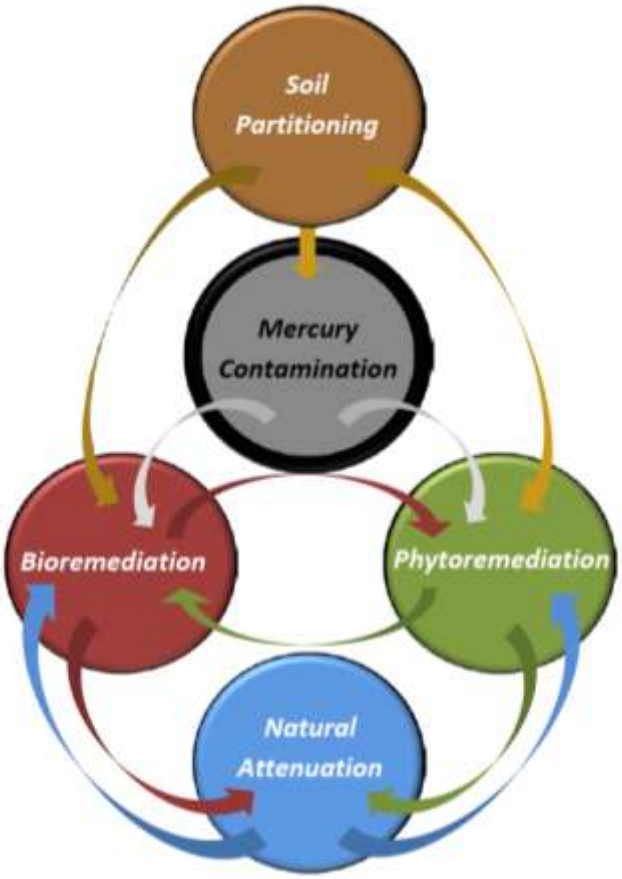
Evaluation of Mercury Contamination

Soil Treatability Studies
Area IV Santa Susana Field Laboratory
Ventura County, California



Final Report
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Prepared by Haizhou Liu
Department of Chemical and Environmental Engineering
University of California, Riverside, CA 92521
Tel: (951) 827-2076 Fax: (951) 827-5696
E-mail: haizhou@engr.ucr.edu

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1. Introduction

A mercury spill occurred at the Santa Susana Field Laboratory (SSFL) circa 2000 when the steam generation facility used for the sodium reactor experiment was being decommissioned. This spill is referred to as "the primary mercury spill" in this document. Mercury that was deposited on the soils and in the subsurface from the primary mercury spill was originally in its elemental state, as indicated by historical records. In addition to the primary mercury spill, other activities at SSFL may have resulted in smaller quantity mercury releases. The valence state of any spilled mercury (regardless of source) and its chemical speciation have likely been impacted by a series of biogeochemical processes in the subsurface since their release.

The purpose of this study is to determine the chemical form(s) of mercury present in Area IV soils. Knowledge of the mercury chemical form will help to evaluate the proper remediation technologies for these soils. This mercury study, along with the other four concurrent treatability studies that were conducted, will support the evaluation of methods for reducing the volume of contaminated soils that may need to be removed from Area IV by more traditional remediation methods, such as excavation and offsite transportation/disposal.

2. Roles and Responsibilities of Study Team

The mercury study team consisted of seven entities. These entities, and their roles and responsibilities, are briefly described below.

- The Department of Energy is a responsible party for Area IV of SSFL and provided funding for the study.
- CDM Smith provided overall project management and contracting, was jointly responsible for preparing the initial mercury contamination study plan, performing field sample collection, conducting the study with University of California-Riverside (UC Riverside) and the contract laboratory, and working with the California Department of Toxic Substances Control (DTSC) to gain regulatory acceptance of the study plan.
- UC Riverside was jointly responsible for preparing the mercury contamination study plan with CDM Smith, conducting the study with CDM Smith and the contract laboratory, and preparing this final mercury study report.
- DTSC is the regulatory agency over Area IV of SSFL.
- California Polytechnic State University, San Luis Obispo (Cal Poly) conducted the bioremediation, natural attenuation, and phytoremediation treatability studies with CDM Smith. As part of their studies, Cal Poly reviewed the analytical chemistry data from this study to determine if the chemical form of mercury present in Area IV soils would be bioavailable or could be converted to a different state that can be readily remediated by bioremediation or phytoremediation.

