

**FINAL REPORT
INCLUDES APPENDIXES A AND B**

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MARKS

**REMEDIAL DESIGN DETAILS -
ADDENDUM 2**

**MERCURY TREATABILITY STUDY
RESULTS**

**SUBUNIT 2A, MEADE STREET
OPERABLE UNIT**

**RICHMOND FIELD STATION,
RICHMOND, CALIFORNIA**

**(TASKS 2D AND 3D, RWQCB ORDER NO. 01-
102)**

Prepared for
University of California Berkeley
Capital Projects
1936 University Ave, 2nd Floor
Berkeley, California 94720-1380

November 6, 2002

URS

URS Corporation
500 12th Street, Suite 200
Oakland, CA 94607

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Mr. Cecilio Felix
November 6, 2002
Page 1 of 11

November 6, 2002

Mr. Cecilio Felix
Associate Engineering Geologist
California Regional Water Quality Control Board
San Francisco Bay Region
1515 Clay Street, Suite 1400
Oakland, CA 94612

Subject: Addendum to the Remedial Design Details for Subunit 2A, Meade Street Operable Unit, University of California, Richmond Field Station, Richmond, California. Results of the Mercury Treatability Study.

Dear Mr. Felix:

URS Corporation (URS), on behalf of the University of California Berkeley (UC Berkeley), has prepared this second addendum to Zeneca, Inc.'s report titled "Remedial Design Details, Meade Street Operable Unit" (RDDR), prepared by Levine Fricke (LFR) and submitted to the California Regional Water Quality Control Board (RWQCB) on January 31, 2002. The RDDR discusses activities to remediate Subunits 1 and 2A of the Meade Street Operable Unit designated in Order Nos. 01-101 and 01-102, respectively. This addendum follows a previous addendum to the RDDR titled "Remedial Design Details – Addendum, Subunit 2A, Meade Street Operable Unit" (RDDR Addendum A) prepared by URS Corporation on August 16, 2002. The RDDR and RDDR Addendum A were submitted to comply with Order 01-102, Task 2d for the upland portion of Subunit 2A and Task 3d for the marsh portion of Subunit 2A. This addendum (Addendum B) provides supplemental information on the results of a treatability study performed for sediment and cinders containing elevated concentrations of mercury at the RFS site.

Zeneca and UC Berkeley own Subunits 1 and 2A, respectively, of the Meade Street Operable Unit. Zeneca is responsible for the remediation of Subunit 1 and Zeneca and UC Berkeley are jointly responsible for the remediation of Subunit 2A. Subunit 2A consists of the southern portion of the upland property and the eastern portion of Western Stege Marsh located directly south of the RFS upland area. The location of the RFS is shown on Figure 1 and the locations and boundaries of Subunits 2A and 2B are shown on Figure 2.

As part of the remediation required under Order 01-102, an excavation plan for Subunit 2A was developed and presented in the RDDR Addendum A. Under the proposed excavation plan, a top layer of clean fill will be excavated, stockpiled, and reused as backfill following the excavation of underlying materials. Portions of the cinders and sediment containing less than 50 mg/kg mercury will be excavated and transported to the Zeneca site, treated as described in the RDDR, placed along with cinders from Subunit 1, and capped. Portions of the cinders and sediment

containing between 50 mg/kg and 260 mg/kg mercury will be excavated, treated to stabilize the mercury on the RFS site, treated as described in RDDR Addendum A, and transported to the Zeneca site to be placed with treated cinders. Finally, portions of the cinders and sediment containing greater than 260 mg/kg mercury will be excavated, solidified to reduce water content and leachability of metals on the RFS site, and transported to a Class I landfill for disposal as a California Hazardous Waste.

When the RDDR Addendum A was submitted, URS was conducting a treatability study to select the particular reagent that will most effectively stabilize the mercury in sediment and cinder containing levels of mercury between 50 mg/kg and 260 mg/kg. Since the submittal of RDDR Addendum A, URS has completed the treatability study. This treatability study report presents the results of the treatability study and contains the following information:

- Section 1.0 Treatability Study Background;
- Section 2.0 Sample Selection;
- Section 3.0 Materials and Methods;
- Section 4.0 Summary of Results;
- Section 5.0 Analysis of Untreated Sediment;
- Section 6.0 Analysis of Treated Sediment;
- Section 7.0 Selected Treatment Alternative; and
- Section 8.0 Quality Assurance/Quality Control of Treated Sediment and Cinders.

1.0 Treatability Study Background

As discussed in RDDR Addendum A, the goal of the upland and marsh remediation activities in Subunit 2A is to remove pyrite cinders and sediment containing chemicals of concern (COCs) that exceed the proposed Remedial Action Objectives (RAO's). Sediment and cinders containing metals in excess of the proposed RAO's were identified for excavation. The cinders and sediment containing elevated concentrations of metals, but containing mercury at concentrations less than 50 mg/kg, will be excavated and transported to the Zeneca site for metals treatment and placement as described in the RDDR. This threshold was established based on treatability studies conducted by LFR and discussed in Appendix D of the RDDR that showed that concentrations of 50 mg/kg mercury should not leach significant concentrations of mercury after treatment with limestone, as is being performed at the site.

Due to the nature of the process being performed by Zeneca to stabilize sediment/cinders, UC Berkeley will perform additional treatment to stabilize the elevated concentrations of mercury (between 50 mg/kg and 260 mg/kg). The purpose of the pretreatment for mercury is to minimize leachability (stabilize) and to solidify (chemically dry) the material for handling and hauling. The benchscale treatability study was performed to investigate different stabilization agents which may be used to treat mercury-contaminated sediment and cinders from Subunit 2A at the RFS site.

Two criteria were developed for the treated material from the RFS site. Treated sediment or cinder must have a pH of less than 9.5, and leachate from the treated sediment or cinder must have a mercury concentration less than 0.25 ug/L. An upper limit was set for pH because some stabilization agents that are mixed with sediment and cinder will increase the pH of the mixed material. Without a limit on pH, the treated material could become too basic. The maximum mercury concentration of 0.25 ug/L for leachate was selected based on the U.S. Environmental Protection Agency (EPA) National Ambient Water Quality Criteria (NAWQC) for Saltwater Aquatic Life Protection. The NAWQC for Saltwater Aquatic Life Protection is 0.025 ug/L for inorganic mercury. The maximum mercury concentration was set at 10 times the national water quality criteria, allowing for dilution and attenuation within the groundwater prior to reaching the marsh.

2.0 Sample Collection

To assess which areas of Subunit 2A contain mercury concentrations between 50 mg/kg and 260 mg/kg requiring treatment prior to transport to the Zeneca site, site investigations were performed at Subunit 2A. The site investigations evaluated the lateral and vertical extent of metals and organics contamination in the sediment and cinders. Based on the analytical results from the site investigations, provided in RDDR Addendum A, the areas shown on Figure 3 as being designated for the Zeneca site will require stabilization treatment for mercury contamination prior to transport and placement.

To identify sediment and cinder samples containing mercury between 50 and 260 mg/kg to be used for the treatability study, six test pits were excavated in Area 4 of Subunit 2A at the RFS site. The sample locations, designated on Figure 4 as TS1, TS2, TS3, TS4, TS5, and TS6, were selected adjacent to borings sampled during previous site investigations containing mercury concentrations within the specified range. Ten discrete samples were collected from these sampling locations (one to four samples from each test pit) at varying depths in both the sediment and cinder layers. The samples were analyzed for Priority Pollutant Metals using USEPA Method 6010 and for selected metals using the Toxicity Characteristic Leaching Procedure (TCLP). The samples were also analyzed for elemental mercury, mercury sulfide, and methyl mercury. The sample depths, sample material (sediment or cinder), and results of the metals analyses are presented in Table 1.

Based on the results of the mercury analysis using USEPA Method 6010, sediment from sampling location TS2 was chosen for the benchscale treatability study. Sampling locations TS1, TS5, and TS6 were not chosen because mercury concentrations in sediment and cinder samples from these locations were greater than the 260 mg/kg limit established by Zeneca for acceptance onto their property. Sampling locations TS3 and TS4 were not chosen because mercury concentrations in sediment and cinder samples from these locations were less than 50 mg/kg, indicating that this material would not require treatment prior to transportation to the Zeneca site. The cinder and sediment samples from location TS2 contained mercury concentrations of 130 and 170 mg/kg, respectively. Since these mercury concentrations are between the thresholds of 50 and 260 mg/kg, sediment and cinder from location TS2 was

considered to be representative of material from Subunit 2A of the RFS site that would be treated using stabilization.

Sediment and cinder for the treatability study were collected from sample location TS2 using an excavator. Sediment and cinder samples were placed in separate buckets and sealed. The sealed buckets were stored in an air-conditioned laboratory trailer on-site at the RFS.

3.0 Materials and Methods

URS contracted to Wilder Construction Company (Wilder) to perform the solidification/stabilization benchscale studies on the sediment and cinder from sampling location TS2 in Subunit 2A. The treatability study was performed in six rounds over a period of approximately 2 months. Wilder mixed sediment and cinder from the buckets in the on-site laboratory trailer to make composite samples, which were used in the stabilization tests. These composite samples, which were approximately half sediment and half cinder, were representative of the materials found at the RFS site. For each sample, Wilder weighed a small volume of composite sediment and cinder (approximately 400 grams total) and mechanically stirred a stabilization agent into the composite. The weight of stabilization agent added was documented as a percent by weight of the composite sample, based on wet weight. For example, if 400 grams of composite sample were used for the test, four grams of stabilization agent were mixed with the composite and documented as one percent by weight. Numerous stabilization agents were used in various quantities. The type and percent weight of stabilization agent used for each test are provided in Table 2.

Wilder placed the mixed samples in 8-ounce sample jars and sent them to Caltest Analytical Laboratory (Caltest), a state-certified laboratory, for analysis. Caltest analyzed the sediment/cinder/stabilization agent samples for pH using U.S. EPA method 9045C and mercury using U.S. EPA Method 7471A. Caltest also performed the Toxicity Characteristic Leaching Procedure (TCLP) described in U.S. EPA Method 1311 on each sample using de-ionized (D.I.) water as the extraction fluid. The TCLP leachate was tested for mercury using U.S. EPA Method 7470A to evaluate the leachability of the treated cinder/sediment mixture.

In addition to the D.I. TCLP mercury analysis, an 8-day leaching test was performed on all samples in the last four rounds of testing. The methodology for this test is described in LFR's *Additional Treatability Study Progress Report* dated January 14, 2002. The 8-day test was designed to replicate the long-term interaction of percolating freshwater (rain) and in-situ sediment. The test was considered an acceptable method for obtaining leachate because the maximum mercury concentration of 0.25 ug/L was based on an ambient water quality goal and the 8-day leachate test was designed to replicate ambient conditions. Wilder performed the test procedure and sent the resulting leachate to Caltest for mercury analysis using approved USEPA method 245.2 (this EPA method was selected in lieu of Method 7470A for mercury in order to achieve the low detection limits necessary to compare to the NAWQC). In the 8-day test, Wilder mechanically mixed approximately 200 grams of composite material/stabilization agent mixture with approximately 200 ml of distilled water in a glass beaker so that the weight to volume ratio

of composite material to water was 1:1. The beaker was then sealed and allowed to sit undisturbed for 8 days. At the end of this period, the mixture was stirred and the aqueous phase sampled and passed through a 0.45 micron filter to remove suspended material. The filtered leachate was sent to Caltest for mercury analysis.

4.0 Summary of Results

Round 1 of the treatability study was performed on July 19, 2002. The objective of this initial round of tests was to identify the treatment additives that are most effective in reducing dissolved mercury concentrations. Nine composite sediment/cinder samples were mixed with stabilization agents. Quicklime, limestone, and elemental powdered sulfur, the selected stabilization agents, were mechanically mixed with each sediment sample, either individually or in combination, at percent weight ratios of one to two percent. The samples were then sent to Caltest where pH was analyzed in each sample. Five of the nine samples were not analyzed further because the pH of the sample was greater than 9.5, the limit that Zeneca would accept. Four of the samples were analyzed further for total mercury in the treated sediment/cinder sample and dissolved mercury in the leachate using the TCLP with D.I. water as the extraction fluid. The D.I. TCLP results for mercury ranged from 2.6 to 6.9 ug/L, higher than the 0.25 ug/L acceptable concentration (Table 2).

