractometer.

### 2.3. MERCURY ADSORPTION IN SOIL PROFILES

Two g samples from each horizon of the profiles were equilibrated in glass bottles with 20 mL of 100 mg Hg L<sup>-1</sup> solutions of 2-methoxyethylmercury chloride (Aretan) or HgCl<sub>2</sub> in four replicates. Earlier determinations showed that standard deviations were less than 9% and 8% for HgCl<sub>2</sub> and Aretan, respectively, when 10 to 12 subsamples from the same sample/solution were analyzed for Hg (Semu *et al.* 1985). The bottles were shaken for 2 hr on an end-to-end shaker. A 2 hr shaking period was found to be optimum after testing several equilibration periods in this study and was adopted for all studies. This time period was also found to be adequate by Hogg *et al.* (1978).

After shaking, the suspensions were filtered through Whatman No. 42 filter paper. The Hg content in the filtrates from the HgCl<sub>2</sub>-treated samples was measured immediately after equilibration. Filtrates from Aretan-equilibrated samples were digested before measurement of Hg content. An aliquot from the HgCl<sub>2</sub> filtrate was pipetted into a 125-mL quick-fit conical flask. Forty mL of distilled water, 3.0 mL of 11 M HNO<sub>3</sub>, and 3.0 mL of 20% Sn(II) chloride solution (in 6 M HCl) were added to the flask (Iskander *et al.*, 1972). Immediately after addition of Sn(II) chloride the flask was connected to a Pye Unicam Hg cold vapor analyzer kit to circulate the Hg vapor through the absorption cell. Mercury was measured using the Pye Unicam SP 191 atomic absorption spectrophotometer equipped with the Philips PM 8220 chart recorder. Standard HgCl<sub>2</sub> solutions in the 0 to 1 mg Hg L<sup>-1</sup> range were regularly included. The difference between Hg found in the filtrates and that originally added to soil was calculated to be the amount adsorbed by the soil. Aliquots from the Aretan filtrates were digested in pyrex boiling tubes with 15 mL of 3 : 1 HNO<sub>3</sub> : HCl for 1.5 hr in a constant temperature (50 °C) water bath (Hogg *et al.*, 1978). This digestion procedure was tested and found to give complete recovery of Aretan-Hg. After digestion, the contents of each tube were quantitatively transferred to the analysis flask and the procedure for Hg measurement described under HgCl<sub>2</sub> was employed.

## 3. Results and Discussion

### 3.1. PHYSICAL, CHEMICAL, AND MINERALOGICAL PROPERTIES

Some of the physico-chemical properties of the soils from three profiles are presented in Table I. The Morogoro profile is quite acidic. The profile is rich in Fe oxide. The clay content is rather uniform down the profile, with the exception of the A horizon.

The Arusha profile has higher pH values than the Morogoro profile. This may account for its relatively higher CEC compared to that in the Morogoro soil, despite almost equal contents of organic C in the two soils and more clay and Fe oxide in the Morogoro soil.

TABLE I  
Physico-chemical and mineralogical properties

Soil	Depth	pH(CaCl <sub>2</sub> )	CEC	Fe oxides	Organic C	Clay	Textural class	Clay mineral
Morogoro (Oxisol)	0-10	5.2	24.6	6.9	2.5	43	Clay	Kaolinite
	10-30	4.2	20.2	6.9	0.9	66	Clay	Kaolinite
	30-50	4.3	18.2	7.7	0.8	67	Clay	Kaolinite
	50-70	4.4	20.6	7.5	0.5	64	Clay	Kaolinite
	70-140	4.4	17.4	7.7	0.4	65	Clay	Kaolinite
	140+	4.1	17.8	7.8	0.4	62	Clay	Kaolinite
Arusha (Inceptisol)	0-15	6.3	32.6	0.9	2.4	5	Loamy sand	Allophane
	15-35	6.4	35.8	0.8	1.7	4	Loamy sand	Allophane
	35-70	6.0	35.2	1.0	0.3	5	Sandy loam	Allophane
	70-95	6.3	24.6	0.9	0.8	5	Sandy loam	Allophane
	95-160	6.4	20.6	0.7	0.4	4	Sandy	Allophane
	160+	6.8	20.6	1.4	1.1	9	Sandy loam	Allophane
Dar es Salaam (Entisol)	0-10	5.7	5.0	0.17	0.8	<1	Sandy	Not determined
	10-36	6.1	4.8	0.16	0.4	<1	Sandy	Not determined
	36-69	5.8	4.0	0.16	0.2	<1	Sandy	Not determined
	69-130	6.0	4.2	0.20	0.1	3	Sandy	Not determined
	130+	5.3	8.4	0.44	0.3	5	Sandy	Not determined

The Dar es Salaam profile is very low in organic C, CEC, and clay. The upper horizons are almost devoid of a clay fraction, which appears further down the profile probably due to transport from the above horizons. There is very little Fe oxide.