- Eurofins Lancaster and Eurofins Frontier Global Services (collectively the "contract laboratory") performed chemical analyses of the mercury study soil samples. The contract laboratory performed their analyses at the aforementioned two Eurofin facilities.
- The Soil Treatability Investigation Group (STIG) was updated on study progress and results.

3. Basis of the Study

3.1 Study Objectives

The objectives of the mercury contamination study were to:

- Determine the current valence state of mercury in contaminated Area IV soils;
- Understand the spatial distribution of mercury valence states at different Area IV sites;
- Quantify the speciation and mobility of mercury at different soil depths; and
- Recommend efficient *in situ* mercury remediation technologies.

3.2 Study Phases

The mercury contamination study phases were:

- Phase 1: study plan preparation, review, and finalizing; STIG meetings concerning the study plan.
- Phase 2: field soil sampling and analysis of samples by contract laboratory.
- Phase 3: UC Riverside review and analysis of sample results; STIG meeting concerning study results.
- Phase 4: final report preparation.

3.3 Study Limitations

Sampling sites for mercury soil depth analysis were focused on sites with known or suspected contamination and that had the potential for *in situ* remediation (e.g., would be amenable to bioremediation or phytoremediation). Due to the areal extent of Area IV, not every potential sampling location could be sampled. However, total mercury analysis was conducted at multiple locations within Area IV in 2011, including at the sample locations selected for this study. The 2011 data were analyzed in conjunction with the data from the samples collected for this study. This study assumes that any mercury found in 2011 did not continue to migrate downward through the soil column between 2011 and 2014 (i.e., contaminant migration has slowed appreciably since the time period immediately following the release).

4. Study Materials and Methods

4.1 Background Information

4.1.1 Valence State of Mercury in Contaminated Soil

As previously stated, a spill of elemental mercury occurred in Area IV when the steam generation facility used for sodium reactor experiments was being decommissioned (in addition to other smaller mercury releases) [1]. *In situ* thermal treatment would be a viable remedial option if mercury still remained in its elemental form, as heat can drive mercury out of the soil and its vapor can be collected and contained for transport and disposal at an offsite treatment facility [2]. However, the valence state of mercury and its chemical speciation have likely been impacted by a series of bio-geochemical processes in the subsurface since the time of any release.

Total mercury concentration in soil has been analyzed in Area IV to some extent. However, total mercury analyses do not fully elucidate the behavior of mercury because mercury's reactivity and subsequent bioavailability are dependent on its speciation. The lack of data on the chemical speciation of mercury in contaminated soil poses uncertainties to the implementation of remediation technologies. Therefore, it is important to understand the current valence state of mercury species and consequently determine the most effective remediation treatment.

Mercury is a ubiquitous contaminant that can enter the environment from a variety of natural and anthropogenic sources. Natural sources include rock weathering, geothermal, and volcanic events [3-4], whereas anthropogenic sources are mainly solid waste incineration, coal combustion, metal smelting, and mining [5]. Once deposited in soil, mercury can exist in three valence states, *i.e.*, 0, +1, and +2.

- Hg(0): elemental mercury can be readily vaporized into a gaseous state. It can be oxidized to Hg(I), and subsequently to more stable Hg(II) forms [6]. Meanwhile, Hg(0) can be formed by reduction of Hg(II) under reducing conditions by abiotic reduction mediated by solid-phase Fe(II) [7], and biotic enzymatic reduction mediated by the presence of fairly ubiquitous mercury resistant bacteria that detoxify their environment by converting inducing concentrations of Hg(II) to Hg(0) [8].
- Hg(I): mercury in its +1 valence state only exists as the metastable dimer Hg_2^{2+} [9-10]. In soil environments, the Hg(I) dimmer is formed as a transient species during the oxidation of Hg(0) to Hg(II), but its relatively short half-life typically prevents it from concentrating to detectable values [6].
- Hg(II): mercury in its +2 valence state is usually the most dominant species in soil and aquifer sediment. Hg(II) can be present in both inorganic and organic forms. Inorganic Hg(II) species include mercuric chloride ($HgCl_2$), mercuric oxide (HgO), mercuric sulfide (HgS), and Hg(II) complexes with soil organic matter. Methyl mercury (CH_3Hg^+) is typically by far the most abundant organic form of Hg(II) in soil and groundwater. Dimethyl mercury, $(CH_3)_2Hg$, is another organic species that is highly volatile and very unstable in the presence of light and