Round 2 was performed on August 1, 2002. The objective of this round was to re-test limestone and quicklime at higher doses, and to test the effectiveness of several proprietary treatment additives. Ten composite sediment/cinder samples were mechanically mixed with stabilization agents limestone, quicklime, BSP, Maeprix, and Keeco, either individually or in combination, at percent weight ratios ranging from 0.5 percent to 40 percent. All samples were tested for pH and mercury using the D.I. TCLP method by Caltest. For samples with pH less than 9.5, the D.I. TCLP results for mercury ranged from 2.2 to 6.9 ug/L. Although the increase in reagents dosage decreased the leachable mercury, the concentration in the water was still higher than the acceptable concentration (Table 2). Two untreated sediment samples were also included in this Round for comparison. The D.I. TCLP mercury concentration of these untreated sample were 18 and 8.6 ug/L.

Round 3 was performed on August 12, 2002. The objective of this round was to re-test the effectiveness of the lime and quicklime under the 8-Day testing procedure believed to be more reflective of field conditions. Limestone and quicklime, considered to be the preferred stabilization agents based on the results of Rounds 1 and 2, were mixed with four composite sediment/cinder samples, either individually or in combination, at percent weight ratios of 0.5 to 20 percent. The pH and D.I. TCLP mercury analyses were then performed by Caltest for all of the samples. In addition, the 8-day leaching test described above was performed for each sample. Wilder performed the mixing and leachate separation for the 8-day test. At the end of the 8-day period, Wilder sampled the leachate after first stirring and filtering it. This leachate was then sent to Caltest for mercury analysis. The results of this 8-day leaching procedure performed during Round 3 ranged from 0.07 to 6.4 ug/L (Table 2), but the pH for the sample treated with quicklime were higher than the allowable limit of 9.5. The dissolved concentrations

were a good indicator of likely concentrations, but were not conclusive because the samples were not vigorously stirred at the end of the 8-day period prior to leachate sampling.

Round 4 was performed on August 20, 2002. The objective of this round of tests was to test the effectiveness of two additional treatment additives, Powdered Activated Carbon (PAC) and Ecobond. Three composite sediment/cinder samples were mixed with Ecobond, powdered activated carbon, and Maeprix in various quantities. Similar to Round 3, the pH, D.I. TCLP, and 8-day leaching analyses were performed; however, unlike Round 3, the 8-day samples were stirred vigorously immediately prior to aqueous phase filtering and sampling at the end of the 8-day period. The 8-day leachate mercury concentrations ranged from 0.05 to 0.10 ug/L, indicating acceptable pH and dissolved mercury concentrations for all of the samples. In fact, the sediment composite used for the Ecobond treatability study passed the 8-day test without a treatment additive. Because this composite was taken from a different soil/cinder batch than the all of the other samples reported in the table, this result confirms the existence of heterogeneity in the leachability of sediment. It also shows that a conservative approach was adopted in this investigation by performing treatability tests on the most soluble soil/cinder composite.

Round 5 was performed on August 27, 2002. This round was performed to confirm that the addition of limestone will lower dissolved mercury concentrations below 0.25 ug/L, while maintaining a pH below 9.5. Limestone was used as a stabilization agent at 10 and 20 percent by weight in Round 3. The 8-day leaching procedure results from Round 3 indicated that the leachate from both of these samples had acceptable levels of pH and mercury; however, the samples in Round 3 were not stirred vigorously at the end of the 8-day period prior to leachate sampling. Thus, in Round 5, the same stabilization agent as in Round 3 was used and the samples were vigorously stirred prior to aqueous phase sampling during the 8-day test. In addition, the sediment and cinder were not composited during Round 5 so that the effect of limestone could be observed on each individual material. Untreated soil and cinder were also tested for comparison. The results for Round 5 show that although acceptable solution pH could be attained, dissolved mercury concentrations ranging from 0.77 to 2.1 ug/L are in excess of the accepted value of 0.25 ug/L.

Round 6 was performed on September 18, 2002. Because the Round 5 results showed that limestone did not consistently produce dissolved mercury concentrations below 0.25 ug/L, this round was performed to test the effectiveness of Powdered Activated Carbon at varying doses (2.5, 5, and 10% PAC) on dissolved mercury concentrations. Due to time constraints, the 8-day testing procedure was shortened to 1 day and samples were sent to Frontier Geosciences for analysis. The 1-day test using 5% PAC resulted in a dissolved mercury concentration of 0.35 ug/L, slightly higher than the target level of 0.25 ug/L and higher than the results of the 8-day test of Round 4 (possibly due to adsorption rates being longer than 1 day). The sample treated with 10% PAC showed a dissolved mercury concentration of 0.15 ug/L, below the required 0.25 ug/L. Finally, the untreated and 2.5% PAC treated samples had conflicting results. The untreated sample showed concentrations of dissolved mercury below the 2.5% PAC. This may be due to laboratory mix-up with the samples.

Round 7 was performed on October 4, 2002. Because Round 6 demonstrated that 5% PAC does not always achieve dissolved mercury concentrations below 0.25 ug/L for soil/cinder containing very elevated levels of mercury, the 1-day tests in this round were performed to determine the effectiveness of a 7.5% PAC dose, and to re-test at 10%. Filtration of the samples in this round was performed using TCLP filters, and the laboratory observed that all but one of the samples was cloudy and contained solid particulate matter. The additional mercury adsorbed to these solids is likely the responsible for the elevated mercury concentrations reported in the qualified data column in Table 2. The one sample that was presumed to be free of particulates based on the clarity of the water (100402-B) was derived from a mixture containing 7.5% PAC. The leachate mercury concentration from this sample was 0.18 ug/L, confirming the effectiveness of higher PAC doses, such as the 10% tested in Round 6.

Round 8 was performed on October 11, 2002. This round was performed because previous tests used sediment with mercury concentrations that are expected to be higher than will actually be achieved after mixing and homogenization has occurred during excavation. Unlike the previous rounds (which used samples from Subunit 2A, Area 4), the samples for this round were taken from Subunit 2A, Area 1. The calculated, depth-averaged concentration for the sediment designated for removal from this area is approximately 38 mg/kg, slightly higher than the concentration of 30 mg/kg measured in this round. Sample preparation for the 1-day tests was performed by URS and the leachates were analyzed by Frontier Geosciences. As shown in Table 2, the untreated sediment produces a pH of 3-4 and mercury leachate of 0.0008 to 0.0016 ug/L, considerably lower than the required concentration of 0.25 ug/L. The addition of 5%, 7.5%, and 10% PAC increases pH to neutral conditions and results in an additional 90% reduction in dissolved mercury concentrations to well below the 0.25 ug/L limit.

5.0 Analysis of Untreated Sediment

Five D.I. TCLP and three 8-day tests were performed on untreated soil, cinder, and composite samples. As shown in Table 2, the two composite samples analyzed during the D.I. TCLP tests of Round 2 produced dissolved mercury concentrations of 8.6 and 18 ug/L. These results were similar to those found during Round 5, where untreated soil and cinder produced dissolved concentrations of 13 and 21 ug/L, respectively. In contrast to these results, the Round 4 tests (which used a composite sample from a different batch of sediment) resulted in lower dissolved concentrations during the D.I. TCLP tests (0.7 ug/L), even though the total mercury contained in the sample was higher (410 mg/kg). These differences were mirrored in the 8-day tests, where dissolved mercury concentrations from untreated soil and sediment in Round 5 were 3.6 ug/L and 1.7 ug/L, but the dissolved concentration measured during Round 4 was only 0.1 ug/L.

To identify the processes responsible for the observed concentrations in the untreated samples, and thus assess the long-term effectiveness of different treatments, additional chemical characterization and speciation modeling was performed using the data and methodology described in Attachment A. The first important result of this analysis is that dissolved concentrations observed during the D.I. TCLP and 8-day tests are predicted to be too low for mercury minerals to be stable (the degree of saturation with respect to minerals is not reported in

this transmittal). Consequently, minerals such as cinnabar or metacinnabar (HgS), which are believed to be the most prevalent forms of mercury based on the concentration of mercury in the soil and the presence of sulfides observed at the site, will partially dissolve over time. This implies that the observed concentrations are a function of slow dissolution reaction rates and the sorptivity of mercury, as discussed below.

The predicted distribution of 150 mg/kg of mercury between dissolved and adsorbed phases is expressed on Figure 5 as the dissolved fraction. The curves on the plot represent the condition where available organic sorption sites are only associated with organic carbon particulate matter (upper curve), and concentrations that may occur if there are additional sorption sites due to organic material coating the surface of some minerals (Davis, 1984) (lower curve). Although concentrations from D.I. TCLP tests are more closely associated with the upper curve, the predicted increase in dissolved mercury at pH 9 for this curve is due to the mercury complex $\text{Hg}(\text{OH})_2^0$, which becomes increasingly important in model simulations where organic coatings are unavailable because there are too few favorable sorption sites for dissolved mercury. Because elevated dissolved mercury concentrations at higher pH cannot be confirmed by the results of this study (the model is calibrated to a restricted pH range), the upper and lower plots on Figure 5 represent estimated uncertainty in model calculations. The most important result of the model simulations is that dissolved mercury is predominantly associated humic and fulvic acids in dissolved organic carbon (DOC). For example, more than 99% of the mercury is predicted to be organically-complexed at pH 7.

Comparison of the dissolved concentrations in Table 2 and Figure 5 shows that predicted concentrations are within the range of the D.I. TCLP results for Rounds 2 and 5, and are higher than the D.I. TCLP tests from Round 4. The lower concentrations in Round 4 are consistent with the presence of greater quantities of cinnabar or metacinnabar (HgS), and the slow dissolution kinetics of the mineral (a process not included in the model). Support for this hypothesis is provided by Ravichandran et al. (1999) which showed that cinnabar dissolves so slowly that dissolved concentrations are below detection limits of 0.5 ug/L in the absence of mechanical agitation. By contrast, other possible mercury forms in the sediment (i.e. elemental mercury or adsorbed mercury) have been shown to equilibrate with water within hours or days (Melamed et al., 1997; Yin et al., 1997).

By accepting the hypothesis that the slow dissolution of cinnabar or metacinnabar (HgS) is responsible for the differences in dissolved mercury concentrations between untreated samples, the higher concentrations of the D.I. TCLP compared to the 8-day tests can also be satisfactorily explained. In this case, the dissolution rate of HgS is a function of mineral surface area and the rate that surface-associated mercury organic complexes can be removed (Ravichandran et al., 1999). Not only does crushing the sample in the D.I. TCLP test increase mineral surface area, but stirring the suspension enhances ligand-promoted dissolution (Stumm, 1992).

To model the fraction of the total mercury in the sample that is reactive in an 8-day test, the total amount of mercury allowed to react in the system was reduced in numerical simulations until predicted concentrations were similar to those measured in the untreated 8-day test of Round 5.

The predicted upper and lower concentrations are shown as dashed lines on Figure 6 as a function of pH. Although the shape of the solubility curve is similar to Figure 5, only 30 mg/kg of the total mercury concentration of 150 mg/kg (about 20%) was found to be “reactive” within the given time frame. Because percolating rainwater will be limited due to the presence of a site cap, and will also have a finite residence time in the soil, the lower concentrations predicted by the 8-day test are more representative of field conditions than the near-equilibrium state represented by the D.I. TCLP tests. Consequently, the results presented on Figure 6 are more representative of probable concentrations than those on Figure 5.

6.0 Analysis of Treated Sediment

Several stabilization agents were applied to the soil/cinder composites to assess their ability to lower dissolved mercury concentrations below 0.25 ug/L, while maintaining a pH below 9.5. D.I. TCLP tests were used for the initial screening in Rounds 1 and 2, with the result that limestone additives achieved the lowest dissolved mercury concentrations within the restricted pH range. 8-day tests using 10% and 20% limestone confirmed that dissolved concentrations could be reduced to a concentration between 0.18 ug/L and 2.1 ug/L.

Measured and modeled concentrations for a mixture of composited soil and limestone during an 8-day test are shown on Figure 6 (uncertainties expressed for laboratory samples are due to not measuring pH). The reason that the predicted concentration is higher than the 8-day laboratory experiments is likely due to surface charge-related processes not being included in the model. For example, Ravichandran et al. (1999) showed that cinnabar is negatively charged below pH 8, and that Ca^{2+} sorbs to the surface, thereby inhibiting dissolution of the mineral. Also, Bob and Walker (2001) demonstrated that calcium carbonate (the primary mineral in limestone) is positively charged, leading to adsorption of DOC and reduction in the availability of organic ligands for mercury dissolution. Finally, analytical results in Rounds 3 and 5 (Table 2) show that there is a clear decrease in dissolved mercury concentration with higher doses of limestone, despite the fact that pH is unchanged. This is presumably due to an increase in available sorption sites for DOC.

