

A Study of the Mercury (II) Sorption and Transport with Oak Ridge Reservation Soil

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ABSTRACT

A series of batch and column laboratory experiments were conducted to determine adsorption coefficients of mercury (II) for Oak Ridge Reservation (ORR) soil. The experimental setup used soil collected from an area offsite of the ORR, in a location upstream of East Fork Poplar Creek (EFPC). The batch equilibrium experiments were conducted in the range of 600 to 5,000 $\mu\text{g/L}$ of initial Hg(II) concentrations at 5°C, 15°C, and 24°C. Adsorption data demonstrated the best fit to the Linear adsorption isotherms, with K_d values in the range of 541 (± 17) mL/g, at equilibrium solution concentrations below 0.025 mg/L of mercury. The effect of temperature was minor and inconclusive. This study indicated that the Linear adsorption isotherm adequately represents the adsorption of total mercury to ORR soils samples. Desorption experiments found that up to 5% of total mercury mass accumulated in soil can be potentially mobilized.

INTRODUCTION

Elemental mercury was released into East Fork Poplar Creek (EFPC) and White Oak Creek (WOC) watersheds as a result of discharges, spills, and accidents associated with the lithium-isotope separation process used in the production of nuclear fusion weapons during the mid-1950's and early 1960's. This soil stock of mercury, from various point and nonpoint sources at the DOE Y-12 plant and the Oak Ridge National Laboratory (ORNL) complex, is the main cause of contamination in the nearby streams [1, 2].

The Oak Ridge Environmental Information System (OREIS) database has documented extensive soil and groundwater contamination with mercury that exists throughout ORR. For instance, the analysis of grab soil samples obtained from a borehole near ORNL buildings 4501 and 4505 for the Bethel Valley Groundwater Engineering Study (May, 2004) documented total mercury (TM) concentrations ranging from 0.043 to 0.334 mg kg^{-1} at a depth of 0 to 4 m.

The initial release of mercury scavenged by soil accelerated the transformation process of less toxic inorganic mercury to organic methyl mercury (MeHg). The concentration of MeHg in soil is generally less than 2% of the TM; however, even in small concentrations, MeHg is highly toxic and tends to bioaccumulate in fish through the food chain. A wide variety of bacterial species ranging from anaerobes to aerobes can synthesize MeHg. Sulfate reducing bacteria have been reported to be important mediators of the biotic methylation process in aquatic systems [3, 4].

The discharge of inorganic mercury to water bodies coupled with an active biotic methylation processes in sediments and the ability of soluble mercury to be readily incorporated into organisms in the aquatic environment are believed to be the leading causes of exceeding the EPA MeHg concentration target of 0.3 mg/kg in fish tissue in the WOC [5,6]. In view of the high concentrations of mercury in soil and the potential health hazards associated with its release to the receiving streams, it is essential to expand the knowledge of mercury adsorption onto ORR soil.

Adsorption (i.e., adsorption and desorption) is a key physico-chemical process in the distribution of soluble mercury at solid-water interfaces (e.g., soils, rocks and sediments) that affects Hg transport in the subsurface [7]. The adsorption distribution coefficient, K_d , which describes the partitioning of a solute

between soil or sediment and water, is estimated as the ratio of the concentration adsorbed onto soil or sediment particles to that dissolved in soil water at equilibrium. The adsorptive properties of mercury depend on a variety of environmental factors such as pH, oxidation-reduction potential (ORP), presence of dissolved organic matter (DOM), and mineral colloids in the soil/groundwater environments [8]. Literature data on mercury adsorption behavior in soils varies significantly [9,10,11,12] with a few studies dealing with ORR soil composed of siltstone, sand, shale, clay and thinly bedded limestone, all predominantly low in organic carbon [13]. The average soil composition of the upper soil zone at the WOC area consists of 27-36% sand, 22-58% silt, and 15-42% clay [14], namely, silt loam, clay loam and loam textures.

