Appendix R
Results of Selective Sequential Extraction Tests Performed on Soil
Date: December 16, 2011

To: Gaston Leone
    Richard Murphy

From: Michael Hay

Re: Results of Selective Sequential Extraction Tests Performed on Soil from the
    Former El Paso Smelter Site, El Paso, Texas

INTRODUCTION
The ARCADIS Treatability Laboratory (Durham, NC) recently performed selective sequential
extraction (SSE) tests on soils collected from the ASARCO Smelter Site, El Paso, TX. The
extractions were performed and the results were compiled by Stephanie Branch, under
guidance from David Liles. This memorandum summarizes the results of these tests and some
of their potential implications.

In the SSE procedure, a soil sample is suspended in a number of extraction solutions, in
sequence, designed to release constituents of concern (COCs) into solution that are bound
within the soil via different and progressively stronger mechanisms (e.g., sorbed to surfaces
with varying strengths, or coprecipitated with certain mineral types). The COCs targeted for
investigation in this study included arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu),
lead (Pb), and selenium (Se); the results for As, Cd, Pb, and Se are described below. Iron (Fe)
and manganese (Mn) results were also obtained and are described below.

These tests were performed to better understand the nature of the association of Site COCs with
the soil matrix. More specifically, they were performed to understand the sensitivity of soil-
bound COCs downgradient of potential treatment zones to changes in aqueous chemistry. This
knowledge is critical in effectively designing in situ treatment remedies. For example, if
certain COCs are weakly sorbed to soils downgradient of a permeable reactive barrier, those
COCs may be desorbed at unacceptable levels if the PRB releases other chemical species that
can exchange for or displace the sorbed COC. Conversely, if COCs are found to be strongly
associated with the soil (e.g., coprecipitated within oxide phases), the tests provide confidence
that those COCs will not be sensitive to minor changes in aqueous chemistry.

SELECTIVE EXTRACTION SOLUTIONS AND PROCEDURE
The following extraction solutions were used in the SSE tests:
1) 1 mol/L (M) MgCl₂, pH 7. Target: Exchangeable (weakly sorbed) ions.
2) 0.1 M NaH₂PO₄, adjusted to pH 5 with H₃PO₄. Target: Oxoanions (such as arsenate
    and arsenite) that are more strongly sorbed to oxide surfaces and can be displaced by
    phosphate.
3) Citrate-bicarbonate-dithionite (CBD): 0.3 M Na-citrate, 0.2 M NaHCO₃, 1 g/g soil Na-dithionite. Target: Metals coprecipitated with iron oxyhydroxides.

4) Microwave digestion in nitric/hydrochloric acid (EPA Method 3051A/6010). Target: All residual metals not extracted in previous steps, primarily associated with crystalline oxides and silicates.

One gram of each soil sample was subjected to the extraction solutions in sequence. Each extraction step involved suspension of sample in the extraction solution (solution volume ranging from 8 – 40 mL), continuous agitation for between 1 and 24 hours, and centrifugation to remove the solution. For solutions 1 and 2, this step was repeated with fresh solution to obtain a more thorough extraction. After decanting the extraction solution, the soil samples were suspended in deionized water for 15 minutes, recentrifuged, and then resuspended in the next extraction solution. The extraction and water rinse solutions within each of the four extraction steps were filtered, combined, acidified, and sent to an analytical laboratory for analysis.

In addition to this extraction series, separate extractions were performed on samples from the same locations using Site groundwater only, collected from well EP-95 (unimpacted area east of I10; see Figure 1). These extractions were performed using a ratio of 70 g soil to 70 mL groundwater. Total metal analyses were also obtained on separate subsamples of raw, un-extracted soil following microwave acid digestion (Method 3051A/6010) to assess mass recovery in the SSE procedure.

For further experimental details and references, see the ARCADIS Best Practice document “Selective Extraction of COCs in Waste or Soil” prepared by Jeff Gillow and the SSE memorandum prepared by the Durham Treatability Laboratory prepared for Richard Murphy, dated October, 2011.

RESULTS

The soil samples collected from the field and submitted for SSE analysis are listed in Table 1, and the locations of the boreholes are shown in Figure 1. All of the samples were collected from the saturated alluvium in order to assess the potential for desorption downgradient of permeable reactive barrier treatment zones. In Figures 2-4, the extraction results are presented in order (from left to right) moving downgradient along the groundwater flow direction, starting upgradient of the Site (east of interstate 10) and moving west to the Ephemeral Pond, then further west into the Parker Brothers Arroyo.