Due to the variability in dissolved mercury concentrations from the limestone treatment, Powdered Activated Carbon (PAC) was also examined as an effective treatment additive. As shown in Table 2, the D.I. TCLP test where 5% PAC was added produced a dissolved mercury concentration of 23 ug/L (Round 4). By contrast, the 8-day tests using the same dosage generated between 0.05 to 0.35 ug/L (Rounds 4 and 6). Although the source of this disparity in concentration is unclear, the higher concentrations in the D.I. TCLP test may be related to additional dissolution of the carbon during the vigorous agitation of the test.

Identification of the processes leading to measured mercury concentrations in the 5% PAC 8-day test were obtained from model simulations using surface properties of PAC from Ekinçi et al. (2002). The predicted reduction in dissolved mercury concentration due to additional PAC binding sites for Hg^{+2} is apparent on Figure 6. Although predicted concentrations are slightly higher than those measured during the 8-day test of Round 4, this may be due to additional

adsorption of DOC onto the PAC in the laboratory experiments. This is a process that is known to occur (Shen and Chuang, 1998), but is not included in the model. A decrease in the availability of DOC for mercury complexing reduces the ability of mercury to dissolve.

7.0 Selected Treatment Alternative

Based on the results of the benchscale treatability study presented in Table 2, the stabilization agent that results in acceptable pH and mercury concentrations in sediment leachates from Area 4 is 5 to 10% PAC by weight. For example, a 5% PAC dose reduces leachate concentrations to between 0.05 and 0.35 ug/L for the most contaminated sediments of Area 4. Results also show that larger doses of PAC produce marginally greater reductions, with dissolved concentrations less than 0.2 ug/L for Area 4 sediment.

Considering the measured total mercury concentrations in Area 1 are less than those in Area 4, it is anticipated that required PAC concentrations will also be less than the 5 to 10% required for Area 4. This is confirmed by the treatability results of Round 8, which show that at 30 mg/kg mercury, no stabilization agent is necessary for sediment from Area 1. Nevertheless, to account for the possibility that concentrations may be higher locally, a PAC dose of 5% will be applied to stabilize the mercury in Area 1. As with the sediment from Area 4, the effectiveness of this treatment will be confirmed by the QA/QC procedures outlined below.

8.0 Quality Assurance/Quality Control of Treated Sediment and Cinders.

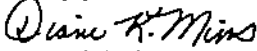
To ensure that the material meets the criteria specified for the stabilization (pH less than 9.5 and leachate mercury concentration less than 0.25 ug/L), quality assurance testing will be performed on the treated cinder and sediment. Treated material will be sampled at a rate of one 4 point composite sample for every 500 cubic yards of treated material. The 1-day leaching test will be performed on all samples, and samples will be sent to a state-certified laboratory for pH and mercury analysis. Material will only be transported to Zeneca after approval by Zeneca and the treatment has shown a reduction in mercury leaching to levels that are protective of the underlying groundwater and nearby surface water. Following mercury stabilization treatment and approval by Zeneca, the material from Subunit 2A of the RFS site will be loaded onto trucks and transported to the Zeneca site.


Based on the treatability study results, the elevated mercury concentrations in the contaminated sediment and cinder at the RFS site can be stabilized to levels that will protect human and ecological health and water quality when the material is treated and transported to the neighboring Zeneca site. In addition, the long-term stability of mercury chemically adsorbed on PAC should be high based on the relative stability of mercury surface complexes compared to other metals (Kerndorff and Schnitzer, 1980). The reduction in dissolved mercury concentrations related to DOC adsorption should also be relatively stable, because the DOC that most readily forms complexes with mercury is also the fraction that preferentially adsorbs to PAC (Kilduff et al., 1996; Schmit and Wells, 2002).

Mr. Cecilio Felix
November 6, 2002
Page 11 of 11

Please call me at (510) 874-3284 or Brad Bessinger at (510) 874-3248 if you have questions or need any additional information.

Sincerely,

URS CORPORATION

Diane K. Mims
Senior Project Manager


Brad Bessinger, Ph.D.
Geochemist

Cc: Mike Hryciw, UC Berkeley Capital Projects
Anna Moore, UC Berkeley Environment, Health and Safety
Pat Schlesinger, UC Office of the General Counsel
Jane Anderson, Zeneca, Inc.
Bill Carson, LFR
John Edgecomb, Esq.
File

Attachments:

Tables

Table 1: Subunit 2A Excavated Sediment and Cinder Metals Analytical Results

Table 2: Analytical Results for Mercury Treatability Study

Figures

Figure 1: Site Location Map

Figure 2: Subunits 2A and 2B Locations and Boundaries

Figure 3: Excavation Plan for Areas to be Excavated and Treated by UC Berkeley

Figure 4: Mercury Treatability Study Sampling Locations

Figure 5: Predicted Mercury Concentrations for Untreated Sediment (D.I. TCLP Tests)

Figure 6: Predicted Mercury Concentrations for Untreated Sediment (8-Day Tests)

Attachment A—Mercury Speciation Model

Attachment B—References

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Table 1.
Subunit 2A Excavated Sediment and Cinder
Metals Analytical Results
 UC Berkeley Richmond Field Station

Sample	Elevation (ft msl)	Moisture (%)	pH	Antimony (mg/kg)	Arsenic (mg/kg)	Beryllium (mg/kg)	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	TCLP Copper (mg/L)	Lead (mg/kg)	TCLP Lead (mg/L)	Mercury (mg/kg)	TCLP Mercury (mg/L)	Nickel (mg/kg)	Selenium (mg/kg)	TCLP Selenium (mg/L)	Silver (mg/kg)	Thallium (mg/kg)	Zinc (mg/kg)	TCLP Zinc (mg/L)	Brook Rand ¹ Total Mercury (mg/kg)	Brook Rand Elemental Mercury (mg/kg)	Brook Rand Hg (Monomethyl) (mg/kg)	Brook Rand HgS (mg/kg)	
RCRA TCLP RT																										
CA TTLC																										
CA STLC																										
TS1-CINDER	-0.64	33%	7.4	<3.0	61	0.190	5.2	6.1	180	0.490	20	0.230	5,700	0.045	29	6.0	<0.050	6.3	<0.25	750	2.90	13.047	<0.00025	0.0507	907	
TS1-SEDIMENT	-2.64	16%	6.0	<2.7	5.3	<0.050	1.1	25	37	<0.100	10	0.084	850	0.0076	27	0.72	<0.050	0.28	<0.25	63	0.550	923	0.000383	0.00676	46	
TS1-SEDIMENT-1	-2.64	26%	7.2	<3.0	6.3	0.110	0.86	15	39	<0.100	8.5	0.170	3,500	0.027	16	0.64	<0.050	0.37	<0.25	64	0.750	1,576	0.00363	0.00635	58	
TS-2-CINDER-2	0.78	32%	7.1	<2.9	87	<0.097	9.6	6.0	4,600	2.6	95	0.540	130	0.0013	27	4.7	<0.050	2.7	<0.24	2,300	5.90	961	<0.00025	0.0130	41	
TS-2-SEDIMENT-1	-0.22	31%	6.9	<2.8	58	0.520	3.4	38	1,600	<0.100	58	0.560	170	0.0021	33	2.9	<0.050	1.3	1.6	670	3.0	133	>0.00025	0.0145	2.0	
TS-3-SEDIMENT	-0.73	39%	8.1	<2.7	94	0.990	4.8	17	600	<0.100	81	0.490	14	<0.001	29	2.1	na	1.8	0.52	1,400	na	na	na	na	na	
TS-4-SEDIMENT		37%	7.2	<3.9	140	1.5	6.2	24	1,100	<0.100	160	1.0	13	<0.001	39	3.6	na	2.7	<0.32	3,300	na	na	na	na	na	
TS5-CINDER	1.21	27%	7.1	3.0	49	0.380	8	1.9	3,800	0.170	44	0.540	350	0.011	25	2.9	<0.050	3.5	<0.24	2,200	4.0	981	<0.00025	0.0146	105	
TS5-SEDIMENT	0.21	16%	8.6	<3.0	3.0	<0.050	1	27	170	0.170	8.9	0.110	380	0.022	34	0.73	<0.050	<0.25	<0.25	50	0.440	311	0.000816	0.00418	2.0	
TS6-CINDER	1.52	31%	7.0	<5.2	320	1.3	25	11	5,900	<0.100	160	0.110	1,300	0.0016	59	12	<0.050	6.6	<4.3	8,400	4.20	1,362	<0.00025	0.0691	65	

¹Results are based on wet weight
 The difference in total concentrations is due to the different extraction techniques used for each method.

**TABLE 2. ANALYTICAL RESULTS
MERCURY TREATABILITY STUDY
RICHMOND FIELD STATION**

Sample No.	Treatment [% by weight]	Additive Form	pH	Mercury (mg/kg)	TCLP-D1 Mercury (ug/L)	8-Day Test Mercury (ug/L)	Qualified Tests Mercury (ug/L)
ROUND 1 - July 19, 2002							
071902-A	1% Quicklime	Powder	12.2	NA	NA		
071902-B	2% Quicklime	Powder	12.4	NA	NA		
071902-C	1% Quicklime, 1% Limestone	Powder	11.9	NA	NA		
071902-D	1% Quicklime, 2% Limestone	Powder	12	NA	NA		
071902-E	1% Limestone	Powder	7.3	140	2.6		
071902-F	2% Limestone	Powder	7.2	150	3.6		
071902-G	1% Sulfur	Powder	8.1	130	6.9		
071902-H	2% Limestone, 1% Sulfur	Powder	7.8	140	3.8		
071902-I	1% Quicklime, 1% Sulfur	Powder	12.2	NA	NA		
ROUND 2 - August 1, 2002							
080102-A	10% Limestone	Powder	7.4	NA	3.6		
080102-B	20% Limestone	Powder	7.4	NA	2.2, 2.7		
080102-C	40% Limestone	Powder	7.6	NA	3.1		
080102-D	0.5 % Quicklime, 15% Limestone	Powder	11.7	NA	0.4, 0.3		
080102-E	5% BSP	Liquid	10.4	NA	25		
080102-F	5% BSP, 10% Limestone	Liquid/Powder	10.5	NA	23		
080102-G	1% Maeprix, 5% Limestone	Liquid/Powder	5.9	NA	5.4		
080102-H	1% Maeprix, 10% Limestone	Liquid/Powder	6.4	NA	5.6		
080102-I	Untreated Composite	-	6.9	260	18, 8.6		
080202-J	5% Kecco	Powder	12.5	NA	6.9		
080202-K	3% Kecco	Powder	12.3	NA	4.2		
ROUND 3 - August 12, 2002							
081202-D	1/2% CaO + 25% CaCO ₃	Powder	10.9	130/100	0.2	0.51	
081202-E	10% Limestone	Powder	NA	NA	NA	0.18	
081202-F	20% Limestone	Powder	NA	NA	NA	0.07	
081202-G	1% CaO	Powder	12	180	8.9	6.4	
ROUND 4 - August 20, 2002							
082602-A	5% PAC	Powder	8.2	150	23	0.05	
082602-B	5% PAC + Maeprix to pH 5 (.5 mL)	Liquid/Powder	7.5	120	12	0.1	
082602-C	EcoBond Untreated	-	7.9*	326*	0.3, 0.13*	0.1 ^{AB}	
082602-D	EcoBond Treated (2, 5, 7 wt.%)	-	NA	NA	0.7, 0.5, 0.19 ¹	NA	
ROUND 5 - August 27, 2002							
090402-A	Untreated Soil	-	NA	110	13	3.6	
090402-B	Untreated Soil + 10% Limestone	Powder	NA	150	1.7	2.1	
090402-C	Untreated Soil + 20% Limestone	Powder	8.5	110	1.5	0.77	
090402-D	Untreated Cinder	-	8.8	190	21	1.3	
090402-E	Untreated Cinder + 10% Limestone	Powder	8.4	170	3.9	0.94	
090402-F	Untreated Cinder + 20% Limestone	Powder	8.4	190	4.8	0.93	
ROUND 6 - September 17, 2002							
091802-A	Untreated Composite	-	9.2	190	NA		0.55 ^{cd}
091802-B	2.5% PAC	Powder	9	133	NA		2.4 ^{cd}
091802-C	5% PAC	Powder	9.1	110	NA	0.35 ^e	
091802-D	10% PAC	Powder	9.4	99	NA	0.15 ^e	
ROUND 7 - October 3, 2002							
100402-A	7.5% PAC	Powder	NA	119	NA		0.58 ^{ce}
100402-B	7.5% PAC	Powder	NA	100	NA	0.18 ^f	
100402-C	10% PAC	Powder	NA	113	NA		28.3 ^{cf}
100402-D	10% PAC	Powder	NA	138	NA		62.7 ^{ce}
ROUND 8 - October 14, 2002							
101102-A	Untreated Composite ¹	-	3.0, 4.0	30	NA	0.00163 ^e , 0.00077 ^f	
101102-B	5% PAC	Powder	5.0, 7.0	NA	NA	0.00018 ^e , <0.00015 ^e	
101102-C	7.5% PAC	Powder	7.0, 7.0	NA	NA	<0.00015 ^e , <0.00015 ^e	
101102-D	10% PAC	Powder	7.0, 7.0	NA	NA	<0.00015 ^e , <0.00015 ^e	