The mineral composition of the clay fractions of the Morogoro profile is given in Figure 1. Kaolinite is the clay mineral in the Morogoro soil, as illustrated by the 001 and 002 reflections of 7.25 and 3.56 Å, respectively. Coarser fractions revealed the presence of goethite ( $\alpha - \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and quartz (Diffractogram not presented for brevity).

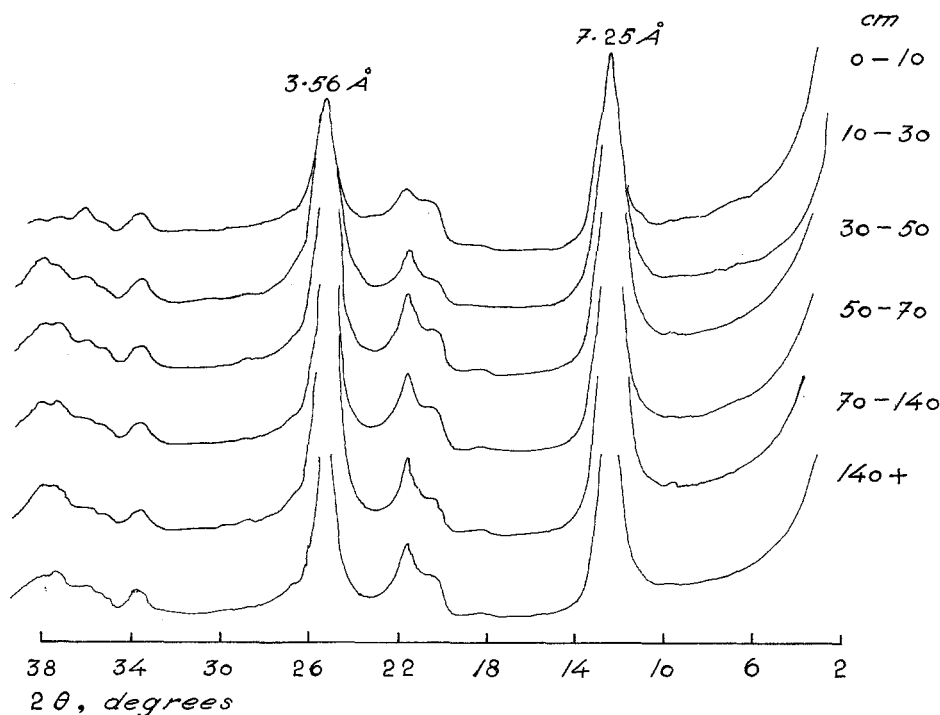


Fig. 1. X-Ray diffractograms of clay ( $< 2 \mu\text{m}$ ) fractions in the Morogoro profile. The 7.25 and 3.56 Å peaks indicate kaolinite.

The clay fraction of the Arusha profile is amorphous. The presence of the 3.26 Å reflection is indicative of allophane (Figure 2). Coarser fractions revealed presence of a number of minerals, where augite [ $\text{Ca}(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$ ] was the dominant one (Figure 2).

### 3.2. MERCURY ADSORPTION IN SOIL PROFILES

Adsorption of Aretan and  $\text{HgCl}_2$  by different horizons of the Morogoro, Arusha, and Dar es Salaam profiles is shown in Figure 3. Generally, all horizons of these profiles adsorbed significantly (at  $P = 0.001$  for Morogoro and Arusha soils and at  $P = 0.01$  for Dar es Salaam soil) higher quantities of Hg from Aretan than from  $\text{HgCl}_2$ . There were

also significant differences in the quantities of these compounds adsorbed both within and between horizons of each profile.

Adsorption of both Hg compounds in the Morogoro profile decreased gradually with depth except in the second horizon where the decrease was more marked. In the Arusha soil, adsorption of both Aretan and HgCl<sub>2</sub> decreased drastically in the second and third horizons, then increased again in the other horizons, showing the lowest adsorption in the third horizon. A more or less similar pattern of Hg adsorption was observed in the Dar es Salaam profile.

