

The role of organic carbon in facilitating mercury sorption and retention in the soil: Some field evidence from Oak Ridge, Tennessee- 10391

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ABSTRACT

Potential binding ability of mercury (Hg) to soil is an important aspect in selecting bioremediation technologies. Two studies were carried out to evaluate affinity of Hg to soil organic carbon. The first study was conducted with soil samples obtained from Hg-contaminated areas close to the Department of Energy Site at Oak Ridge, Tennessee. The soil samples were analyzed for total Hg and total organic carbon (TOC), and later tested for Hg desorption in aqueous phase. The second study was conducted using peat (*Sphagnum* moss) as a carbon source for sorption of Hg in the aqueous phase. The study was undertaken as a confirmatory test to understand the interaction of Hg with the organic carbon under controlled conditions. Both studies revealed higher degree of association of Hg with peat/soil organic carbon, for a given condition. The soil samples were found to contain higher concentrations of Hg with increasing percentages of TOC in the soil. The soils with TOC of 1.18% and 6.05% had total Hg concentrations of 0.92 and 436 parts per million (ppm), respectively. Furthermore, desorption of Hg from the contaminated soils was directly related to TOC content of the soil. The results revealed an inverse relationship between Hg desorption from the soil and the TOC content of the soil, thus indicating the role of soil organic carbon in binding and retaining Hg in the soil. In a similar way, Hg sorption on peat substrate increased with increasing concentrations of Hg in the aqueous phase, thus showing a high affinity of Hg towards organic carbon. The ratio of the initial to final concentrations of Hg in the aqueous phase was as high as 144.09 for the experiments conducted at 0.50 ppm aqueous Hg concentration. Such Hg-TOC relationships might have a significant impact on the bioavailability of Hg in soils, hence on the ability of microorganisms or plants to uptake, transform or mobilize Hg during remediation process.

INTRODUCTION

Mercury is a global pollutant that has serious health concern, mainly due to its ability to undergo biological transformation (into harmful forms), bioaccumulation and biomagnification through the ecological food chains [1]. In the past, two mass poisoning events took place; one in Minamata Bay in Japan during 1950s due to consumption of Hg contaminated fish, and the other in Iraq due to consumption of wheat grains treated with methyl Hg based fungicides during 1971–1972. The Hg contamination problem is still a concern in different parts of the world.

The Department of Energy (DOE) Y-12 Site is a manufacturing and developmental engineering facility at Oak Ridge that was built in 1943 as a part of the Manhattan Project. The site occupies approximately 800 acres on the northeast corner of the DOE Oak Ridge Reservation adjacent to the city of Oak Ridge, Tennessee. The original mission of the installation was electromagnetic separation of uranium isotopes and weapon components manufacturing as part of the national effort to produce the nuclear weapons. During 1950-63, tons of elemental mercury (Hg) were used in a column exchange process (Colex) for lithium-6 isotope separation and purification [2]. The accidental spills of Hg caused extensive contamination of the site and the nearby East Fork Poplar Creek (EFPC). Although several remedial measures were put in place to reduce the Hg contamination in the EFPC, recent studies indicate that the creek and its partial watershed area are still contaminated with Hg above the cleanup standard level [3, 4]. Given the fact that these areas receive on average 55.1 inches of rainfall and 11.1 inches of snow annually, the persistent nature of Hg in the Oak Ridge soil environment requires evaluation. The Hg binding ability of soil has been reported for various contaminated sites elsewhere [5, 6, 7]. In this context, two different studies were carried out to evaluate the affinity of Hg towards Oak Ridge soil. The first study was conducted with soil samples obtained from Hg-contaminated areas close to the DOE Site at Oak Ridge, Tennessee. These soil samples were analyzed for total Hg and total organic carbon (TOC) to determine a statistical relationship, and later were tested for Hg desorption in aqueous phase. The second study was conducted using peat (*Sphagnum* moss) as the organic carbon source for the sorption of Hg in aqueous phase to understand the role of organic carbon in retaining the soil Hg.

