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**INVESTIGATION OF ANOMALOUS BIOAVAILABILITY OF MERCURY IN
LEFPC FLOODPLAIN SOILS**

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BACKGROUND

An initial bioavailability study was conducted to measure the bioavailability of mercury in LEFPC soil in early 1994 (Barnett and Turner, 1995; Department of Energy, 1994a). Twenty soil samples were taken from the floodplain from a variety of locations and leached by a procedure designed to simulate a child's digestive tract, the critical pathway for human health risk from mercury in the floodplain. The study indicated that the bioavailability (the percentage of mercury released by leaching during the procedure) was low, with an average of approximately 5%. This study was critical in the recommendation to include a bioavailability factor (other than the default value of 100%) in calculating the remediation goal option (RGO), and in raising the RGO from 50 to 180 ppm.

Although the average bioavailability of mercury in LEFPC was low, one soil leached an unusually high percentage of mercury. This soil, designated sample ZN3210127, leached 46% of the mercury, compared to 14% for the next highest soil, with only five others leaching greater than 5%. The only unusual circumstance noted about this soil was it was the only soil of the twenty which had detectable levels of mercury vapor in the headspace of the sample container, and it was the most upstream sample, taken at N-32156, E-00 (survey locations refer to the designation from the RI report (Department of Energy, 1994b)), approximately 15 m below where the creek passes under the Y-12 Plant north perimeter guard road.

PURPOSE

The purpose of this report is to describe a scoping study of the bioavailability of mercury in soils near this site in the floodplain of the upper part of the creek to determine if the sample from the original study was in error (e.g. contaminated during sampling or analysis) or if the area itself was unusual. Upper part of the creek in the context of this report refers to the creek where it passes under Bear Creek Road to approximately the NOAA site. A secondary purpose of this study was to compare the results of mercury analysis in soils and water from standard methodologies with results obtained by a rapid field method (Kriger and Turner, 1995) which has been proposed for use during remediation.

APPROACH AND METHODS

On February 20, 1995, samples were taken from ten locations in the floodplain of the upper area of the creek. The sample locations are described in Table 1. Jacobs Engineering surveyed the location of these samples as part of another sampling effort (Jacobs, 1995). Unlike the RI sampling effort along the creek, these samples were "biased" in that depth horizons of the soil which were suspected to contain the highest concentrations of mercury were sampled, rather than taking composite samples over a given depth (e.g. 0 - 16 inches) in the soil. Such biased sampling was also employed

Table 1 Location of Samples

Sample	Location
BA-1	N-32156 W-00
BA-2	Approx. 3 m downstream from BA-1
BA-3	Approx. 10 m downstream from BA-1
BA-4	Approx. 15 m downstream of BA-1, approx. 2 m from the creek
BA-5	In bank between carwash and dentist's office
BA-6	Approx. 10 m upstream of BA-1, approx. 5 m below guard road
BA-7	Approx. 30 m upstream of N-30844 W-00 on opposite bank
BA-8	Approx. 2 m away from the creek from BA-7
BA-9	Approx. 7 m upstream of N-30844 W-00
BA-10	Approx. 27 m downstream of N-30844 W-00
BA-11	N-33468 E-02
BA-12	Approx. 10 m north of monitoring well An:E-2

1. Survey locations refer to the designation from the RI report (Department of Energy, 1994b)

during the original bioavailability study (Barnett and Turner, 1995). A Jerome Model 431-X mercury vapor analyzer was used to measure any detectable ($> 1 \mu\text{g}/\text{m}^3$) levels of mercury in the in situ soil gas phase and in the headspace above the samples. The samples were collected in clean glass jars, transported back to the laboratory, homogenized, and refrigerated. The soils were processed on February 21 and 22, 1995 through the pH 2.5 leaching portion of the original bioavailability study (Barnett and Turner, 1995), and both solid and leachate mercury were analyzed with by rapid field method (Kriger and Turner, 1995). The original bioavailability study consisted of an additional leaching at pH 6.5, which was not performed for this study. However, the bioavailable mercury at pH 2.5 is generally a good indicator of the total bioavailability, since the majority of the samples in the first study leached more mercury at pH 2.5 than at pH 6.5. The bioavailable mercury was estimated as twice the mercury leached at pH 2.5, a conservative assumption for most samples in the original study. Subsequently, two more samples were taken from the creek (locations also described in Table 1), and, along with five of the first ten samples, leached in a similar manner. The leachates from this batch and all twelve of the soils samples were submitted to the Y-12 Plant analytical laboratory for mercury analysis by SW-846 Method 7470 and 7471 for comparison with the values determined in the rapid field method.