### 3.3. RELATIONSHIP BETWEEN MERCURY ADSORPTION AND SOIL PROPERTIES

The relationship between Hg adsorption and variation in physico-chemical properties was not consistent between the three profiles (Table II). In the Morogoro profile, adsorption of both Aretan and HgCl<sub>2</sub> was positively correlated with the distribution of organic C ( $r = 0.962$  and  $0.960$  for Aretan and HgCl<sub>2</sub>, respectively) and CEC ( $r = 0.847$  and  $0.854$  for Aretan and HgCl<sub>2</sub>, respectively). The correlation of adsorption with CEC

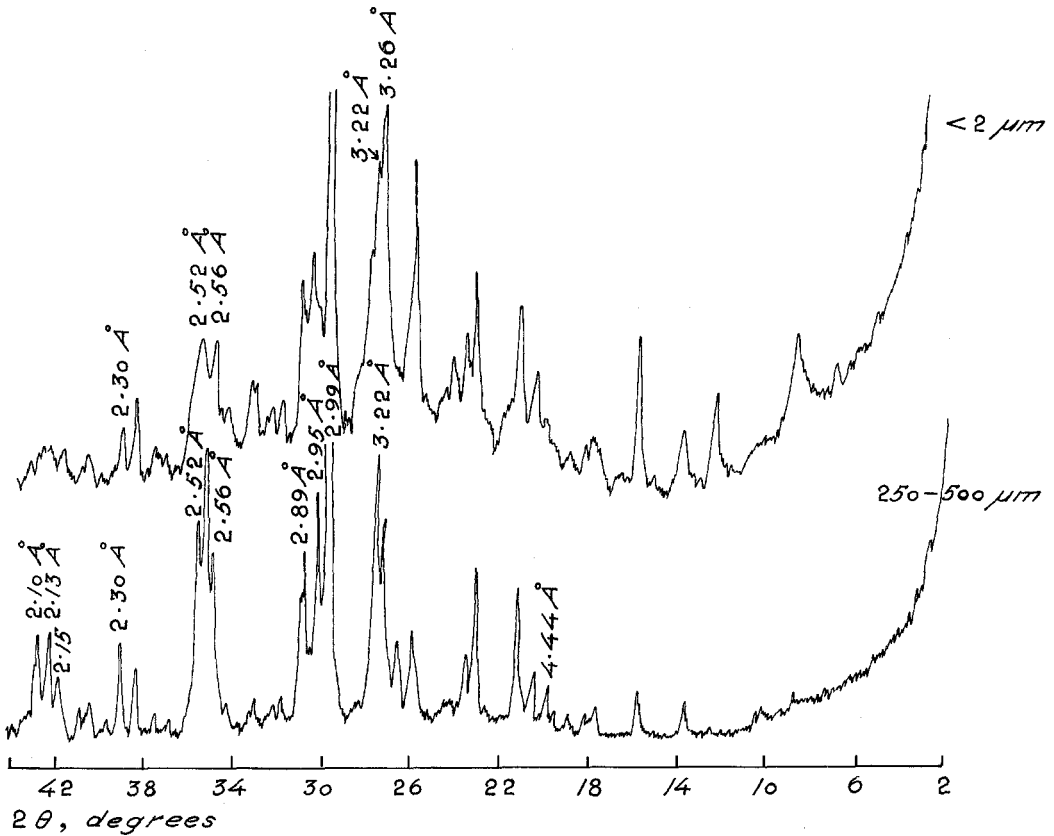


Fig. 2. X-Ray diffractograms of the <2 and 250-500 μm fractions of the B horizon (15-35 cm) of the Arusha profile. The 3.26 Å peak is for allophane, while the rest of the labeled peaks indicate augite [Ca(Mg, Fe) Si<sub>2</sub>O<sub>6</sub>].

may imply that adsorption by ion exchange may be involved in this soil, as was reported by Aomine and Inoue (1967) with PMA in Japanese soils. Adsorption of Aretan was also positively correlated ( $r = 0.821$ ) with pH. This indicates that either there were different mechanisms (e.g. adsorption vs precipitation) or a given mechanism operating differently at different pH values to result in the observed correlation. This positive correlation was contrary to other results (Semu *et al.*, 1985) where adsorption of Aretan changed little with increasing pH. This discrepancy may be rationalized by considering that the results referred to were obtained when pH of the same soil (surface horizon) was adjusted to different pH levels with little change in other soil properties, whereas