typically only concentrates to detectable values in marine sediment and deep seawater [11]. During the methylation process, inorganic Hg(II) is transformed to the methyl mercury molecule.

Prior studies on mercury speciation in other contaminated soils have identified a variety of Hg(II) species after the deposition of elemental Hg(0) in soil [6]. For example, after a spill near a plant using elemental mercury for manufacturing thermometers, an average of 80% of the total mercury in soil was detected as Hg(II) 20 years after the spill. Fractionation analysis also showed that 60% of Hg(II) was bound to sulfide as HgS and 30% bound to soil organic matter, with 10% existing as methyl mercury [12]. The same study also found that the surface layer of soil (0-20 cm) was characterized by higher mercury concentrations than that of the subsurface soil (60-80 cm).

In another study to examine mercury speciation after an elemental Hg(0) spill in Oak Ridge, Tennessee, similar results showed that a majority of the Hg(0) had been oxidized to Hg(II) in soil samples [13]. Studies from different contaminated sites also found that the major Hg(II) species in soil included HgS, $HgCl_2$, $HgSO_4$, HgO, and Hg-organic complex [14-16]. Depending on its concentration, the residual Hg(0) (i.e., what is left after oxidation and volatilization) can either exist as concentrated spherical particles or adsorb to the surface soil particles. It was observed in the aforementioned study that the adsorption of Hg(0) on soil particles was enhanced with decreasing soil particle sizes [17]. The total mercury concentration in contaminated soils referenced in many of these previous studies had similar ranges to those detected in Area IV soils.

4.1.2 Speciation of Mercury(II) in Contaminated Soil

The biogeochemistry of mercury in soils and sediments has been found to be dominated by inorganic and organic Hg(II) complexes. A summary of the important biogeochemical processes that determine the valence state of mercury and its speciation is presented in Figure 1. Hg(II) is generated via the oxidation of Hg(0). Hg(II) can be abiotically reduced to Hg(0) by iron-containing minerals in soil in anoxic conditions [18]. Bacteria can also promote Hg(II) reduction by catalyzing electron transfer from an electron donor to Hg(II) [19, 21]. The speciation of Hg(II) complexes depends on multiple parameters in the subsurface including oxygen level, ionic composition, soil organic content, and microbial activities. The speciation of inorganic Hg(II) compounds in soil is affected by the presence of various inorganic ligands.

Under oxidized surface soil conditions, chloride (Cl^-), hydroxide (OH^-) and sulfate (SO_4^{2-}) have the largest influence on Hg(II) speciation. Consequently, $HgCl_2$, HgOHCl, $Hg(OH)_2$ and $HgSO_4$ are the predominant forms of inorganic mercury [14-16]. Under anoxic subsurface soil and sediment conditions, in the presence of sulfide (S^{2-}) that is produced by sulfate-reducing bacteria [22-23], Hg(II) speciation is controlled by cinnabar $HgS_{(s)}$ [13,24]. Its dissolved uncharged complexes, *e. g.*, HgS^0 and $Hg(HS)_2$, are capable of passively diffusing into bacterial cells [25-26] and undergoing methylation to form methyl mercury by sulfate-reducing bacteria [22-23] and in some cases iron-reducing bacteria [27-28]. In addition, active uptake of mercury sulfide by sulfate-reducing bacteria is an important pathway for methylation in anoxic conditions [29].