In addition, testing of soil samples determined that maghemite and hematite are the major iron minerals, and that some clay and silt soils are heavily coated with iron and manganese oxides [15,16]. Mineral compositions of ORR soil, represented by silicate clay minerals, iron, aluminum, manganese oxide, quartz and soil organic carbon, are mostly responsible for the retention of cationic mercury via electrostatic forces and complexation [17,18,19,19]. Soil cation exchange capacity (CEC) mainly originates from clay minerals and is positively correlated with mercury adsorption since mineral surface exchangeable cations such as Ca^{+2} , Mg^{+2} , Na^{+} , and K^{+} can be replaced by ionic mercury [17]. However, the adsorption coefficients of inorganic mercury in soil with high organic content are generally higher than for minerals and metal oxides regardless of soil pH and texture [21].

The mobility of mercury is greatly reduced by adsorption onto solids in the subsurface. An alternative approach to estimate adsorption is based on tracer tests that are conducted in laboratory or field settings, which can yield retardation factors in the groundwater environment. Retardation is defined as the ratio of the contaminant's average linear velocity to groundwater average linear velocity. It is related to K_d by:

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (\text{Eq. 1})$$

Where R is the retardation factor, V_w is the groundwater velocity, V_c is the contaminant velocity, ρ_b is the bulk density (g/cm^3), and θ is the total porosity. For the ORR vadose zone, the ratio of ρ_b/θ varies between 5 to 10 g/cm^3 [14].

Seasonal temperature fluctuations are one of the environmental factors affecting mercury adsorption in soil. Previous studies at ORR have found year-round temperature fluctuations in the range of 12°C -24°C and 6°C -24°C for ground and surface waters, respectively.

The overall objective of this work was two-fold: a) to conduct batch-equilibrium experiments to evaluate isotherms representing the amount of Hg (II) adsorbed to ORR soil at various temperatures, and to assess the effect on Hg(II) adsorption; and b) to investigate the potential desorption of inorganic mercury adsorbed on soil in leachability tests. The development of mercury fate and transport numerical models, for the surface and subsurface domains, requires a definition of adsorption parameters measured at site-specific conditions.

MATERIALS AND METHODS

Experiments were conducted using surface soil (from a 0-15 cm depth) collected offsite of the ORR in a location upstream of EFPC (84°17'29.667" W, 36° 0' 3.467" N). The classification of the soil texture is defined to be eroded Collegedale clay and silt loam. Soil sample physicochemical properties are presented in Table I. Soil bulk density was determined to be about 1300 kg/m^3 in accordance with the Blake and Hartge method [22].

Table I. Sample Soil Physico-Chemical Properties

Parameters	Units	Values
pH		5.6
CEC	meq 100/g or Cmol/kg	29.1
Organic carbon	% (mg/g)	2.63 (26.3)
Total Sulfur	%	0.07
Bicarbonate alkalinity (HCO ₃ ⁻)	mg/kg	312.5
Aluminum	mg/kg	2027
Calcium	mg/kg	1005
Iron	mg/kg	5765
Manganese	mg/kg	355
Sulfate	mg/kg	162
Sand	%	28.8
Silt	%	43.7
Clay	%	27.5
Texture		Clay loam

Soil samples were air-dried and crushed to pass through a 1-mm sieve before being used in experiments. In all batch experiments, 1 g of air-dried soil was mixed with 2 mL mercury stock solution to achieve a soil/solution ratio of 0.5 g/mL. Six TM concentrations ranging from 600 µg/L to 5000 µg/L were prepared by diluting a 1000 mg/L Hg(NO₃)₂ stock solution with reverse osmosis (RO) pretreated tap water. All batch experiments were performed in triplicate using 12 mL vials tightly capped with Teflon PTFE-lined caps. The experiments were repeated twice resulting in 36 samples prepared for each temperature. A parallel no-soil control set was prepared in duplicate to determine initial TM for each concentration and mercury losses on vials caps and walls. Batch adsorption experiments were performed using a temperature controlled Benchtop Refrigerated Incubator Shaker (New Brunswick Scientific¹) at 150 rpm to evaluate the effect of temperature on Hg(II) adsorption. The effect of temperature on Hg(II) adsorption was tested at 5°C, 15°C, and 24°C. After shaking each set of vials for 24 h, the samples were then centrifuged at 2000 rpm for 15 min to allow the fluids to separate from the suspended solids. The supernatant fluids were then filtered through a 0.45 µm PTFE syringe filter to remove remaining suspended particulate. The weights of the water withdrawn and of the solid phase were measured. Experimental and control samples were preserved with 5% HNO₃, stored in a refrigerator at 5°C and then analyzed with a Total Mercury Analyzer DMA-80² per EPA Method 7473. Mass balance and recoveries were determined for each vial. The TM uptake by soil, S , was calculated through the mass balance equation:

$$S = \frac{C_0 - C_e}{m_s} V \quad (\text{Eq. 2})$$

Where C_0 and C_e are respectively the initial and equilibrium concentrations (mg/mL), V is the volume of solution (mL), and m_s is the experimental mass of soil (g).

Linear, Freundlich and Langmuir isotherms are the most commonly used equilibrium relationships to represent adsorption behavior at equilibrium in variety of disciplines [23, 24]. The simplest and most widely used relationship in environmental applications in water environments is the Linear isotherm,

¹ <http://www.nbsc.com/> visited 11.09.08

² <http://www.milestonesci.com/> visited 11.09.08

$$= \quad \quad \quad (Eq.3)$$

which yields

$$= - = \frac{\quad}{\quad} = (\quad) \quad \quad \quad (Eq.4)$$

where C_e is the dissolved concentration in solution at equilibrium, S is the weight of sorbate divided by the weight of sorbent (mg/g), and K_d is the distribution coefficient.

The Freundlich isotherm can be explained as being an empirical generalization of the Linear isotherm and is expressed as follows:

$$= \quad / \quad \quad \quad (Eq.5)$$

where K_f and $1/n$ are empirical constants. The linearized form of the Freundlich equation yields:

$$= \quad + (1/ \quad) \quad \quad \quad (Eq. 6)$$

The Langmuir isotherm equation describes the adsorption of gases onto clean solids and implies uniform adsorption on the saturated monolayer surface [7]. A basic assumption of the Langmuir theory is that adsorption occurs at specific homogenous sites of the sorbent and once a metal ion resides in a site, no further adsorption can take place [25]. The constants are characteristic of the Langmuir equation and can be determined from a linearized form of Eq. (7), as follows:

$$\frac{1}{S} = \frac{1}{S_{max}} + \frac{1}{C_e K_L S_{max}} \quad \quad \quad (Eq. 7).$$

where C_e is the equilibrium concentration (mg/mL), S is the amount of mercury ion adsorbed (mg/g), S_{max} is the S for a complete monolayer (mg/g), and K_L is the adsorption equilibrium constant (mg/mL). A linear plot of $1/S$ versus $1/C_e$ results in a straight line with a slope of $1/(K_L S_{max})$ and intercept of $1/S_{max}$ [26]:

$$- = \frac{\quad}{\quad} \times - + \frac{\quad}{\quad} \quad \quad \quad (Eq. 8)$$

The method of detection limit was calculated as 0.627 ng and verified using the five point check [28]. This value is higher than the detection limit of 0.02 ng Hg reported in the User Manual by the manufacturer of the DMA-80 Direct Mercury Analyzer [29].

Desorption experiments were also conducted with the purpose of determining the potential leachability of inorganic mercury accumulated in mercury preloaded soil. The leaching solutions were prepared with pH 4.93 and 2.88 according to EPA Test Method 1311 Toxicity Characteristic Leaching Procedures (TCLP).

RESULTS AND DISCUSSION

Batch Adsorption Experiments

The results from the adsorption experiments are illustrated in Figures 1, 2, and 3. Fig. 1 is a plot of the measured equilibrium concentrations, both adsorbed and in solution. This figure strongly suggests that linearity prevails in the equilibrium relationship between adsorbed and solution concentrations for the range of experimental initial concentrations, namely 600-5000 µg/L.