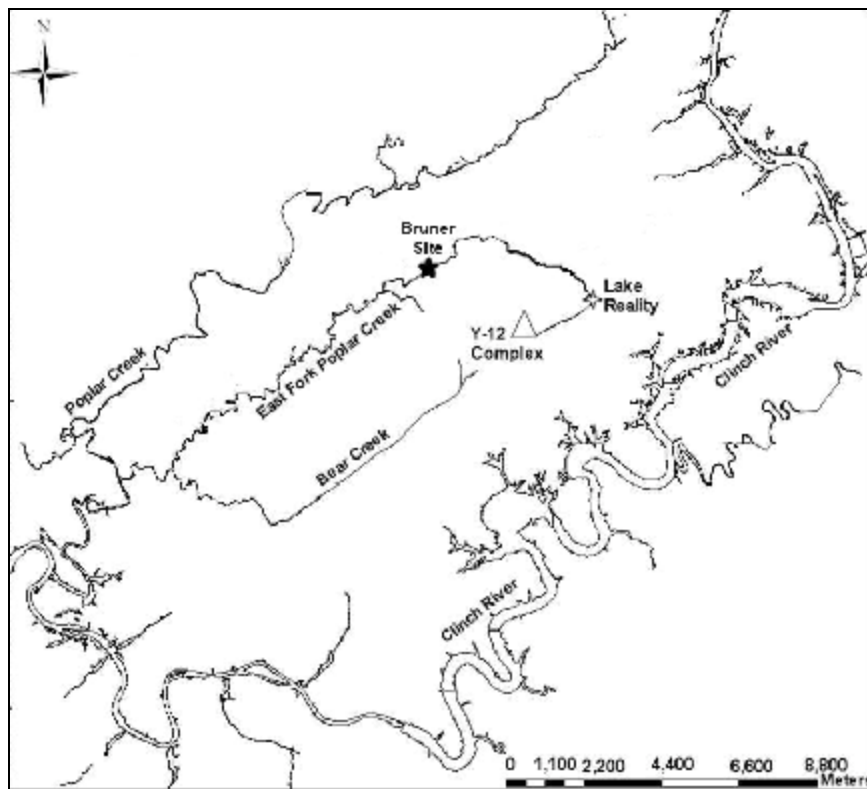


Fig. 1 Geographical location of the Bruner Site, which is located at a distance of 8.26-8.39 km from the Y-12 Complex (Hg source zone).

MATERIALS AND METHODS

The soil samples were obtained from the floodplain areas known as Bruner Site as shown in Fig. 1. The site is located at a distance of 8.26-8.39 km from the Y-12 Complex that has Hg point-sources including the headwater zone for the entire EFPC. This site was reported to have Hg contaminations that were well above the background levels [3, 8]. The soils were collected following a quadrat method. The method consisted of collecting 55 samples of top soils (10-15 cm thick in depth) from 11 quadrates of 5,000 sq. ft (464.52 m²) each. All the samples were placed in double-layered zip-lock bags and stored under dry ice refrigeration, and later shipped to the laboratory for experiments and analysis. For the adsorption studies, peat (*Sphagnum* moss) was obtained from a local commercial source (Home Depot).

For the Hg leaching experiments, the soils samples were air dried and screened through 2 mm sieve. From the sieved soil sample, 1 gram was placed in 40 mL glass vials and 20 mL deionized water was added to each vial. The vials were tightly capped and placed on a magnetic shaker for a continuous 48 hours agitation. The vials were centrifuged to separate solid and liquid phases. The aqueous phase was decanted, filtered through PTFE syringe filter (0.4 μm), and analyzed for total Hg.

For the adsorption studies, five sets 40 mL vials were prepared in triplicates with 0.1 gm sterilized (autoclaved) peat and 20 mL deionized water. The vials were capped and placed on a magnetic shaker (100 rpm) for 24 hours to homogenize the mixture. To each set, a different concentration of Hg (0.5, 1, 4, 8, and 16 mg/liter) was added. Each concentration was run in triplicate for a total of 15 vials (5 x 3 = 15). The vials were placed on a magnetic shaker at 100 rpm for the 24 hours experiment. Later, the experimental vials were centrifuged and the aqueous phase analyzed for Hg.

Total Hg was analyzed using Milestone Model DM-80 Direct Mercury Analyzer, following EPA method 7473. Briefly, a known amount of homogenized sample was placed in a nickel boat, which was then placed on a tray of the auto-sampler. The samples were analyzed in triplicate, and the results were averaged for each sample. Total carbon (TC) content of the soil as well as peat was analyzed using TOC Infrared Analyzer (Shimadzu- TOC-VCSH) attached to solid sample process module (Shimadzu-SSM-5000A), following EPA Test Method 9060. As inorganic carbon (IC) was found to be very low compared to TC in the soils, TC was taken to be equivalent to total organic carbon (TOC). Statistical analysis of analytical data was done using statistical software packages (SPSS 14.0).

RESULTS AND DISCUSSIONS

Fig. 2 presents the THg concentrations and the TC contents in the soil samples that were collected at the Bruner Site. It should be noted that the higher levels of Hg were associated with the soil samples with higher TC content. The average Hg concentration and carbon content for S8 samples was 45.10 mg/kg and 2.91%, respectively. Similarly, for the S7 samples, the average Hg and TC values were 35.98 mg/kg and 2.71%, respectively. The TC observed for soil samples taken from S1 and S2 was less, and coincided with reduced Hg concentrations. The average Hg

concentration for S1 soil samples was 0.92 mg/kg and the corresponding TC was 1.18%. A similar trend was observed for S2 soil samples having Hg concentration of 2.17 mg/kg and an average TC content of 1.0 %. Similarly, the mean and standard deviation were 24.00 mg/kg and 23.00 mg/kg, respectively, for soil Hg concentrations in the 11 quadrates. The mean for the % TC was found to be 2.27%, with a standard deviation of 0.89% for all the above quadrates.