In addition to complexation with inorganic ligands, Hg(II) can be bound by soil dissolved organic matter (DOM), which is primarily composed of humic substances [30-31]. Among different functional groups in humic substances, the reduced-sulfur moieties (e.g., thiol, sulfide, and bisulfide groups) have the highest Hg(II) binding constants and dominate the speciation of Hg(II)-DOM complexes [32-34]. As a result of this strong association, Hg-DOM complexes are a major control on the fate and transport of Hg in soil and sediment, except under high sulfidic conditions [30].

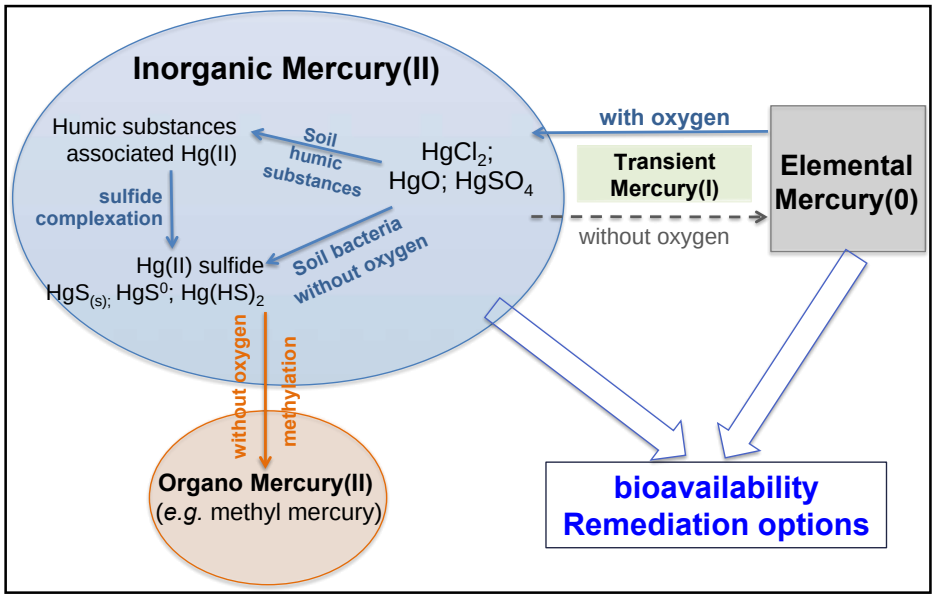

Figure 1: The valence states of mercury and its speciation in contaminated soil controlled by different biogeochemical processes.

4.1.3 Mobility and Bioavailability of Mercury in Contaminated Soil

The valence state and speciation of mercury significantly affect its solubility and bioavailability in soil, and consequently impact the choice of remediation options. Meanwhile, mercury adsorption to soil mineral surfaces also affects its mobility and bioavailability. Prior studies have found that an increase in chloride concentration and a decrease in pH can decrease mercury adsorption and therefore increase the labile fraction of mercury [15-16], which can potentially create a more favorable environment for mercury uptake by plants and application of phytoremediation. Iron-containing minerals in the clay fraction of soil particles have a strong capability of adsorbing mercury [35]. In addition, the mobility and bioavailability of mercury can be quite different in varying depths of the vadose zone. It is expected that in vegetated areas, the surface soil layer near the roots of vegetation has higher DOM content and thus a potential for higher concentrations of Hg(II)-DOM complexes. Consequently, the amount and chemical composition of DOM in soil play a major role in the transport of mercury through soil profiles [36].

4.2 Field Sampling

This study anticipated significant heterogeneity of total mercury concentrations throughout Area IV soils, so a review of the existing soil analytical chemistry data set was conducted. Soil samples for this study were then collected and analyzed from four locations previously sampled in 2011.

The sample locations for this study included:

- Two locations near the aforementioned primary mercury spill site (SL-284-SA6 and STS-73-SA6)
- One location in subarea 5B near the 17th street pond and drainage area (SL-212-SA5B)
- One location in subarea 5D North (STS-113-SA5ND).