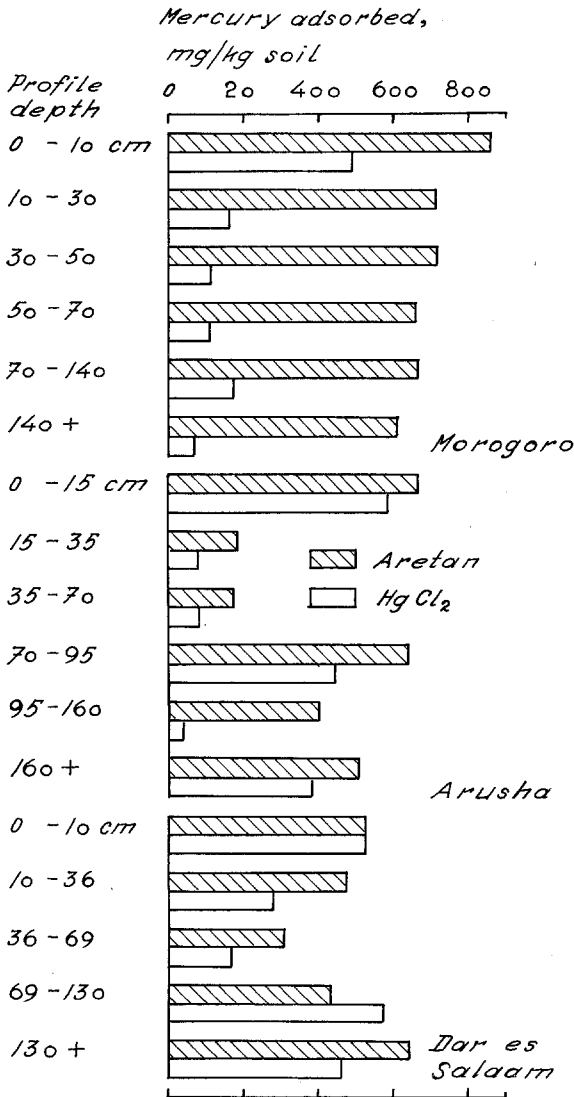


Fig. 3. Mercury adsorption in different horizons of Morogoro, Arusha, and Dar es Salaam profiles.

TABLE II

Correlation coefficients between some soil physico-chemical properties and adsorption of Aretan and HgCl<sub>2</sub> in the Morogoro, Arusha, and Dar es Salaam profiles

Soil property	Morogoro		Arusha		Dar es Salaam	
	Aretan	HgCl <sub>2</sub>	Aretan	HgCl <sub>2</sub>	Aretan	HgCl <sub>2</sub>
Clay	-0.791	-0.927 <sup>b</sup>	0.356	0.468	0.661	0.468
Organic C	0.962 <sup>b</sup>	0.960 <sup>b</sup>	0.358	0.582	0.375	0.339
Fe oxide	-0.742	-0.687	0.077	0.281	0.761	0.306
pH	0.821 <sup>a</sup>	0.803	-0.457	-0.496	-0.275	-0.275
CEC	0.847 <sup>a</sup>	0.854 <sup>a</sup>	-0.494	-0.134	0.872	0.271

<sup>a</sup> Significant at  $P = 0.05$ .

<sup>b</sup> Significant at  $P = 0.01$ .

those reported here were obtained with horizon samples having wide variation in pH as well as other soil properties (Table I).

A somewhat similar contradiction was reported for PMA where in one study the adsorption by clays changed little with pH (Aomine and Inoue, 1967), but the opposite was true in another study (Inoue and Aomine, 1969). The equilibrium concentration of Hg in the present study was different from that reported by Semu *et al.* (1985). Inoue and Aomine (1969) suggested that the mechanism of adsorption could be different, depending on the concentration of PMA.

Adsorption of HgCl<sub>2</sub> by the Morogoro profile showed a significant negative correlation ( $r = -0.927$ ) with clay content. This implies that the clay of this soil, namely kaolinite, was generally not involved in the adsorption of HgCl<sub>2</sub>, as was also observed by Feick *et al.* (1972) and Trost and Bisque (1972) with Hg(II), and by Trost and Bisque (1972) and Fang (1978) with metallic Hg vapor. Aomine and Inoue (1967) and Stuanes (1976) have given evidence showing that soils' mineral matter contributed little in the adsorption of Hg(II), while it was substantially involved in the adsorption of PMA (Aomine and Inoue, 1967). The same deduction may be made from the results of the present investigations.

In the Arusha and Dar es Salaam profiles, adsorption was not significantly correlated ( $P = 0.05$ ) with any of the soils' physico-chemical properties, despite significant differences in adsorption among horizons of each profile. This lack of significant correlation may strengthen the suggestion (Khalid *et al.*, 1977; Farrah and Pickering, 1978) that other reactions, like precipitation, may also be involved in Hg retention by soils, in addition to purely adsorption processes.

The substantial capacity for Hg retention by these profiles implies that these soils may be able to prevent leaching of Hg.

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