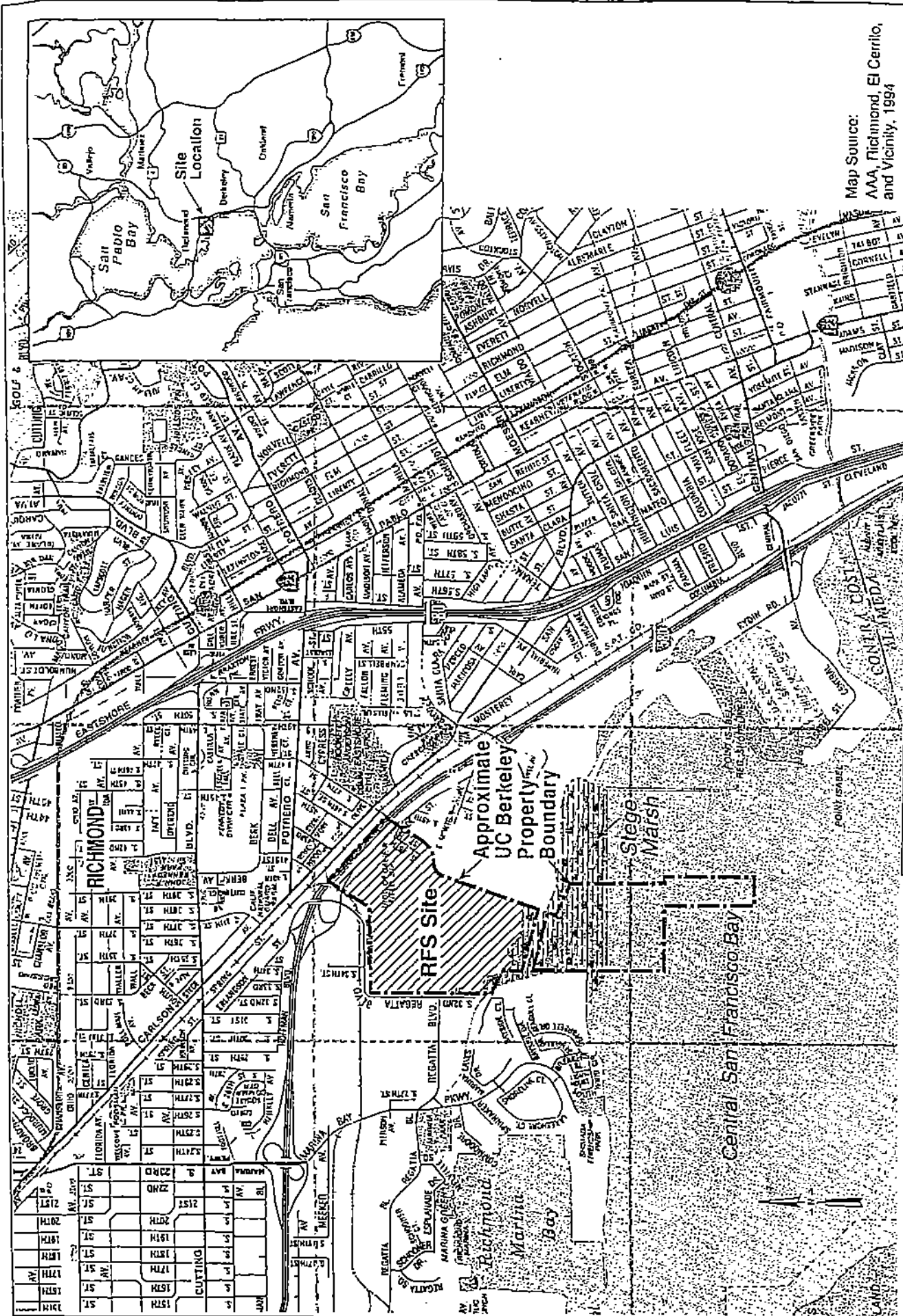
NOTES:

BSP = Best Sulfur Products proprietary additive; Maeprix = Sevenson proprietary phosphate additive; Kecco = proprietary additive that also contains calcium oxide;

Quicklime = calcium oxide; Limestone = calcium carbonate; TBA = To be analyzed;

¹Sample from different composited batch with higher total mercury concentration; ²Untreated sample was tested; ³1-Day Tests performed

⁴Untreated and sample treated with 2.5% PAC may have been switched in the laboratory; ⁵Samples were filtered using a TCLP filter instead of a 0.45 um filter, with lab reporting visible particulate matter in the samples that appears to have produced elevated mercury concentrations due to mercury adsorbed to the solids; ⁶Sample from Subunit 2A, Area 1 and PAC same as will be used at site



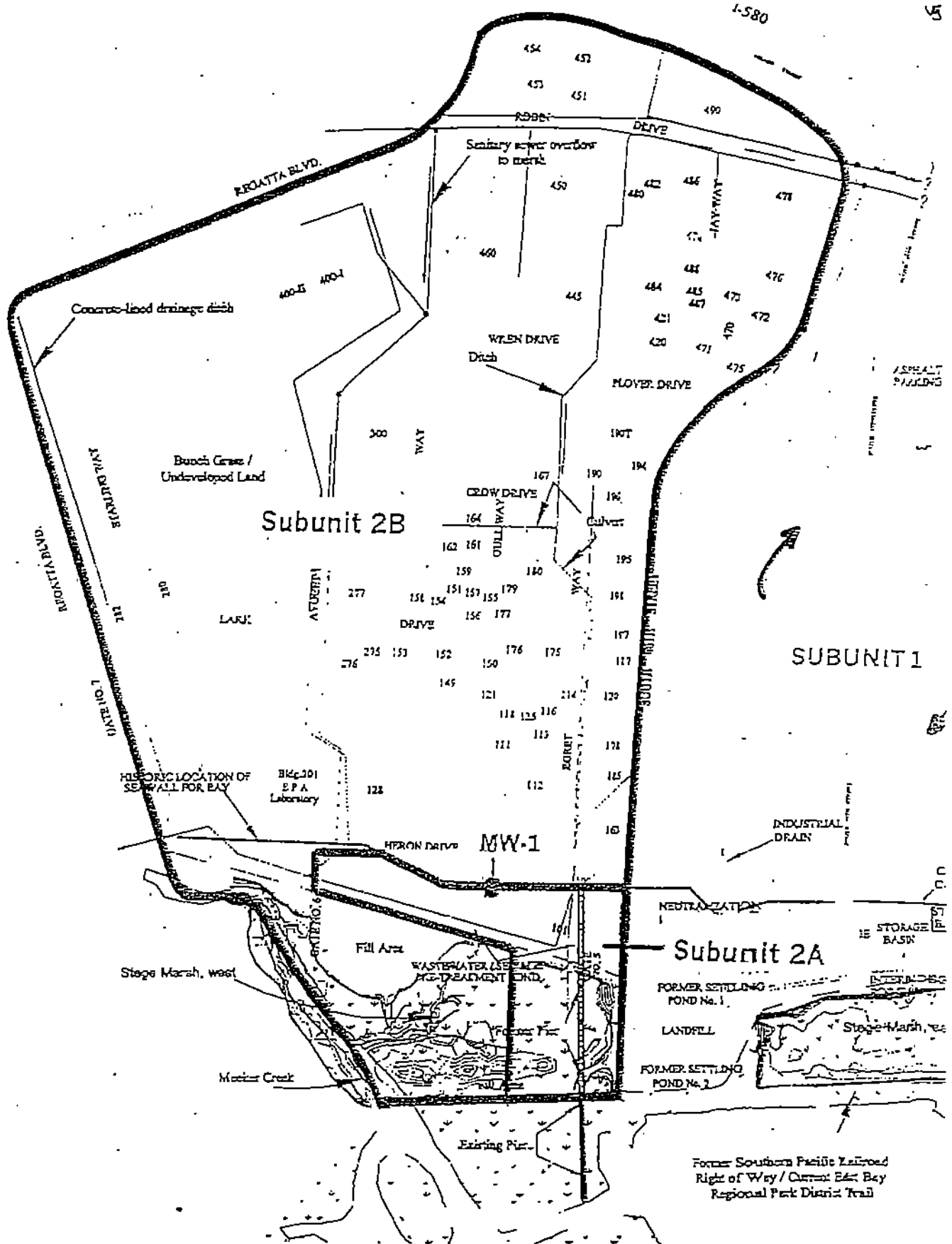
Map Source:
AAA, Richmond, El Cerrito,
and Vicinity, 1994