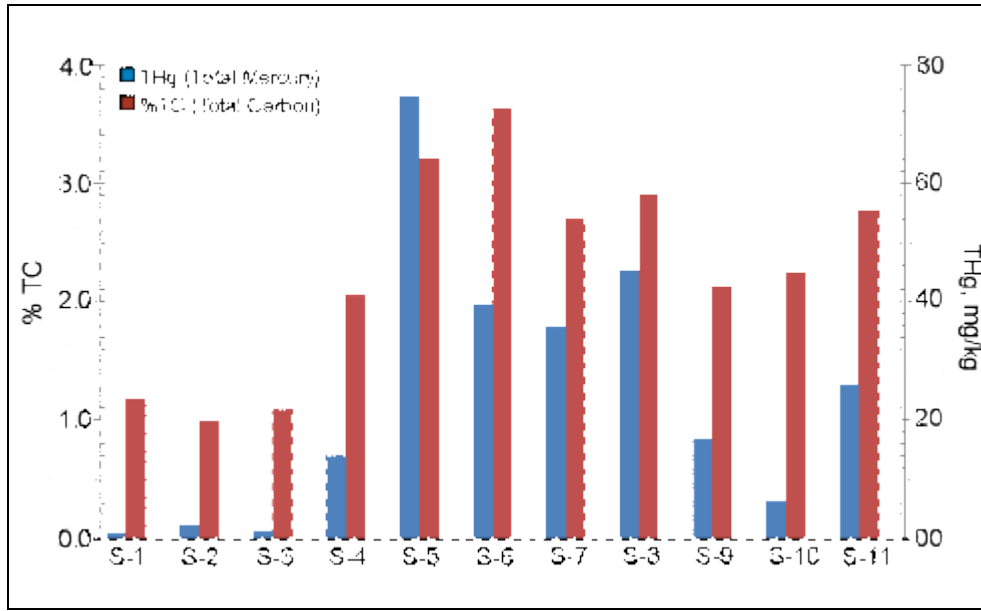


Fig. 2 Soil mercury concentrations and total carbon content for each quadrate (Labeled S1-S11)

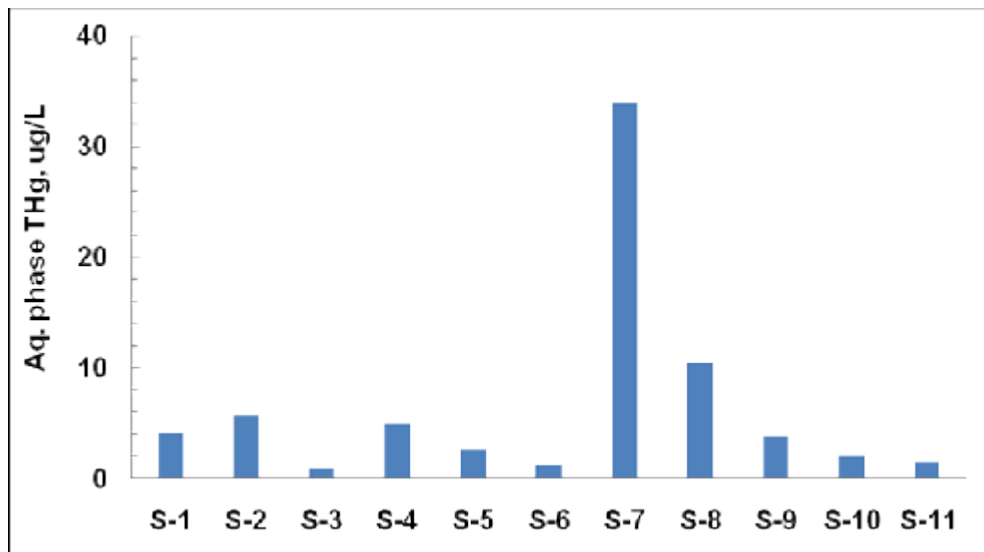


Fig. 3 Aqueous THg concentrations (average) for the leaching experiments conducted on the soils from each quadrate, S1-S11

The mean for the percent leachable Hg for all the quadrants (n = 11) was 3.13%, with a standard deviation of 5.73%. The correlation between the TC percentage in the soils and percent leachable Hg from the same soils was -0.61, which was significant (p < 0.05). However, no significant correlation was observed between the THg concentrations in the soils and percent leachable soil-Hg. The aqueous phase THg concentrations in the soil samples collected from different quadrates are presented in Fig. 3. The low leachable fraction of soil Hg in Oak Ridge soils may be attributed to the complexation of Hg with the soil organics. The transformation of Hg into various other forms, including organic matter bound Hg (>50%) has been reported by Leu et al [3] for some of the soils from Oak Ridge. They have reported 1.87-7.33% of THg as water soluble fractions in these soils, which very well accommodate the value (3.13%) that was obtained in our study.