RESULTS AND DISCUSSION

The results of the solid and leachate concentrations obtained using the rapid field method and SW-846 methods are shown in Table 2. A comparison of the results indicates the potential for utilizing the rapid field method during remediation. The agreement between the rapid field method and SW-846 results for soil mercury concentrations was excellent. Four of the ten samples had exactly the same values, and nine of the ten agreed within 10%. The leachate samples also showed good agreement, four of the five agreeing within 25%. The fairly large relative error of the fifth leachate sample was a result of the relatively low concentration of the sample. The agreement of the results between the rapid field method and SW-846 is even better considering the notorious problems of mercury variability in natural materials, and the fact that the rapid field method and SW-846 measurements were made on different sub-samples and thus incorporated sub-sample variability as well as analytical variability. The rapid field method was also much faster and less expensive; the rapid field method results were obtained in a matter of hours, while the samples submitted to the Y-12 Plant laboratory cost $> \$100/\text{sample}$ and the results were not available for at least two weeks.

As shown in Table 2, it should be noted that eight of the ten soils from the upper part of the creek had concentrations in excess of the currently proposed LEFPC RGO of 400 ppm. However, the mapping of soils for remediation was based on depth-composited (sixteen inch cores) samples, rather than the discrete samples collected in this study.

The bioavailability results are shown in Table 3. Sample BA-1 is from the same location as sample ZN3210127 from the original study. ZN3210127 leached 29% of its mercury at pH 2.5, and BA-1 leached 33 - 35%. This is remarkable agreement, and

Table 2 Solid and Leachate Concentrations - Field and SW-846 Results

Sample	Field Hg Solid (mg/kg)	SW-846 Hg Solid (mg/kg)	Difference (%)	Field Hg Leachate (ug/l)	SW-846 Hg Leachate (ug/l)	Difference (%)
BA1	2500	2500	0.0	660	630	4.8
BA2	620	570	8.8	46	-	-
BA3	920	790	16	71	94	-25
BA4	200	220	-9.1	12	-	-
BA5	510	550	-7.3	0.73	0.62	18
BA6	1300	1300	0.0	230	-	-
BA7	1800	1800	0.0	510	410	24
BA8	250	250	0.0	15	9	67
BA9	550	520	5.8	28	-	-
BA10	1000	980	2.0	160	-	-
BA11	-	2700	-	-	210	-
BA12	-	1700	-	-	280	-

Table 3 Results of Second Bioavailability Study

Sample	Field % Leached	SW-846 % Leached
BA1	33	35
BA2	11	-
BA3	11	13
BA4	7.2	-
BA5	0.2	0.2
BA6	21	-
BA7	27	28
BA8	6.2	4.9
BA9	4.8	-
BA10	17	-
BA11	-	11
BA12	-	23

clearly illustrates the sample from the original study was not the result of sampling or analytical errors. In addition, the average mercury leached from the ten soils from the upper part of the creek at pH 2.5 was 14% compared to only 3% from the original study which included samples from the entire length of the creek. Six of the ten samples had higher leachable mercury than nineteen of the twenty samples from the original study. Sample BA-11 is from the same location as sample ZN3340223 in the original study, between NOAA and the Ford dealer. ZN3340223 leached approximately 5% at pH 2.5, and BA-11 leached 10%. Sample BA-12, just upstream (behind the Ford dealer), leached 22%. The leaching results and the detection of mercury in the soil vapor as well as in the headspace above several of the soil suggests the mercury in the upper part of the creek is biogeochemically different than the mercury in the lower part of the creek. This difference is manifested in mercury volatility and water solubility and would probably also be manifested in bioavailability as well. The reason for the difference is unknown beyond speculation at this point. It's also interesting to note that the leachability is somewhat sporadic. For example, BA-1 leached 33% while samples BA-2, 3 and 4 located within 15 m downstream leached at most 12%.

CONCLUSIONS

1. The mercury in the floodplain soils in the upper reaches of the creek is more volatile, soluble and potentially more bioavailable than in the lower reaches of the creek.
2. There are discrete concentrations of mercury in the upper floodplain in excess of the proposed RGO of 400 ppm. The concentration of mercury in sixteen inch composite samples from the sampled sites, however, are unknown, and may not exceed 400 ppm.
3. The results of water and soil mercury analysis obtained with the rapid field method are comparable with results obtained by standard methodologies.

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