UNIVERSITY OF CALIFORNIA,
BERKELEY
RICHMOND FIELD STATION
SITE LOCATION MAP

Project No. 51-09967067.00
University of California
Richmond Field Station






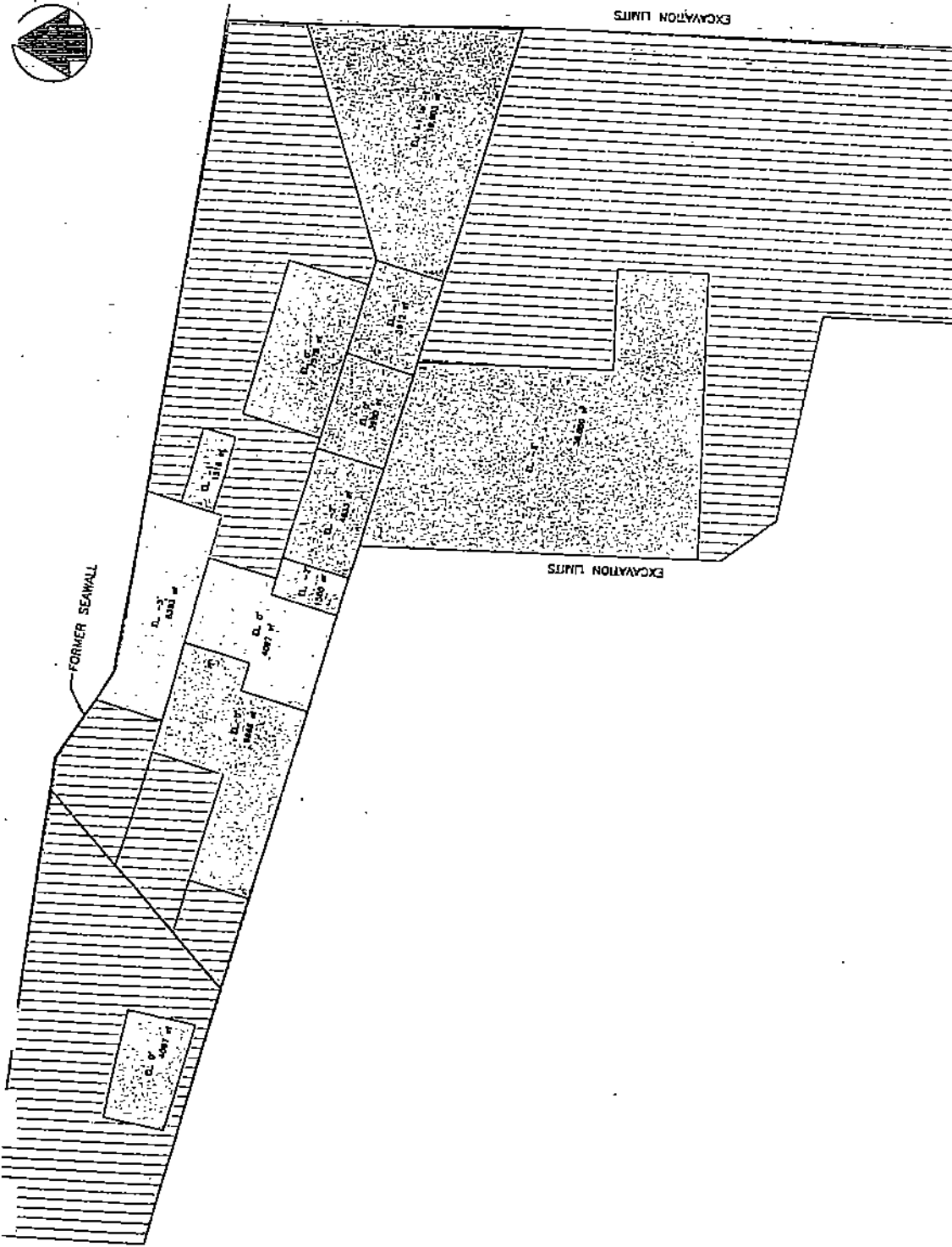
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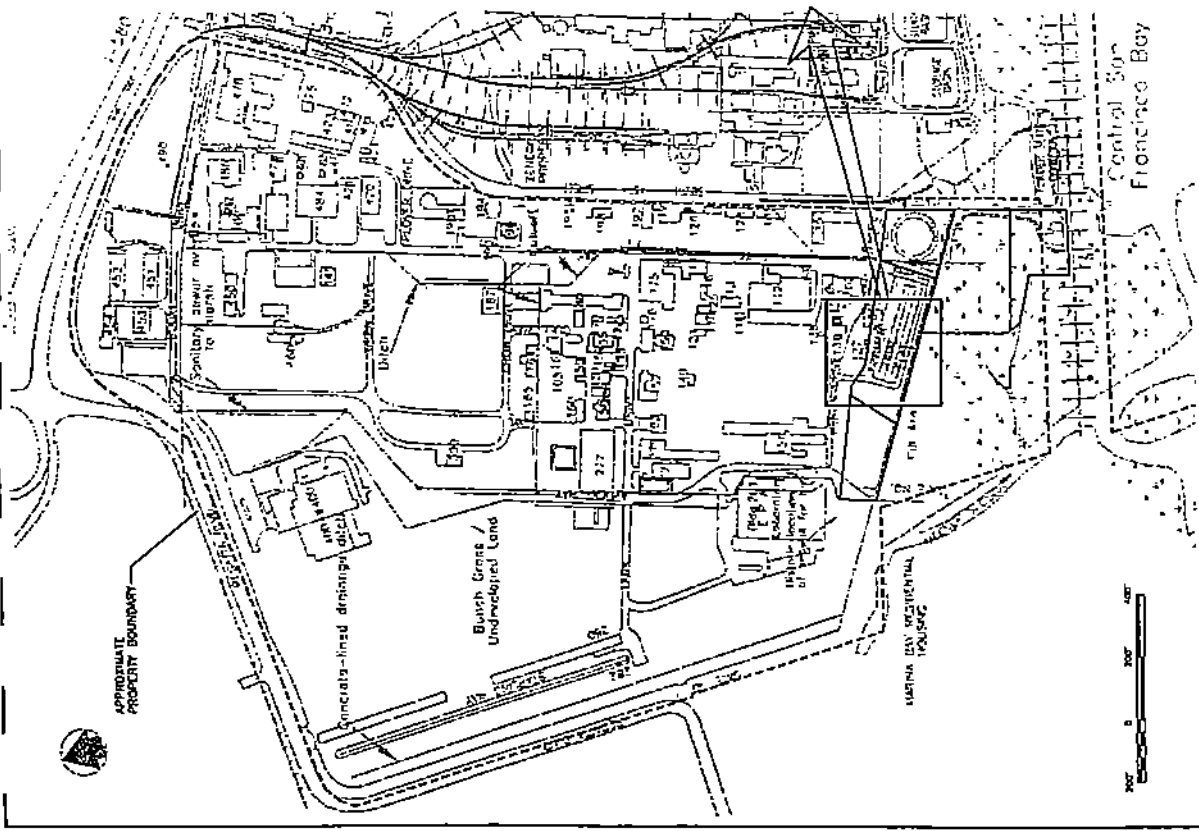
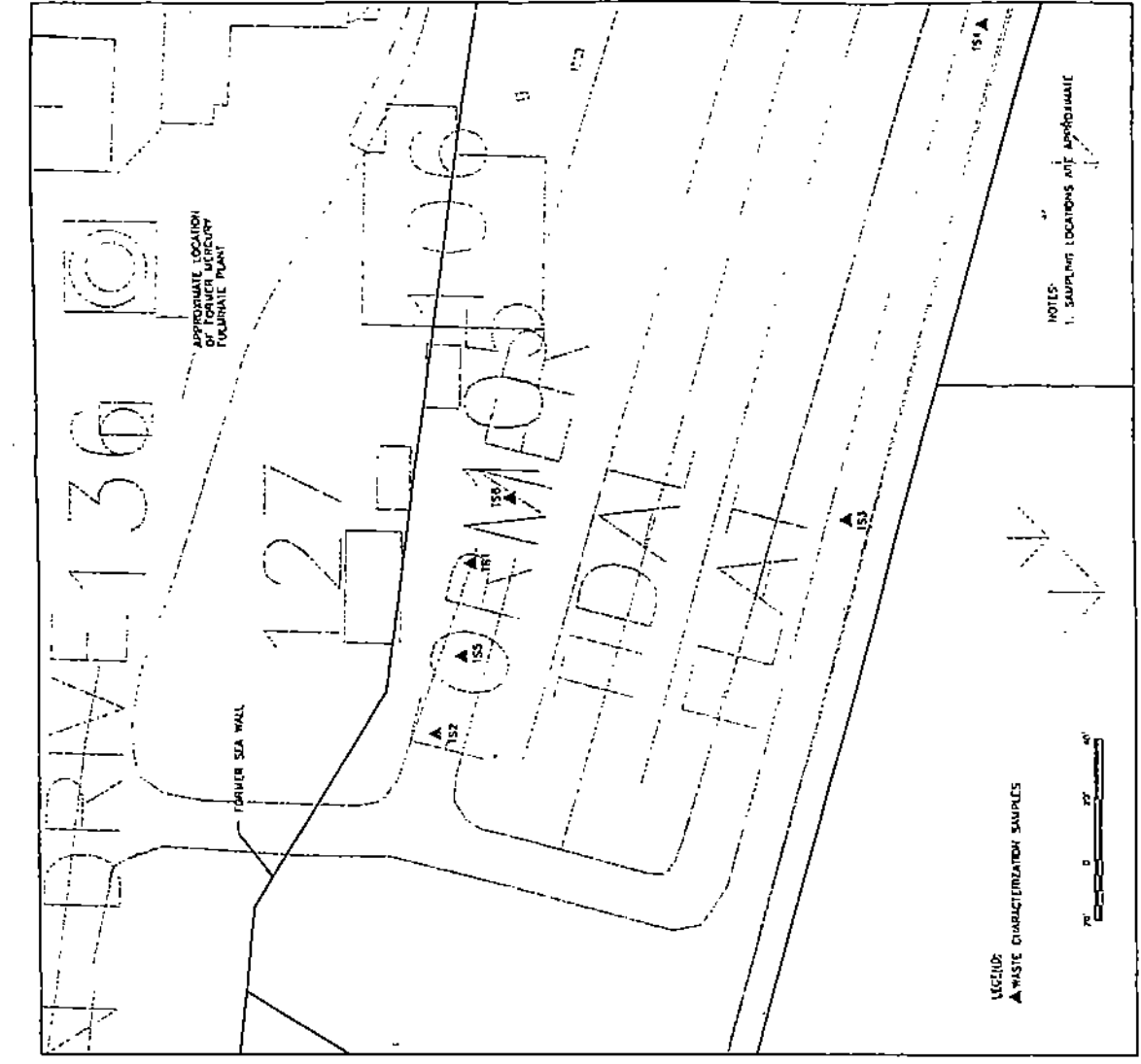
Subunits 2A and 2B
Locations and Boundaries

1. ELEVATIONS SHOWN IN MFGVD 28.

-  NO EXCAVATION
-  TO LANDFILL
-  TO TREAT AND IMBA TO ZEPHYRA



 500 17th Street, Suite 200 Oakland, California 94612		University of California, Berkeley Richmond Field Station EXCAVATION PLAN FOR AREAS TO BE EXCAVATED AND TREATED BY UC BERKELEY	DATE: 01/15/03 DRAWN BY: [Name] CHECKED BY: [Name] SCALE: AS SHOWN SHEET NO.: 3
UNIVERSITY OF CALIFORNIA RICHMOND FIELD STATION	PROJECT NO. UC-001574	SHEET NO. 3	DATE: 01/15/03



