Interaction of Soil and Mercury as a Function of Soil Organic Carbon: Some Field Evidence

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Mercury (Hg) contamination of soil is a potential threat to human as well as environmental health. In the past, two major episodes of mass poisoning were related to consumption of Hg contaminated fish in Minmata Bay in Japan during 1950s and consumption of wheat grains treated with methyl Hg based fungicides in Iraq in 1971–1972. Recently, no such major incident has been reported, however, the Hg contamination problem persists globally, and so also the threat. Oak Ridge in Tennessee (USA) is one such place with a significant Hg contamination problem. During 1950–1963, tons of elemental Hg were used in a column exchange process (Colex) for ^{6}Li isotope separation and purification (Hollerman et al. 1999) The accidental spills of Hg and other chemicals caused extensive contamination of the site; as a result it was included in the US EPA's National Priorities List of Superfund Sites in 1989.

In this study, we examine the extent of Hg contamination in a selected site at Oak Ridge to determine if there is any trend in Hg contamination of soil with respect to soil organic carbon distribution. This information will assist in understanding Hg mobility and bioavailability in the area concerned.

Materials and Methods

The study site known as the Bruner Site is a floodplain area along the Lower East Fork Poplar Creek (LEFPC) at Oak Ridge, TN, and offsite from the Y-12 Site of the Depart-

ment of Energy (DOE) Oak Ridge Reservation. The LEFPC originates within the boundary of the DOE, meanders offsite for most of its length, and then ends in confluence with the Poplar Creek. The LEFPC was the major Hg carrier that contaminated the floodplain and other riparian areas. This study was done in 2004, and the details of the sampling locations are shown in Fig. 1.

In order to collect soil samples, 11 quadrates of 5,000 sq. ft (464.52 m^2) each were laid down at the Bruner site. This included areas of flood plain on either side of the stream, as well as areas that differed in vegetation cover
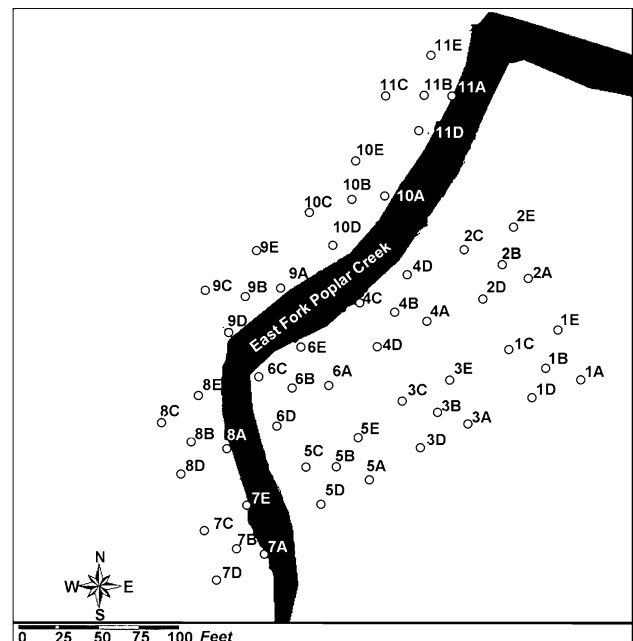
Fig. 1 Map of sampling locations at the Bruner site, Oak Ridge (1–11 represent quadrate numbers).

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(trees vs. grass). Within each quadrate the top soil (10–15 cm) was sampled with an auger from five different spots (n = 5) along the diagonals of the quadrate at 25 ft intervals (Fig. 1). The samples from the perimeter of the quadrates were excluded in order to avoid duplication with the adjacent quadrates, which had common boundaries. From the 11 quadrates, a total of 55 samples were collected (only 54 analyzed). The samples were stored under dry ice refrigeration, and later shipped to the respective laboratories for analysis.

The soil samples were separately homogenized and divided into two portions. One of the portions was used in Hg analysis and reported on a wet weight basis. The other one was utilized in determining moisture content, pH, and soil total organic carbon (TOC). Total Hg (THg) was analyzed using a Milestone Model DM-80 Direct Mercury Analyzer, following EPA method 7473. Briefly, a known amount of homogenized soil 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. The samples from the center of each quadrate (labeled B) were also analyzed for Methyl Hg (MeHg) using CV-GC-AFS (FGS-070) following EPA 1630 method. TOC was analyzed in TOC Infrared Analyzer (Shimadzu). Other parameters, such as moisture content and pH were determined through routine laboratory procedures. Statistical analysis of analytical data was done using a software package (SPSS 13.0).