For location SL-284-SA6, samples were previously taken from five depths on November 30, 2011: 0.5 to 1.5 ft, 4 to 5 ft, 9 to 10 ft, 14 to 15 ft, and 15.5 to 16.5 ft. Sampling for this treatability study was then conducted on May 19, 2014 (this date applies to all mercury treatability study samples) with one sample taken from the soil depth of 0.5 to 1.5 ft.

For site STS-73-SA6, samples were taken from 4 to 5 ft on July 21, 2011. The samples for this treatability study were taken from 0.5 to 1.5 ft and 3 to 4 ft. For the treatability samples from this location, the sample ID is "STS-73-SA6RS," where RS means "resampling." These samples had to be re-collected due to shipping issues with the first set of treatability study samples collected from this location. A duplicate sample was also taken at this location and was named "STS-373-SA6."

For site SL-212-SA5B, samples were previously taken from 0 to 0.5 ft on December 20, 2011. The samples for this treatability study were taken from two soil depths: 0.5 to 1.5 ft and 3 to 4 ft.

For site SL-113-SA5ND, sampling was previously conducted on June 10, 2011 and samples were taken from two soil depths: 0 to 0.5 ft and 4 to 5 ft. The samples for this treatability study were taken from 3 to 4 ft.

The sample locations are presented in Figure 2.