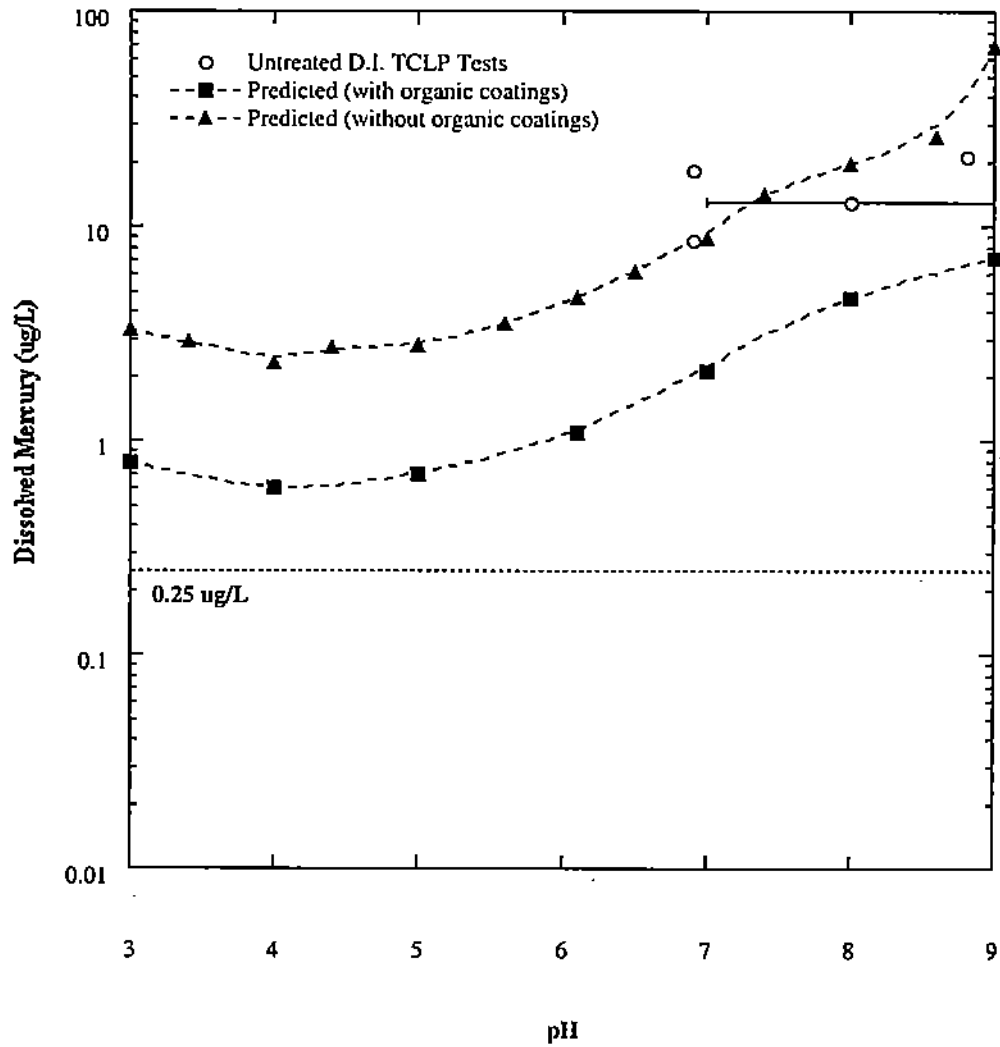
Project No. 51-08967067.01

URS

MERCURY TREATABILITY STUDY
SAMPLING LOCATIONS

RICHMOND FIELD STATION
RICHMOND, CALIFORNIA

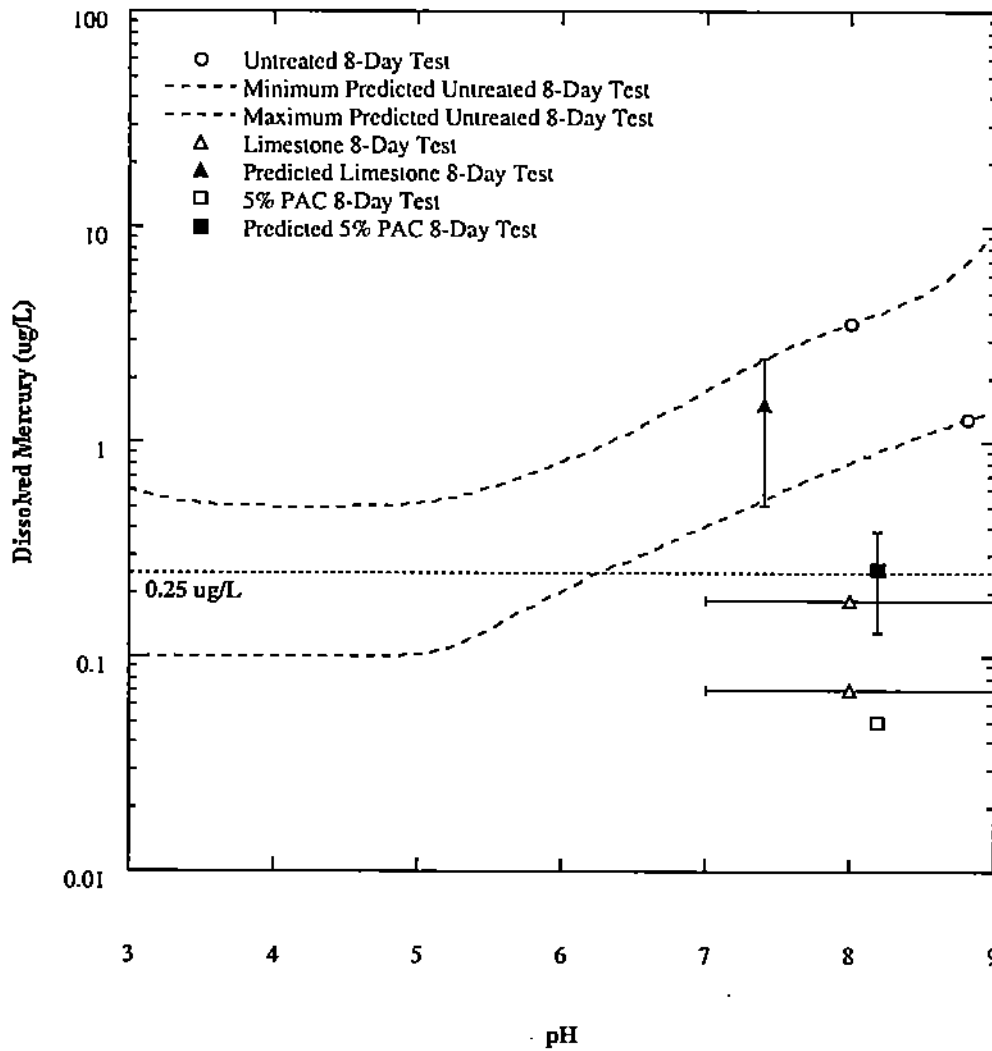
FIGURE
4



Job No. 26813393.8A330
 Richmond Field Station
 Treatability Study

PHREEQC Predicted Dissolved Mercury (ug/L)
 Sediment Weight to Water Volume (1:1)
 Total Mercury Concentration is 150 mg/kg

FIGURE
 5



URS

Job No. 26813393.8A330
 Richmond Field Station
 Treatability Study

PHREEQC Predicted Dissolved Mercury (ug/L)
 Sediment Weight to Water Volume (1:1)
 Total Mercury Concentration is 30 mg/kg

FIGURE
 6

Attachment A. Mercury Speciation Model

A-1 Introduction

In order to gain an understanding of the processes controlling dissolved mercury concentrations in the D.I. TCLP and 8-day tests (and thus gain insight into the effectiveness of different treatment alternatives), the distribution of mercury between dissolved, adsorbed, and mineral phases was calculated numerically using the USGS-supported modeling software PHREEQC (Parkhurst and Appelo, 1999).

A-2 Method and Processes Modeled

Introduction

PHREEQC uses a thermodynamic database (Allison et al., 1990) and a chemical description of solid and aqueous phases determined through laboratory analysis, to predict the distribution of each element in solid, surface, aqueous, and gaseous phases. PHREEQC is based on chemical thermodynamics and the energetics of possible chemical reactions that are supplied to the program through the thermodynamic database. PHREEQC uses this information, along with the total elemental compositions of the system being modeled, to minimize the overall energy of the system. PHREEQC simultaneously solves expressions relating the mass of each element to its possible distribution between different forms (mass balance equations), expressions representing the Gibbs free energy change of prescribed reactions (mass action equations), and an expression for electrical neutrality of the system (the charge balance equation).

PHREEQC models several types of chemical processes. The first are aqueous phase reactions, which are chemical reactions between dissolved species. The model also includes ion exchange reactions, which are heterogeneous adsorption/desorption reactions normally associated with binding between dissolved species and mineral phases with fixed charges (i.e. clay minerals (Deutsch, 1997)), and included surface complexation reactions, a type of adsorption/desorption reaction characterized by aqueous species attaching themselves via chemical bonds to functional groups present on the surface of sorbing phases. Finally, the model includes precipitation and dissolution reactions, which are processes where aqueous species are irreversibly transformed to or from the solid phase, respectively.

Aqueous Reactions

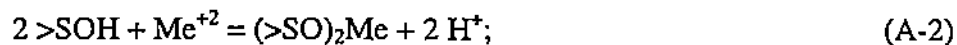
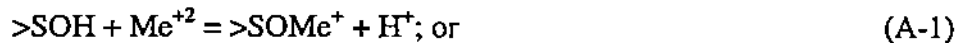
The primary modification to the thermodynamic database required for this study was the recalculation of mercury sulfide complexes (Benoit et al., 1999), inclusion of equilibrium constants for mercury polysulfide complexes (Paquette and Helz, 1997; Jay et al., 2000) and methylmercury (Stumm and Morgan, 1996), and calculation of stability constants for organo-mercury complexes. Incorporation of the organo-mercury complexes was made possible by previous research has identified classes of organic ligands and measured their collective stability constants (e.g. Glaus et al., 2000). The most important class of dissolved organic matter identified in this study includes humic and fulvic acids, which can comprise up to 50% of all DOC (Dellis and Moulin, 1989), and contain carboxyl and phenol binding sites that have a high affinity for trace metals (Spark et al., 1997a and 1997b).

Adsorption and Desorption Processes

Mercury adsorbs to soil because there is an electrostatic attraction between positively charged ions and negatively charged surface interfaces. The surface charge on soil results from two processes: 1) ionic substitution of Al^{+3} for Si^{+4} in the crystal lattice of clays; and 2) the ionization of protonated surface functional groups such as aluminol and silanol sites at crystal edges of clays (Stumm and Morgan, 1996), carboxyl sites on hydrous ferric oxides (Dzombak and Morel, 1990), and carboxyl and phenol sites on organic matter (Davis, 1984).

Ion exchange is the process where trace metals such as mercury replace major cations on permanently charged clay interfaces. It is normally modeled by assuming that all exchange sites in the mineral are occupied (Appelo and Postma, 1993). There is thus no net surface charge, and after the number of exchange sites has been defined, equilibria can be calculated from a set of exchange constants using mass action, mass balance, and charge balance equations.

Surface complexation is the process where trace metals compete with H^+ ions and other cations to form surface complexes with oxygen atoms:



where [$>S$] denotes the mineral surface. This surface complexation process is pH dependent. As pH increases, an adsorption edge is observed in laboratory experiments where trace metals more effectively compete for the surface hydroxyl groups.

Surface complexation processes are difficult to model because surface sites can have net surface charges that must be balanced within a diffuse region extending into the solution (Adamson, 1990). Because the dielectric permittivity of this diffuse region is necessarily different than the bulk medium, the electrical potential energy of an ion in the vicinity of a charged surface is also modified. Consequently, the reactivity of the ion changes, and surface equilibrium constants must be corrected for surface charge (Koretsky, 2000). The constant capacitance model, the diffuse double layer model, and the triple layer model are three methods for correcting for changes in the vicinity of a surface (Schindler and Stumm, 1987).

Due to the fact that the database for all possible surface reactions is currently incomplete, and because there is uncertainty about the type and number of surface sites in soils, two simplifications have been employed to successfully model natural systems. The first is the use of empirical surface complexation constants derived specifically for the soil of interest (Davis et al., 1998; Celis, et al., 2000). The second is the use of a non-electrostatic model (James and Parks, 1975; Davis et al., 1987). This latter approach has been shown to be viable because the chemical contribution to the Gibbs free energy of adsorption is much larger than the electrostatic contribution for moderately or strongly sorbing ions such as mercury.

For adsorption to clay or organic matter, this study used the non-electrostatic model developed by Tipping and Hurley (1992) and Appelo et al. (1998). In addition to being similar to the processes of interest in this study, the model of Appelo et al. (1998) is calibrated within a wide range of electrolyte concentration and a pH from 3 to 10. Because exchange constants for mercury were not included in their database, they were derived in this study from the sorption

experiments of Nguyen et al. (1994). Exchange constants for other trace metals were not calculated because mercury is more strongly-bound (Tipping, 1998), and primarily competes with hydrogen ions for surface sites (Kerndorff and Schnitzer, 1980).

Precipitation and Dissolution Processes

The thermodynamic database of Allison et al. (1990) was used for most minerals. The exceptions were stability constants for mercury solid phases, which were taken from the SUPCRT database (Johnson et al., 1992), supplemented by the recent thermodynamic compilation of Bessinger and Apps (2002).

A-3 Model Calibration

Aqueous Reactions

Equilibrium constants for organo-mercury complexes were derived in this study from adsorption experiments between mercury and organic carbon by assuming that the stability constants between the functional groups on solid phase organic carbon are the same as dissolved organic carbon. With this assumption, the amount of organically complexed mercury was calculated by multiplying the total amount of mercury adsorbed to organic matter by the fraction of the organic matter that is dissolved. This study used the relationship between DOC and TOC derived by Moore et al. (1992) for number of soils with varying pH (3.8 to 8.5), and organic content (0.1 to 4.3%). The DOC fraction obtained from these calculations was subsequently modified for pH-dependent sorptivity using the experimental results of Jardine et al. (1989), regressed to fit to a Langmuir isotherm of the form:

$$S = S_{\max} \left(\frac{C}{K + C} \right) \quad (1)$$

Where S is the amount of humic adsorbed (mg/kg), C is the equilibrium dissolved concentration (ug/L), and K is the dissociation constant for the mineral-humic complex (Jones et al., 1998). Predicted partitioning of DOC is shown on Figure A1, and the pH-dependent function used for calibration on Figure A2. The general shape of the curve on Figure A-2 is consistent with the pH-dependent mercury sorption behavior experimentally observed by Lee et al. (2001). Although ionic strength can alter the adsorption isotherm, ionic strength has been shown to be of secondary importance relative to pH (Jardine et al., 1989).

Ion Exchange Reactions

The ion exchange constant for Hg^{2+} adsorption to clay was derived from the experimental study of Nguyen et al. (1994). Their described experiments were re-specified in PHREEQC (using the ion exchange constants for other species from Appelo et al. (1998)), to obtain the exchange constant that minimized the least squares fit to the data. The value derived in this study is shown in Table A1, and the fit to the data in Table A2.

Surface Complexation Reactions (Hydrous Iron Oxides)

This study used the diffuse double layer model of Dzombak and Morel (1990) to simulate the sorption of mercury to iron hydroxides. Stability constants for the interaction of iron minerals and most species were taken from the PHREEQC thermodynamic database. The constants for

Hg²⁺ were derived from the experimental sorption study of Bonnissel-Gissinger et al. (1999). The exchange constants reported in Table A1 were found by re-speciating the experiments in PHREEQC, and then minimizing the least squares fit to the data. The graphical fit to the data is shown on Figure A3.

Surface Complexation Reactions (Organic Matter)

This study used the non-electrostatic surface exchange model Appelo et al. (1998) to simulate the sorption of mercury to organic matter. Because this model does not contain exchange constants describing interactions between mercury and organic matter, they were generated as part of this study.