Results and Discussion

The THg concentrations in soil samples differed significantly within the study site compared to TOC (Table 1), as indicated by the plots in Figs. 2 and 3. The concentration of Hg ranged from 0.11 to 103.26 mg/kg (n = 54) with a mean of 24.31 ± 3.47 mg/kg (mean ± 1 standard error throughout this study). As shown in Table 1, the mean Hg concentrations in each of the six grassy quadrates (Q1–Q4, Q10 and Q11) were 0.92 ± 0.45, 2.17 ± 0.57, 1.34 ± 0.77, 13.90 ± 7.73, 6.37 ± 1.5, and 26.02 ± 5.73 mg/kg, respectively. For the same quadrates, the soil organic carbon (%f_{oc}) was 1.24% ± 0.11%, 1.00% ± 0.14%, 1.09% ± 0.26%, 2.06% ± 0.74%, 2.25% ± 0.27%, and 2.82% ± 0.35%, respectively. The Hg concentrations and soil organic carbon increased significantly in the case of quadrates Q5 through Q9, which had forest cover. The mean Hg concentrations were 74.64 ± 8.52, 39.55 ± 8.46, 35.99 ± 7.15, 45.10 ± 7.84, and 16.70 ± 6.84 mg/kg, and f_{oc} was 3.21% ± 0.22%, 3.63% ± 0.32%, 2.71% ± 0.38%, 2.91% ± 0.31%, and 2.13% ± 0.38%, for Q5–Q9 quadrates, respectively. The t test, $t(52) = 6.43$, $p < 0.001$, showed a significant difference for mean mercury concentrations between the grassy and forested quadrates. The mean Hg concentrations were 42.40 ± 4.98 and 8.71 ± 2.30 mg/kg for the areas under trees and grasses, respectively. Since the data was skewed (skewness = 1.03), a Mann–Whitney U test was also performed, giving $z = 5.00$, $p < 0.001$, which supported the results from the t test. Similarly, the mean f_{oc} was higher for the quadrates with trees (2.92% ± 0.17%) than for the grassy ones (1.76% ± 0.19%). The t test was significant, $t(52) = 4.45$, $p < 0.001$. The Mann–Whitney U test gave $z = 4.00$, $p < 0.001$, similar to the results from the t test. Our findings on f_{oc} differed from that of Marland et al. (2004) who have reported soil carbon in 0–20 cm depth to be higher for pasture (~3 kg/m^2) than in forest (~2 kg/m^2) in the Oak Ridge Reservation. The deviation in our results

Table 1 Summary statistics of the data for soil total Hg (THg, μg/kg), methyl Hg (MeHg, μg/kg), organic carbon (f_{oc}%), and pH

Quadrates	n	Min.	Median	Mean	Max.	SD	Skew
Grasses							
THg	29	105.53	3905.91	8713.54	43649.64	12401.36	1.93
MeHg	6	0.38	0.89	2.27	9.41	3.53	2.36
f_{oc}	29	0.34	1.49	1.76	4.95	1.04	1.35
pH	29	5.40	7.21	7.02	7.97	0.79	–0.56
Trees							
THg	25	976.79	38423.53	42395.22	103255.40	24877.31	0.39
MeHg	5	1.41	9.33	7.82	11.60	3.94	–1.36
f_{oc}	25	1.03	2.92	2.92	4.55	0.84	–0.27
pH	25	6.49	7.61	7.54	7.93	0.26	–2.75
All							
THg	54	105.53	12836.22	24306.91	103255.40	25473.06	1.03
MeHg	11	0.38	1.63	4.79	11.60	4.56	0.36
f_{oc}	54	0.34	2.29	2.30	4.95	1.11	0.30
pH	54	5.40	7.53	7.27	7.97	0.65	–1.35