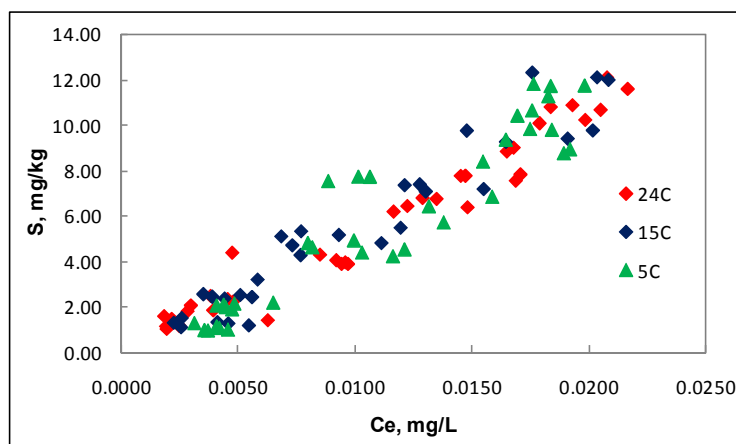


Fig. 1. Experimental results for both adsorbed and equilibrium concentrations for mercury in ORR Soil at 5, 15, and 20°C.

The curve fitting of batch experiments resulted in linear isotherms with R-square values ranging between 0.87-0.95 (Fig. 2). The calculated distribution coefficients (K_d) were between 522-554 mL/g. The determined K_d values were similar to those reported from batch equilibrium experiments for soils comparable in mineralogical composition, OM content and CEC [31,32]; however, obtained values were lower than previously reported for organic soils [33,34].

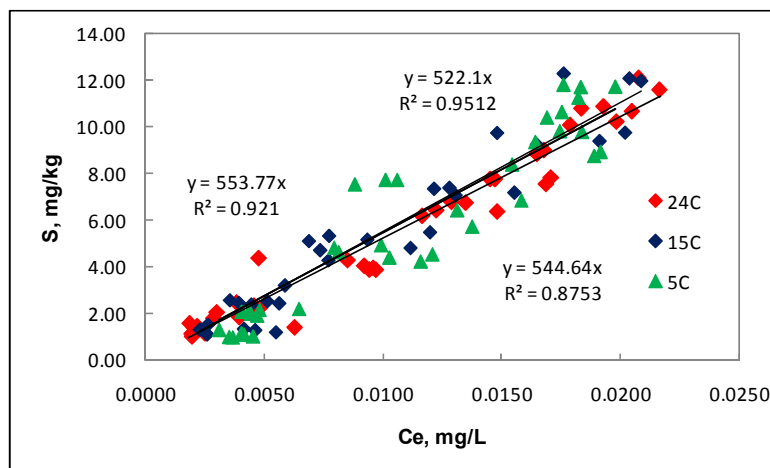


Fig. 2. Linear isotherms for mercury in ORR soil at 5°C, 15°C, and 20°C.

The calculated K_d values at equilibrium showed differences between 4% and 6% amongst the three test temperatures, namely 5°C, 15°C and 24°C; all the studied mercury solution concentrations were below 0.025 mg/L. A positive dependence of adsorption on temperature was observed in other adsorption studies of heavy metals [26,35]. However, the batch equilibrium experiments, hereby reported, confirmed that at low TM concentrations (<0.025 mg/L) in solution, the distribution coefficient, K_d , did not change significantly with a temperature increase from 5°C to 24°C. Furthermore, the Freundlich isotherm fitted the experimental data equally well, with exponents near 1 and indexes of determination as high as those calculated for the Linear isotherm. Because neither the Linear nor the Freundlich isotherms provide an estimate of the maximum adsorption capacity of the soil, S_{max} , the estimate was attempted to be obtained from a regression of the data with the Langmuir isotherm model. The adsorption data for 5°C, 15°C, and

24°C were then regressed for a linearized form of the Langmuir isotherm (Fig. 3). The regression results show very low indexes of determination for all temperatures, which reaffirm the Linear isotherm as the best relationship to represent the equilibrium behavior of mercury in the ORR environments based on the samples used in this study.