Figure 2 shows the SSE results for As. All samples (impacted and unimpacted) exhibit low amounts of As release by native groundwater. In the upgradient unimpacted zone, the majority of the soil-associated As is present in the CBD-extractable fraction. The fact that this As was not released by MgCl₂ and phosphate solutions demonstrates that the As is present as a co-precipitate within metal (primarily Fe) oxyhydroxides, rather than in an adsorbed form. This is consistent with the low dissolved As concentrations observed in well samples and suggests that As is not mobile in this area and is representative of background conditions.
In contrast, soils from source areas such as the Ephemeral Pond (EPH-SB02) and impacted soils downgradient contain substantial concentrations of As in sorbed forms, which are expected to be more mobile depending on geochemical conditions. The majority of this form is released within the phosphate extraction. This is not surprising, as both arsenate (As(V)) and arsenite (As(III)) are well-known to form inner-sphere complexes on oxide surfaces via hydroxyl ligand exchange, yielding a strongly-adsorbed surface complex. However, the MgCl₂ extraction demonstrates that a significant amount of As (up to 6 mg/kg soil [EPH-SB02]) may also be present in a weakly sorbed/ion exchangeable fraction. Note that the CBD-extractable As content for most impacted soils is similar to the unimpacted soil value, suggesting that the majority of this fraction in impacted soils may actually be due to background As. On the other hand, the residual As fraction (released in the microwave acid digestion) was considerably higher in the impacted soil relative to background, particularly in the most highly impacted areas (ephemeral pond, PBA-SB06). This suggests that some contaminant As does get incorporated into a more recalcitrant form in the soil.

SSE results for Cd, Pb, Fe, and Mn are shown in Figure 3. Pb appears to follow similar trends to As, exhibiting high concentrations underneath the ephemeral pond and at PBA-SB06, near the fluctuating water table. The majority of the Pb is not easily desorbed and is only released on dissolution of mineral phases by CBD extraction and acid digestion. Cd on the other hand does not correlate with As and Pb, exhibiting a hotspot at PBA-SB10. The majority of the Cd appears to be located on cation exchange sites within the soil. Results for Fe and Mn illustrate that the CBD extraction was able to dissolve a large fraction, though not all of the Fe- and Mn-oxides present within the soil. For Fe in particular, the majority of the metal was released in the subsequent acid digestion. The results also demonstrate that some Mn is present within ion-exchangeable and specifically-sorbed forms.

Total soil, SSE, and 1:1 soil-groundwater extraction results were also obtained for Se on all samples. Total Se concentrations by 3051A acid digestion/6010 analysis were below the analytical detection limit in all cases, indicating total Se concentrations of < 2.7 mg/kg. All SSE extraction solutions also had Se concentrations below the detection limit, with the exception of the CBD extraction. However, reagent blanks (i.e., extraction solution not reacted with soil) were also submitted for analyses, and Se concentrations in the CBD blanks were of the same magnitude as the CBD extractants, indicating that most, if not all of the Se detected in the CBD extraction was due to reagent contamination. This contamination most likely originated in the Na-dithionite reagent; although the treatability laboratory attempted to obtain the most pure form available, the reagent was of limited purity (85% technical grade).

Although the CBD extractions were inconclusive for Se, the MgCl₂ and NaH₂PO₄ extractions indicate less than 0.7 mg/kg of Se released by each method (based on detection limit), suggesting that the readily-desorbable Se fraction is minimal. This is also confirmed by the 1:1 groundwater extractions. Se was detectable in all solutions in this extraction, since 1) the samples did not need to be diluted as strongly for ICP analysis, and 2) the groundwater used had a background Se concentration of 0.02 mg/L. After correction for background Se in the groundwater, the 1:1 groundwater extractions indicate a groundwater-labile soil Se concentration of less than 0.04 mg/kg in all cases except EPA-4 (unimpacted area). EPA-4 indicated a higher labile soil Se concentration (0.13 mg/kg), but that sample also failed an ICP
quality-control check (M7 error), suggesting that the sample may have been reading artificially high for Se.

TOTAL COC RECOVERY BY THE SSE METHOD

To assess the total COC recovery and potential mass loss during SSE, the total SSE-extracted COC concentrations (i.e., the sum of individual extractant values) were compared to total COC concentrations obtained on separate samples by acid digestion (3051A, as in SSE step 4). Careful consideration of these data is important, as it has key implications for the reliability of the SSE results. These results are shown in Figure 4, where the first panel gives the total SSE-extracted value as a fraction of the total acid digestion value.

In the case of As, the total recovery by SSE was within 80% for most samples, but was as low as 64% (ephemeral pond replicate 1). Part of this difference may be attributable to natural sample variability, particularly since only 1 gram of soil was used in the SSE experiments; this would account for the two samples where SSE results were 20% greater than total soil values. However, the majority of the total soil values were higher than the sum of SSE values, suggesting some systematic error in the SSE results. Specifically, the treatability laboratory suspects that some soil was lost in the repeated centrifugation, decanting, and filtration steps of the SSE procedure.