Normal Q-Q Plot of total Hg

Normal Q-Q Plot for Organic Carbon
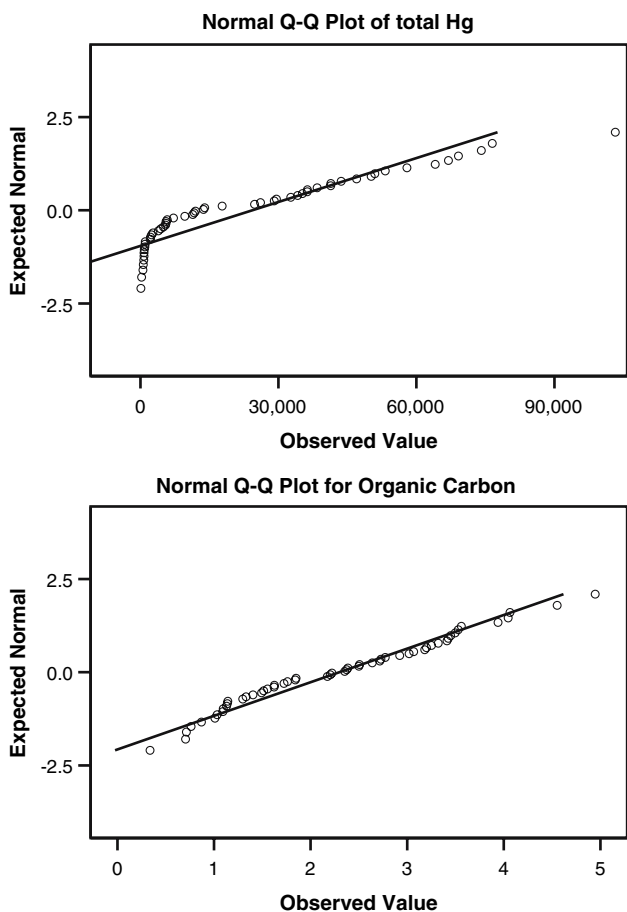
Fig. 2 Normal probability plots for data on total Hg (μg/kg) and % organic carbon in the soils studied (n = 54)
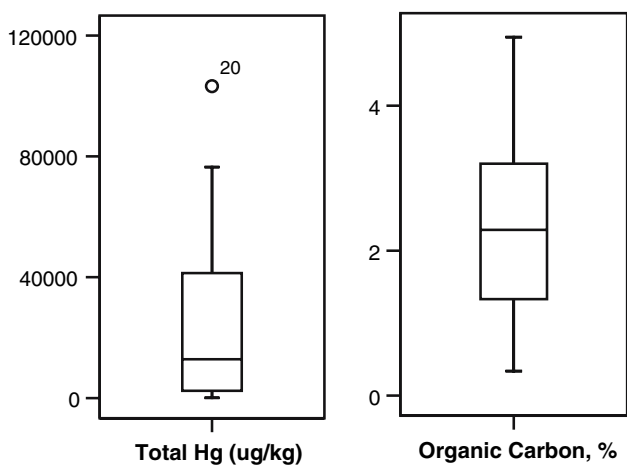
Fig. 3 Box plots for the data on total Hg (μg/kg) and soil organic carbon (f_{oc}%) for all the samples (n = 54)

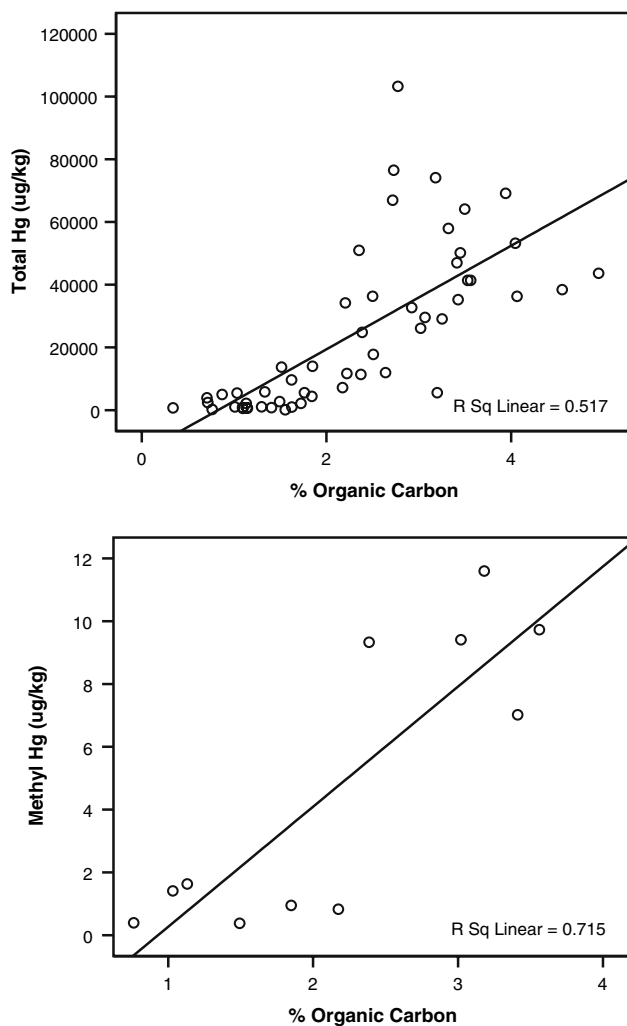could be due to the fact that the grass in our case is not maintained naturally, but from time to time is mowed.