Results from the sorption study are summarized in Table 1. As the concentration of Hg increased, sorption of Hg onto peat increased. This trend is best seen as a simple linear sorption isotherm constructed from the experimental data in Fig. 4. The ratio of the initial to final concentration of Hg in the aqueous phase was as high as 144.09 for the experiments conducted at the lower Hg concentration (0.5 mg/L). This ratio declined progressively with increasing Hg concentration and was attributed to an increased competition of Hg for peat sorption sites. Nonetheless, peat showed a high sorption capacity for Hg. The greater affinity for Hg sorption is due to the organic carbon fraction (f_{oc}) in the peat substrate; the major organic constituents being lignin and cellulose [9]. Chen et al. [10] reported that as f_{oc} increased, sorption also increased for a given contaminant and that the amount of sorption onto peat was as a result of ion exchange and complexation. The peat had 44% TC. The TC value was the same for all the experiments, since a uniform amount (0.1 g) of peat was used in all the experiments.

Table I. Results from the batch adsorption experiments

Initial aqueous Hg concentration (mg/L)	0.50	1.00	4.00	8.00	16.00
Final aqueous Hg concentration (mg/L)	3.47×10^{-3}	0.02	0.49	1.95	3.79
Solid phase Hg (mg/g)	0.20	0.39	1.40	2.42	4.88
Initial Hg / Final Hg in aqueous phase (ratio)	144.09	50.00	8.16	4.10	4.22

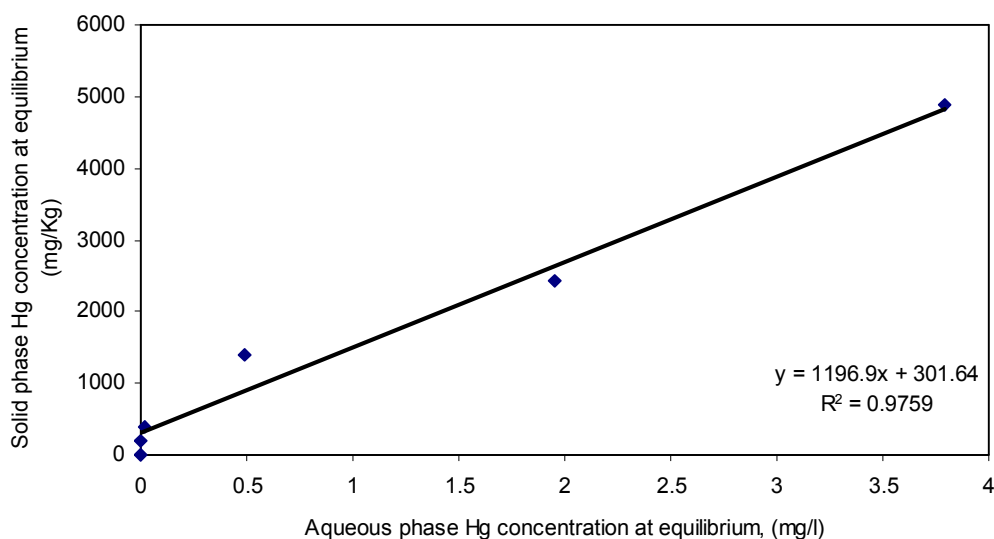


Fig. 4 Linear sorption isotherm for Hg and peat

CONCLUSIONS

It was found that the leaching of Hg from the contaminated soils was directly related to the organic carbon content of the soil. Study results showed an inverse relationship between Hg leaching and soil organic carbon (measured as total carbon). This suggests that bioavailability of Hg is controlled by the organic content of the soil. The degree of Hg leaching from the soil is also an important factor to consider in Hg uptake by plants. The greater the Hg leaching the more Hg that will be available for plants to take up. This is also an important factor that must be considered in understanding the movement of Hg in any contaminated site. In organic rich soils, Hg retention will be high, and in areas of low organic content and high rainfall, Hg mobility can be relatively high. Often, the mobile fraction of Hg is related to the bioavailable Hg in the soil. Sorption experiments also showed that Hg had a high affinity for peat which represents the organic matter in the soil.

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