Ideally, experiments used for calibration would have achieved equilibrium between solid and aqueous phases and would have sufficiently characterized the chemistry of the system to quantitatively interpret the results. Calibration would subsequently proceed by speciating the experiments using the PHREEQC model, and adjusting the equilibrium constants describing mercury-humic interactions until the difference between modeled and measured solubility was minimized. Unfortunately, the two experimental studies that examined the solubility of mercury in the presence of humic acid did not achieve equilibrium between solid and aqueous phases. In Ravichandran et al. (1998), cinnabar only partially dissolved under oxic experimental conditions, and in Melamed et al. (1997), metallic mercury was dissolved for eight days, with continual increases in dissolved mercury concentration observed during the experiments (Melamed et al. (1997) also did not adequately characterize the nature or amount of dissolved organic matter in their experiments).

Considering the limitations imposed these experiments, organic exchange reactions were derived from adsorption experiments on multi-mineralic soils. By utilizing the reaction constants previously derived for clay and iron oxyhydroxide interactions, it was possible to isolate the effects of mercury adsorption to organic matter. The experiments of Hogg et al. (1978) (along the linear part of their adsorption isotherms) were re-speciated as before. The resulting predictions are shown on Figure A4, and exchange constants for six types of exchange sites are shown in Table A1. Despite the fact that the same constant was used for all six surface types (Appelo et al., 1998), the constants are variable with respect to H⁺, allowing the model to capture pH-dependent sorption.

A-3 Model Verification

Although the experiments of Ravichandran et al. (1998) could not be used to obtain absolute equilibrium constants between mercury and humic acid, minimum values could be obtained. Exchange constants were obtained by first taking advantage of the fact that the experiments of Ravichandran et al. (1998) achieved a state of partial equilibrium, where concentrations of dissolved species did not change after 8 days. Using the total dissolved mercury concentration of their experiments, and their observation that dissolved mercury was never observed above the detection limit of 0.5 ug/L in the absence of humic acid, minimum exchange constants were calculated using PHREEQC and the total dissolved mercury concentration, with the stipulation that the inorganic fraction not exceed the detection limit. Minimum constants were found to be equal to 11.0, two orders of magnitude lower than those derived during calibration. Because

these are minimum values, they are consistent with the model developed in this study (where a value of 13.4 was used). Modeled and experimental results both in the absence and presence of Ca^{2+} are displayed on Figure A5. Inclusion of competing divalent cations decreases solubility by 85%.

A-4 Model Simulations

Model simulations were designed to replicate a mixture of sediment and DI-water with the same relative proportions of soil and water used in the D.I. TCLP and 8-day tests. The objective of using this mixture was to identify the dissolved species and adsorbing surfaces responsible for observed mercury concentrations. The effect of pH on dissolved mercury concentrations was incorporated in model simulations by titrating either HNO_3 or NaOH into the system. Additional simulations were also performed to ascertain the effect of adding limestone or PAC to the mixture.

To improve the accuracy of predictions, additional chemical characterization of uncomposited soil and cinder was performed. Analytical results on soil and cinder are presented in Table A3. Although sediment mercury concentrations were higher than those in the majority of composited samples, a value of 150 mg/kg was used during the simulations. It is important to note that the chemical analysis reported in this table is not charge balanced; however, this error was deemed to be less significant than the uncertainty of including a more comprehensive suite of elements necessary to achieve charge balance (because surface adsorption reactions for most elements are unknown within the framework of the model).

Because it has been shown that organic coatings on the surfaces of minerals can mask their sorptive behavior (Davis, 1984), calculations were performed with two concentrations of organic sorption sites, the higher concentration assuming that the cation exchange capacity originally assigned to the clays is instead related to organic matter. Resulting predictions are expressed as upper and lower estimates on Figures 5 and 6.

Confirmation of the validity of this approach is provided by the fact that predicted dissolved concentrations are within the range of those observed in the D.I. TCLP and 8-day tests. Although dissolved concentrations are higher than the 8-day tests, this is expected because the model only calculates equilibrium conditions and natural chemical processes are time-dependent.

Table A1. Surface Complexation Stability Constants Used by PHREEQC

Surface Type	Number of Site Types	Reaction ^a	log K
Clay	1	$Hg^{+2} + 2X' = HgX_2$	9.87
Fe _{hydroxide}	2 (weak, strong)	$ZOH + Hg^{+2} = ZOHg^+ + H^+$	(4.0, 7.0)
	2 (weak, strong)	$ZOH + Hg^{+2} + H_2O = ZOHgOH + 2 H^+$	(-3.3, -0.3)
	2 (weak, strong)	$ZOH + Hg^{+2} + Cl' = ZOHgCl + H^+$	(5.8, 8.8)
Organic ^b	6 (Ya...Yf)	$Hg^{+2} + 2Y' = HgY_2$	13.4

^aX, Y, Z denote surfaces; ^bSame constant used for all six sites

Table A2. Predicted and Measured Mercury Adsorption on Clay (Nguyen et al. 1994)

Case	Solution Composition	Measured Adsorbed (%)	Predicted Adsorbed (%)
1	Hg Only; pH = 4.5	92	99
2	Hg Only; pH = 5.5	100	99
3	Hg + 10 x 10 ⁻⁵ NaCl; pH = 4.5	68	68
4	Hg + 10 x 10 ⁻⁵ NaCl; pH = 5.5	100	98
5	Hg + 5 x 10 ⁻⁵ CaCl; pH = 4.5	70	68
6	Hg + 5 x 10 ⁻⁵ CaCl; pH = 5.5	100	98

^aX, Y, Za, and Zb denote surfaces; ^bSame constant used for all six sites

Table A3. Measured Chemical Parameters of Soil and Cinder and Properties Used in PHREEQC

Parameter	Soil Sample	Cinder Sample	PHREEQC
pH	6.6	7	7
Ca(mg/L)	110	76	93
Mg(mg/L)	79	59	69
K(mg/L)	13	12	13
Na(mg/L)	420	350	385
HCO3(mg/L)	260	230	245
Cl(mg/L) ^a	690	400	545
SO4(mg/L)	160	570	365
DOC(mg/L)	20	14	17
pH	6.3	6.1	6.2
Sulfide(mg/kg)	910	180	NA
Mercury(mg/kg)	280	570	150
Fe(%)			1
Clay(%)	8.3	NA	8.3
TOC(%)	1.9	2.0	2.0
CEC(meq/kg)	120	120	120
porosity			0.4
bulk density			1.9

^aQA/QC qualifier on sample

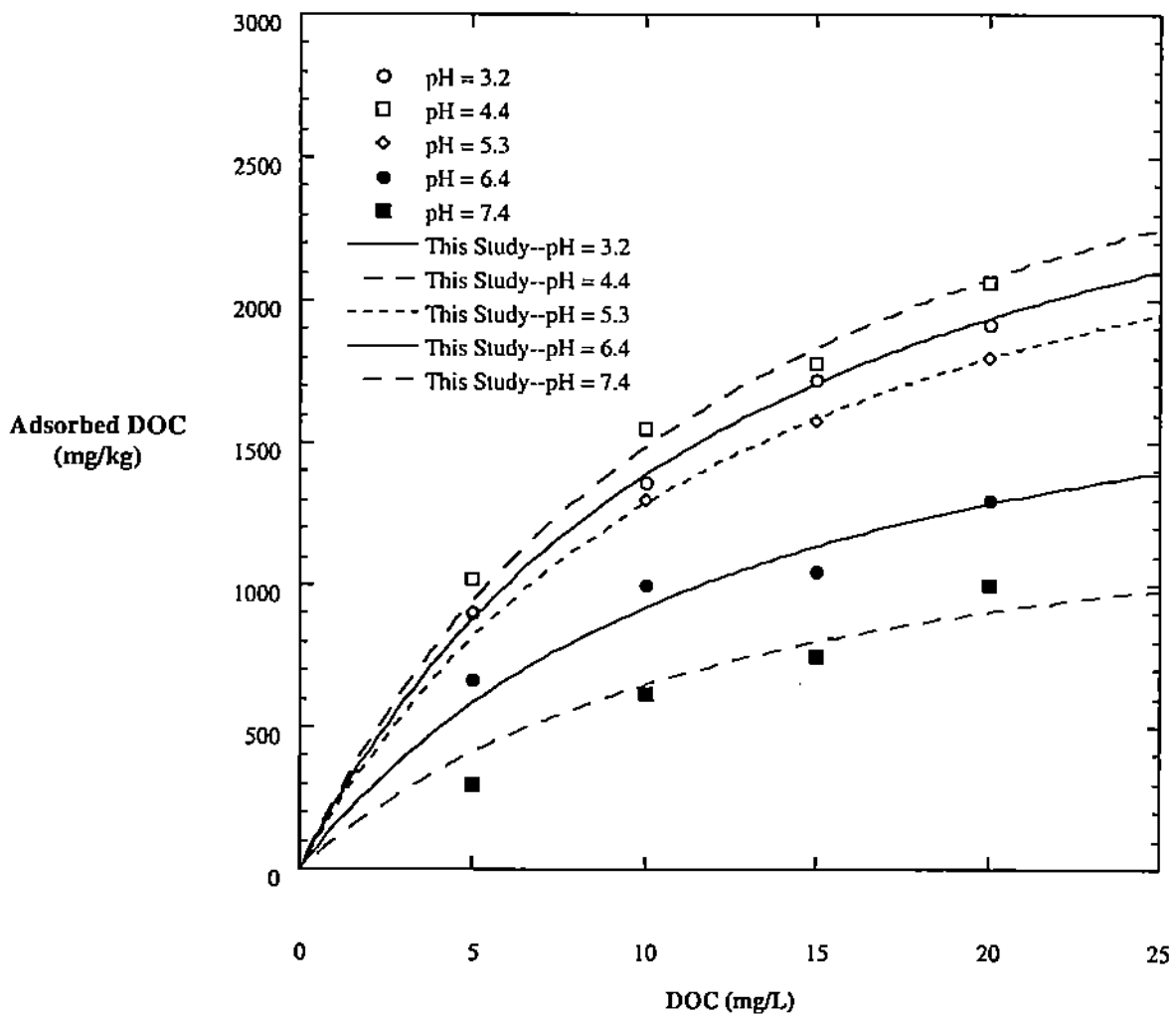


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Treatability Study

Description of Stability Constants Derived during
Calibration (TOP) Calibration Results (MIDDLE)
and PHREEQC Input Parameters (BOTTOM)

TABLES
A1 - A3



URS

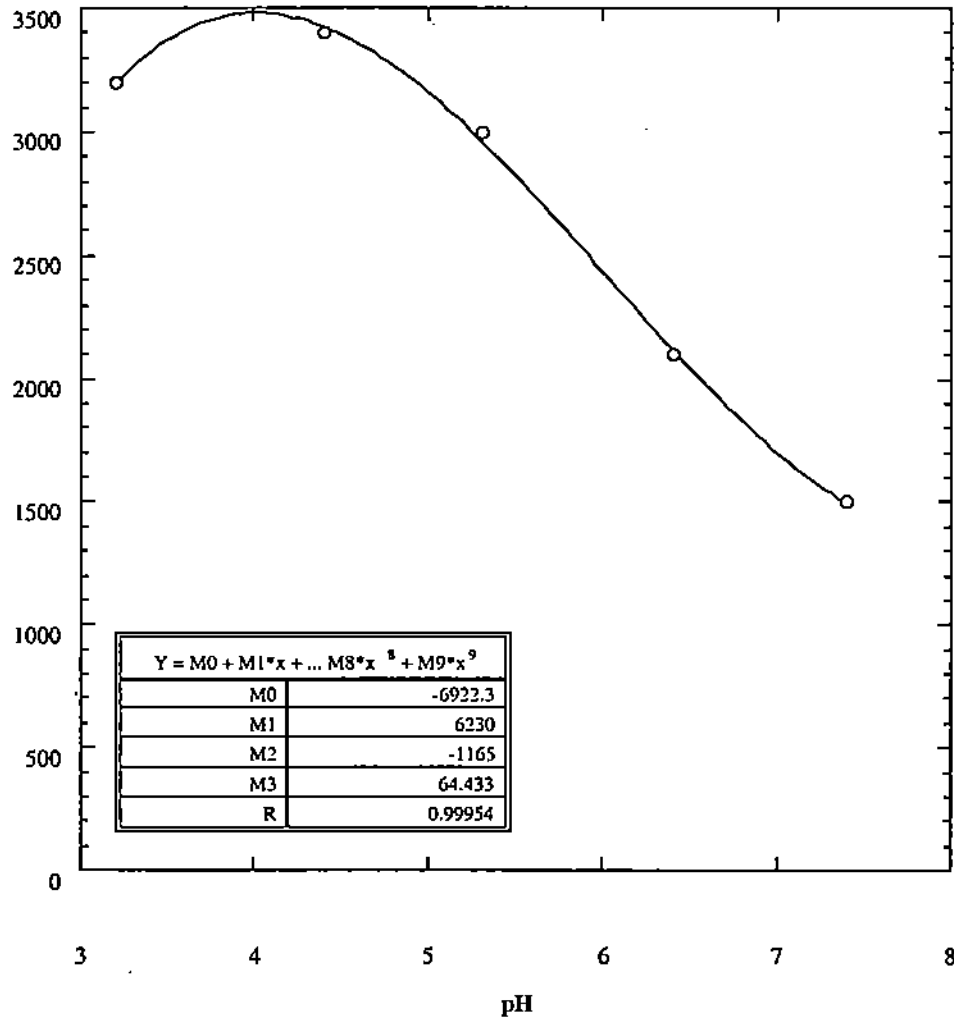
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PHREEQC Predicted DOC Concentration as a
Function of pH and the Experimental Results of
Jardine et al. (1989)