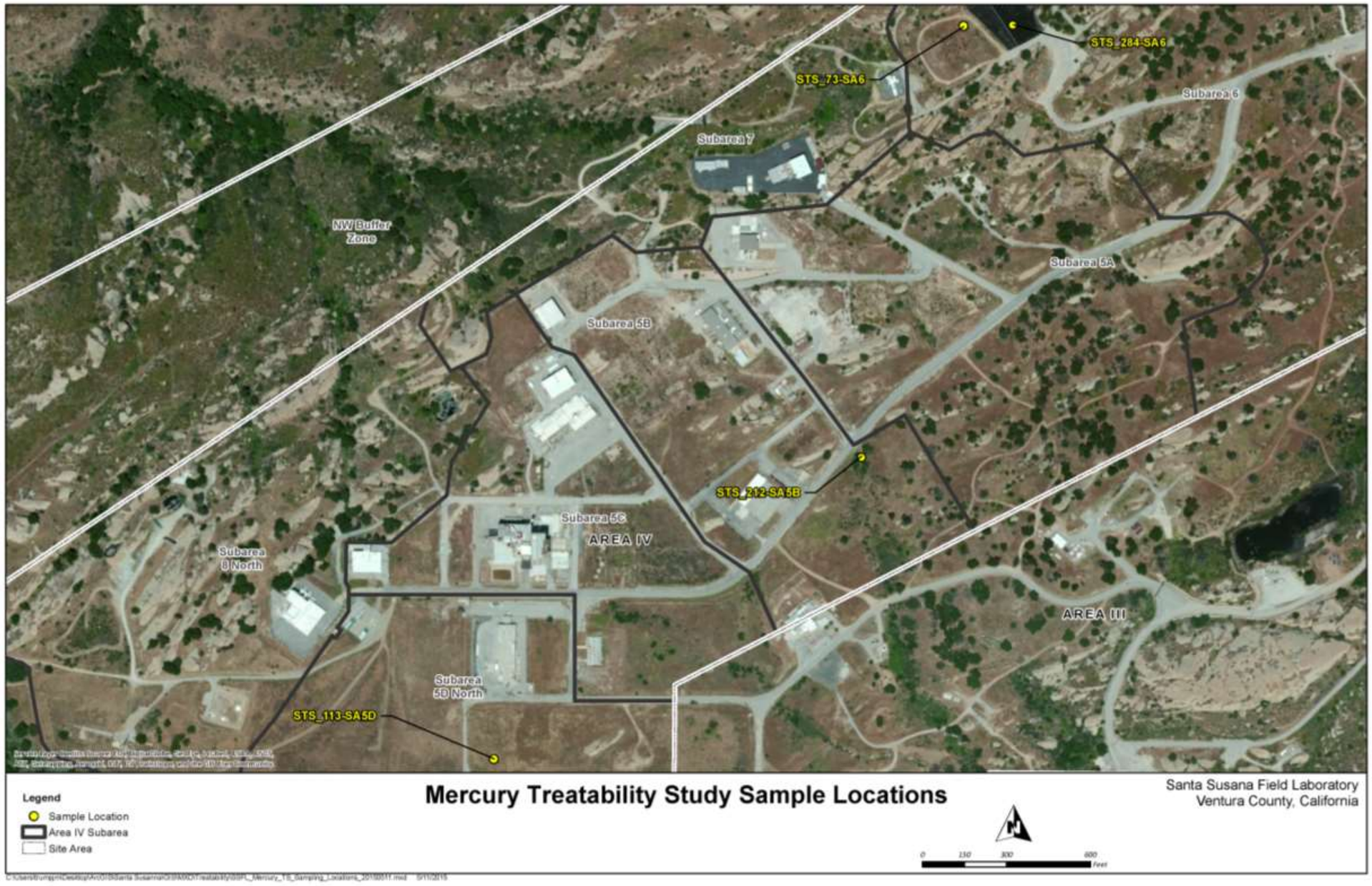

Figure 2: Mercury Treatability Study Sample Locations

4.3 Soil Analytical and Quality Assurance Procedures

Chemical compositions of soil samples were analyzed for the analytes presented in Table 1. The mercury complex speciation process is detailed in the next two subsections.

The field sampling and analytical methods included procedures from the quality assurance project plan (QAPP) outlined in the Master Field Sampling Plan for Chemical Data Gap Investigation, Phase 3 Soil Chemical Sampling at Area IV, Santa Susana Field Laboratory; Ventura County, California; April 2012 [39]. These have previously been approved by DTSC for other studies that have been or will be conducted at SSFL (Phase 3 QAPP). Routine analytical procedures were based on this Phase 3 QAPP. Analytical method reporting limits are presented in Appendix A of this document. Quality control objectives are also presented in Appendix B of this document.

Table 1: Minimum required sample mass, target sample volume, and analytical methods.

Analyte	Soil[a] - required mass (grams)	Analytical Method
Total Mercury	3	Cold vapor atomic absorption spectroscopy EPA Method 7471B
Elemental Mercury	10	EPA Method 1613
Methyl Mercury	3	EPA Method 1630 Aqueous Ethylation, purge and trap and cold vapor fluorescence spectrometry
Mercury Complex Speciation	10	Modified EPA standard method 3200
Percent Moisture	10	ASTM D2216
Nitrogen	75	ASTM D5373
Organic Carbon	50	SM 5310B
pH	20	EPA Method 9045
Metals	5	EPA Method 6010C/6020A/7471B Inductively Coupled Plasma (ICP) -Atomic Emission Spectrometry (AES), ICP-Mass Spectrometry (MS), Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
Anions	10	EPA Method 9056
Total	**196**	

a: These masses are based on estimated soil moisture of 12%

4.4 Analysis of Mercury Valence State

Analysis of the valence state of mercury was conducted by Eurofins (the contract laboratory). The following standard analytical methods were used to determine the valence state of mercury in soil samples.

- Total mercury: total mercury in soil samples was measured based on EPA method 7471A, which is based on cold vapor atomic absorption spectroscopy (CVAFS). In this method, the soil sample is mixed with high-purity water, nitro-hydrochloric acid and potassium permanganate. The soil sample is digested and then oxidized to convert the various mercury forms to labile Hg(II). Mercury Hg(II) is then reduced to Hg(0) by adding stannous sulfate and purged from solution in a closed system using inert gas. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer, where the absorbance of radiation at the 253.7 nm wavelength by mercury vapor is measured as a function of mercury concentration.
- Elemental mercury Hg(0): Analysis of elemental mercury is similar to the EPA method 1613E that is based on cold vapor atomic fluorescence detection, but the step of adding $SnCl_2$ is eliminated so that only mercury existing in its original elemental state is trapped on a gold trap and its vapor is analyzed after desorption by fluorescence detector. Elemental mercury Hg(0) is sparingly soluble in water and has a significant vapor pressure at room temperature. It is therefore a suitable candidate for extraction and concentration by purge and trap methodology. The Hg(0) vapor readily fluoresces under irradiation from a mercury vapor lamp, a property that allows for very sensitive and specific detection of the element by cold vapor atomic fluorescence spectrometry.
- Hg(II): The concentration of Hg(II) is calculated as the difference between total mercury and elemental Hg(0) measured based on the previous described steps.