The mean MeHg concentration was 4.79 ± 1.38 μg/kg (n = 11). The minimum and maximum values were 0.38 and

Table 2 Pearson correlations among total Hg (THg, μg/kg), Methyl Hg (MeHg, μg/kg), and organic carbon (f_{oc}%) in the soil

Quadrates/all				Quadrates/grass		Quadrates/trees	
	THg	MeHg	f_{oc}	THg	f_{oc}	THg	f_{oc}
THg	1.000	0.863**	0.719**	1.000	0.874**	1.000	0.474*
MeHg		1.000	0.846**				
f_{oc}			1.000		1.000		1.000

Significance at 5% level and 1% level are indicated with "*" and "**" respectively

11.60 μg/kg, respectively (Table 1). The MeHg concentrations were significantly high in the case of forested areas compared to grasslands. The mean MeHg concentration for the forested area was 7.82 ± 1.76 μg/kg, and that for the areas under grass cover was 2.26 ± 1.44 μg/kg. The lowest concentration, 1.41 μg/kg in the case of forested areas, and the highest concentration, 9.41 μg/kg in the case of grassy areas were the extreme outliers that caused greater degrees of skewness and standard deviations in the data. As discussed earlier, the forested area was also characterized by higher organic carbon content. This can influence both microbial activities and retention of MeHg in the soil. In fact, the correlation between MeHg and f_{oc} was found significant ($p < 0.01$) as shown in Table 2. Correlation scatter plots for THg, MeHg and f_{oc} in Fig. 4 show a positive trend, indicating increase in THg and MeHg concentrations with increasing f_{oc} in the soil. Similar findings have been reported earlier for different study sites (Palmieri et al. 2006; Shi et al. 2005; Cai et al. 1999; Rae and Aston 1982). It is known that soil organic carbon enhances the capacity of the soil to bind metals (Bolt and Bruggenwert 1976). The correlation between THg and f_{oc} was significant ($r = 0.719$, $p < 0.001$) for all the quadrates studied (Table 2). However, the correlation between the THg and f_{oc} in case of grassy quadrates (Q1–Q4, Q10 and Q11) was better ($r = 0.874$, $p < 0.01$) compared to the quadrates that were dominated with trees and shrubs ($r = 0.474$, $p < 0.05$). As discussed earlier, the standard deviations in THg concentrations was more than double for the forested areas than for the grasslands, indicating more variability in Hg concentrations under forest cover. Tack et al. (2005) have reported that mercury contents in soils with high organic carbon contents vary over a wider range than those in soils with lower organic carbon contents. In our case, the forested areas contained nearly 40% higher organic carbon than the grassy areas, which might explain the difference in correlation coefficients as stated above. It is known that leaf litters and other organic debris contribute more carbon to the soil under tree stands. Wu et al. (2004) also reported large amounts of plant debris in the top soil developed under forest compared to grassland. Further, they reported greater light fractions of organic carbon in the soil under forest cover. The light fraction is a readily decom-

posable substrate for soil microorganisms, which in our case may have influenced the Hg/TOC ratio in soils under forest cover, giving a lower coefficient of correlation.

Fig. 4 Correlation scatter plots for the data on total Hg and organic carbon, n = 54, and methyl Hg and organic carbon, n = 11

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