The results for Cd, Pb, Fe, and Mn also demonstrate incomplete recovery or loss of metals by the SSE procedure (Figure 4). Recovery was the lowest for Fe and Pb, where for one sample the recovery was only 18%. Comparison with the results in Figures 2 and 3 suggests that the discrepancies are greatest for those metals that exhibit large contributions in the 3051A extraction step. This is consistent with the notion of a compounded error resulting from repeated centrifugation/filtration steps. The loss of mass throughout the extraction procedures would have the greatest impact on the last step, whereas the first step would not be affected at all. It is also possible that the Fe and Mn oxides are disproportionately present within smaller size fractions that do not settle as easily on centrifugation. Fe, Mn, and metals that tend to be strongly associated with them would then be more susceptible to loss when the extraction supernatant is removed and filtered. Similar results for Fe and Pb were obtained in a previous SSE study performed for ARCADIS, where Fe recovery ranged from 58 – 90% and Pb recovery ranged from 28 – 133%. A literature review to assess whether these levels of mass recovery are typical in SSE experiments is warranted, as well as a reevaluation of the experimental procedures to determine steps that can be taken to enhance recovery and decrease variability, such as the use of larger soil volumes.

SUMMARY AND IMPLICATIONS

A substantial fraction of soil-bound As in impacted areas is present within readily exchangeable and specifically-bound forms. This observation should be taken into account when designing treatment strategies upgradient of impacted areas. The readily exchangeable fraction (MgCl₂ extraction) may be particularly sensitive to changes in cation/anion balance or TDS, while the specifically-sorbed fraction (NaH₂PO₄ extraction) will be more sensitive to concentrations of oxoanions such as phosphate and, to a lesser extent, carbonate and sulfate. Cd, which is predominantly present on cation exchange sites, as well as a small proportion of the Mn, will also be sensitive to shifts in the solution cation balance, whereas Pb is more
strongly bound within the soil matrix. Although COCs within the CBD-extractable fraction should not be considered available for desorption, this fraction may be sensitive to release if the redox conditions were to shift to favor Fe and Mn reduction. Finally, although low recoveries were observed for some COCs by SSE, this problem seems to have a minimal effect on estimations of the desorbable fractions. In light of the lack of complete recovery by SSE, the observed extraction concentrations should be considered conservative minimum values.

Attachments
### TABLE 1

**SOIL BOREHOLE SAMPLES FOR SSE ANALYSIS**  
**FORMER ASARCO SMELTER SITE**  
**EL PASO, TEXAS**

<table>
<thead>
<tr>
<th>SOIL BORING a</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA-4</td>
<td>East of I10, effectively unimpacted background soil.</td>
</tr>
<tr>
<td>EPH-SB02-(15-16)b [2X]c</td>
<td>Beneath ephemeral pond.</td>
</tr>
<tr>
<td>PBA-SB13-(30-32)</td>
<td>Downgradient of slag pile.</td>
</tr>
<tr>
<td>PBA-SB12-(28-30)</td>
<td>Downgradient of slag pile.</td>
</tr>
<tr>
<td>PBA-SB10-(15-17)</td>
<td>Downgradient of slag pile.</td>
</tr>
<tr>
<td>PBA-SB06-(15-17)</td>
<td>Downgradient of slag pile. Level is near fluctuating water table.</td>
</tr>
<tr>
<td>PBA-SB06-(28-30) [2X]</td>
<td>Downgradient of slag pile.</td>
</tr>
<tr>
<td>PBA-SB08-(19-20)</td>
<td>Downgradient of slag pile.</td>
</tr>
<tr>
<td>PBA-SB08-(24-25)</td>
<td>Downgradient of slag pile.</td>
</tr>
</tbody>
</table>

Notes:  

a Soil borehole samples submitted for SSE analysis, given in order along the groundwater flow direction.  
b Numbers in parentheses give sampling depths in feet below ground surface.  
c Samples with [2X] indicate that the SSE experiments were run in duplicate.
Figure 1. Locations of boreholes from which samples were collected for SSE analyses (gold circles). Groundwater was collected from well EP-95 (red circle).
**Figure 2.** Concentrations of arsenic released by each extraction, given on a soil mass basis.
Figure 3. Sequential extraction results for Cd, Pb, Fe, and Mn.
Figure 4. Sequential extraction mass balance/SSE recovery results for As, Cd, Pb, Fe, and Mn. The sum of COC concentrations observed in sequential extractions is compared to total COC by acid digestion.