FIGURE
A1

Smax (mg/kg)
(Jardine et al. 1989)

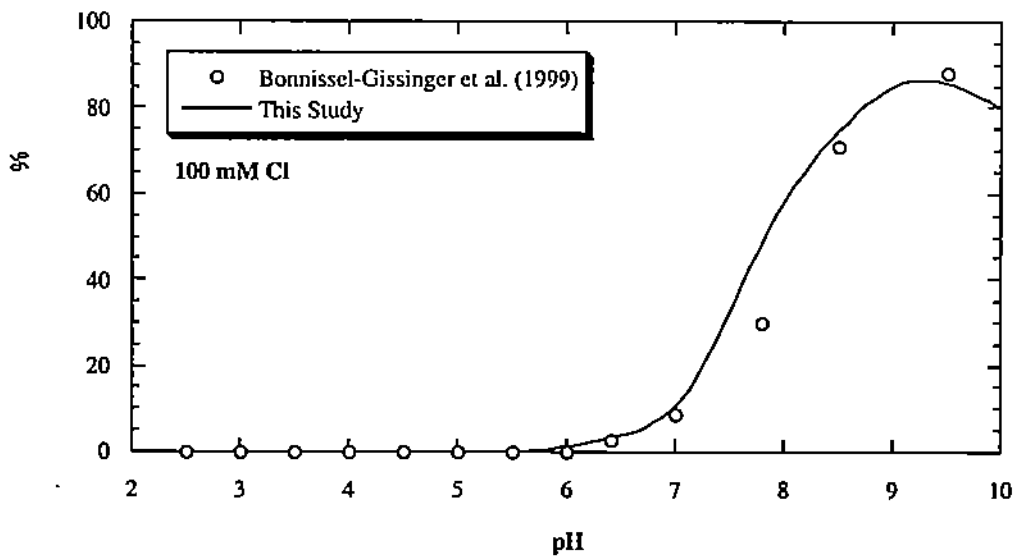
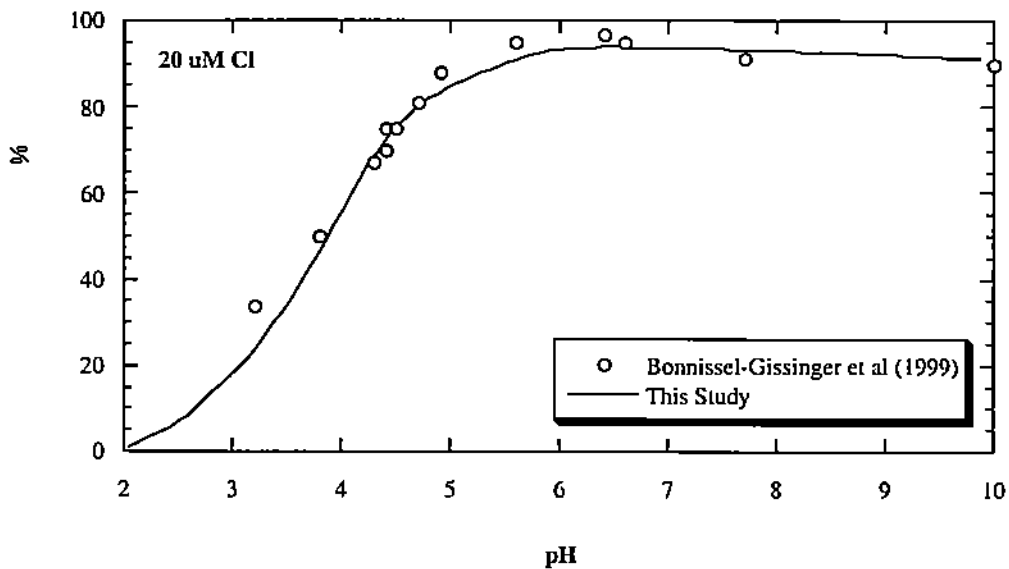


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Smax (Maximum Adsorption Capacity) Function
Used during PHREEQC Modeling to pH 8.0
(Constant Smax Used for pH > 8.0)

FIGURE
A2

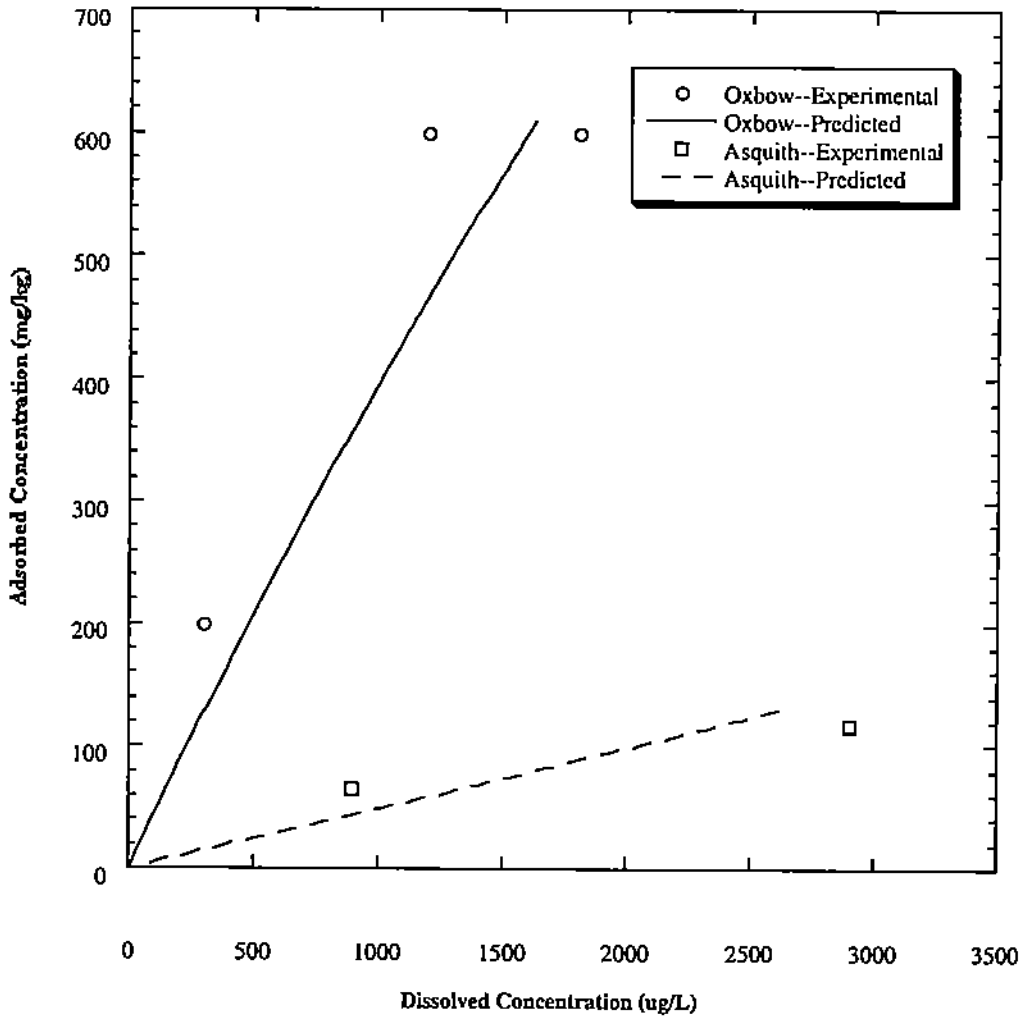


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PHREEQC Predicted Mercury Distribution and
 Experimental Mercury Distribution on Iron
 Hydroxide (Bonnissel-Gissinger et al., 1999)

FIGURE
 A3

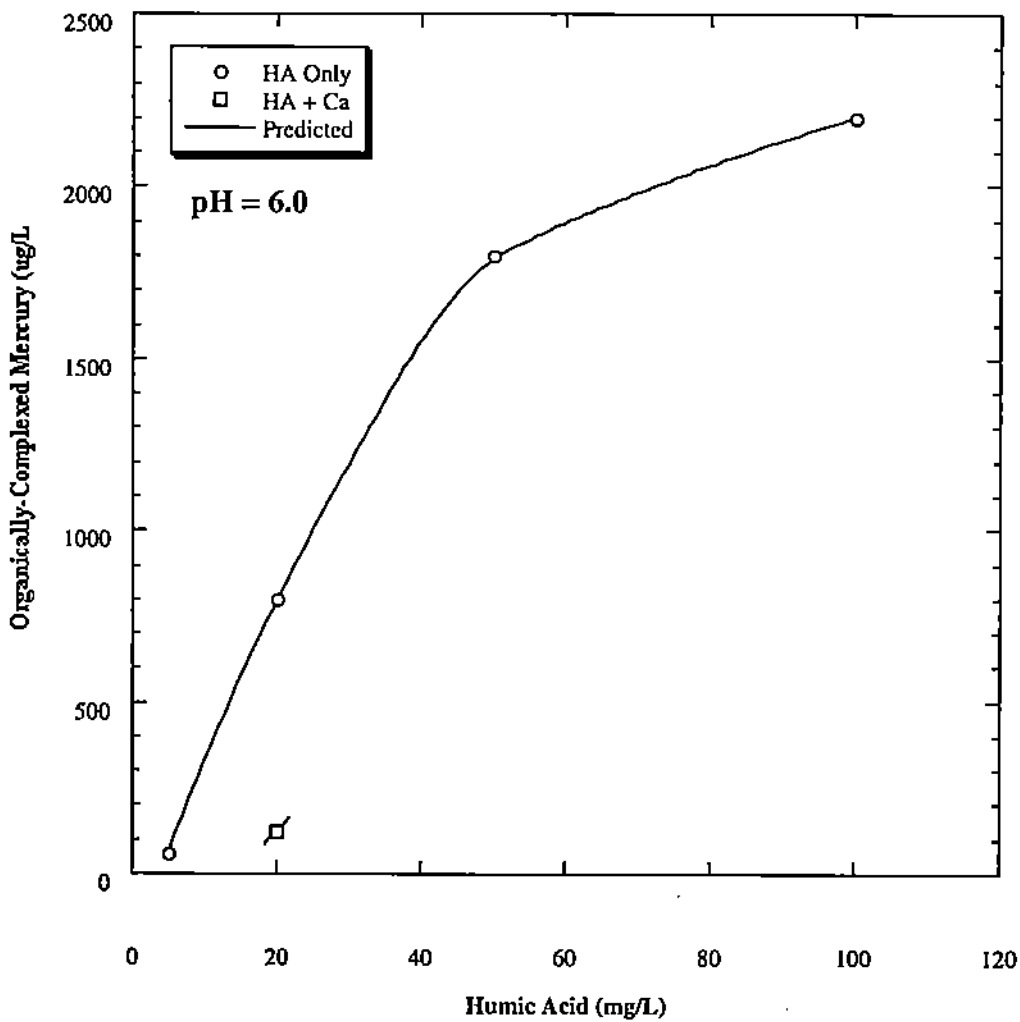


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PHREEQC Predicted Mercury Distribution and
 Experimental Mercury Distribution for Two Soils
 (Hogg et al. 1978)

FIGURE
 A4



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PHREEQC Predicted Organically-Complexed
Mercury Concentrations and Experimental Data
of Ravichandran et al. (1998)

FIGURE
A5

Attachment B. REFERENCES

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