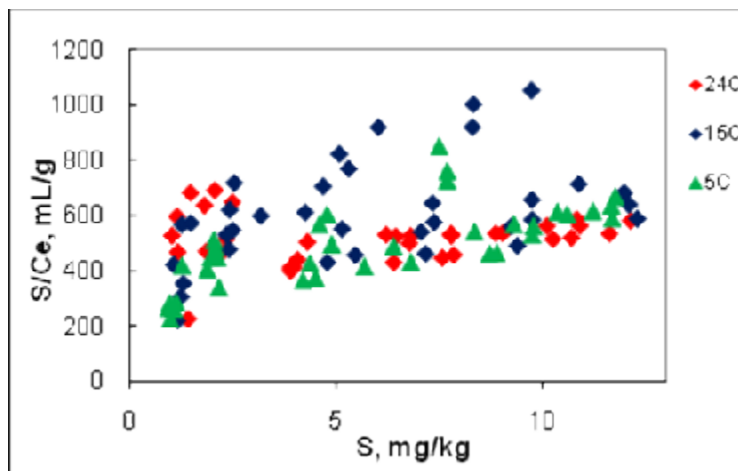


Fig. 3. Langmuir adsorption isotherms for mercury in ORR soil at 5°C, 15°C, and 20°C.

Table II summarizes the results from the regression analysis for the Linear, Freundlich, and Langmuir isotherm at the various temperatures. The agreement of the data with the Linear isotherm and the low correlation for the Langmuir is conclusive.

Table II. Results from the Regression of the Data to the Linear, Freundlich and Langmuir Isotherms.

Isotherm	T, C	K_d , L/g	K_f	1/n	K_L	S_{max}	R^2
Linear	5	544.6					0.88
	15	553.8					0.92
	24	522.1					0.95
Freundlich	5		1517.05	1.25			0.91
	15		867.56	1.08			0.86
	24		362.2	0.91			0.96
Langmuir	5				28.03	11.74	0.51
	15				22.16	21.6	0.2
	24				2.61	192.29	0.011

Desorption Experiments

Prior to the tests, appropriate leaching solutions, at pH values of 2.88 and 4.93, were prepared in accordance with EPA Method 1311. The pH of the slurry that formed after the mixing the solution with 5.0 g of air-dried soil and 96.5 mL of distilled-deionized water (DIW) was 8. After addition of 3.5 mL 1N HCl, the resulting pH reduced to 5.3. If the pH of the slurry is greater than 5.0, the suggested extraction fluid to determine mercury leaching should be at a pH of 2.88. This solution fluid was prepared by mixing 5.7 mL of glacial acetic acid with DIW to a volume of 1 liter. The leaching test procedure used 5.0 g of air-dried soil that had been previously subjected to a continuous influent mercury concentration of 5.0 mg/L to columns, reaching adsorbed concentrations of 550 to 720 µg/g. The mercury-adsorbed soil was then mixed with 100 mL of leaching solution at pH 2.88. Each test included duplicates that were rotated

for 24 hours. The filtered liquid material (extract) was next analyzed for TM. The soil-extracted (or recovered) TM mass was measured in the range of 3.7-4.9%. This low range of recovery represents a potentially mobile TM fraction of the adsorbed mercury in the ORR soil samples.

CONCLUSIONS

Sorption of mercury was studied in batch and continuous flow columns using ORR soil samples. The batch studies were conducted at 5°C, 15°C, and 24°C. The adsorption data of mercury fitted best to the Linear isotherm compared to the Langmuir isotherm. The Freundlich fitted comparably well to the Linear isotherm. The obtained K_d values for the studied temperature range vary within 524 and 558 mL/g, and showed a low difference within the temperature range of 5°C to 24°C, at the studied mercury solution concentrations (below 0.025 mg/L). Desorption experiments pointed out that up to 5% of TM mass accumulated in soil can be potentially re-mobilized under standard leaching test conditions.

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