4.5 Analysis of Mercury Complexes

The mobility and bioavailability of mercury in soil is significantly impacted by the speciation of Hg(II) complexes. Analysis of the speciation of mercury complex was conducted by Eurofins. In addition to the analysis of the valence state of mercury, a sequential extraction procedure to determine mercury speciation in the study soil samples was conducted. The sequential extraction process separates the following fractions: readily soluble mercury (mainly mercury chloride and mercury hydroxide), mercury bound to humic substances (*i.e.*, Hg(II)-DOM complexes), mercury sulfide, organic mercury, and elemental mercury. In this process, the soil sample is sequentially extracted by chloroform, methanol, hydrochloric acid, sodium hydroxide and sodium sulfide.

One previous study using this extraction method successfully separated the contribution of mercury between a.) mercury bound to humic substance and b.) mercury sulfide in soil samples [37]. It is found that the mercury bound to humic substances comprised a significant contribution of the mercury percentage, especially in the top layer of soil. On the other hand, mercury sulfide was the dominant mercury form in the samples from lower layers of the soil profile in the same

aforementioned study. It is believed that when mercury is bound to humic substances, it can increase its bioavailability and make phytoremediation possible, whereas mercury sulfide is much less mobile and therefore much less bioavailable. This same analytical procedure was used in this study to determine mercury(II) speciation in Area IV soil samples and to help recommend potential follow-on work to identify potentially feasible mercury remediation techniques.

The laboratory analytical procedures used to extract different fractions of mercury are illustrated in Figure 3. The mercury complex fractions that this study analyzed for and their associated mobility are briefly discussed below:

- Fraction 1: elemental mercury in vapor phase. This is the most volatile mercury fraction and is very mobile.
- Fraction 2: methyl mercury. Methyl mercury is typically the most abundant organic form of mercury in soil. Methyl mercury can accumulate in organic tissues and is toxic to organisms.
- Fraction 3: water soluble mercury (*e.g.*, $HgCl_2$, $HgSO_4$). Fraction 3 associated mercury complexes are soluble in water and are inorganic. Fraction 3 complexes have weak bonds with soil particles and are the most bioavailable complex fraction.
- Fraction 4: acid soluble mercury (*e.g.*, HgO, $Hg(OH)_2$ and $HgCO_3$). Fraction 4 associated complexes are inorganic and can be removed from soils with weak acids. The weak acids could be used to make these complexes more bioavailable. Mercury needs to be labile and in solution in order to be bioavailable. With respect to phytoremediation, plants (as well as bacteria) must solubilize bound mercury to uptake it. Plants can do this in multiple ways. First, they can release root exudates, which are organic acids. The organic acids lower the local pH and also chelate metals. Similarly, the root exudates can also dissolve carbonate minerals that sorb Hg^{2+}. Second, roots can promote bacterial activity around the root that promotes solubilization. The bacteria produce polymers that strongly bind to the target contaminants, which then allow the plant to uptake the contaminant into the root.
- Fraction 5: soil humic substance associated mercury (*e.g.*, Hg-humics). Fraction 5 complexes are predominantly organic compounds. The organic Fraction 5 complexes are extractable and can change chemical form (i.e., they are labile). Humic substances are not very mobile in soil and are part of the organic soil fraction. Therefore, the mercury sorbed to humic substances may not be very mobile unless there is a breakdown of the humic acids.
- Fraction 6: surface bound elemental mercury (*e.g.*, Hg^0, amalgamated mercury). Fraction 6 complexes are not extractable. This fraction of mercury is essentially immobile in the soil.
- Fraction 7: sulfide mercury (*e.g.*, HgS). Fraction 7 complexes are bound to minerals, and are among the least bioavailable mercury complex fractions.

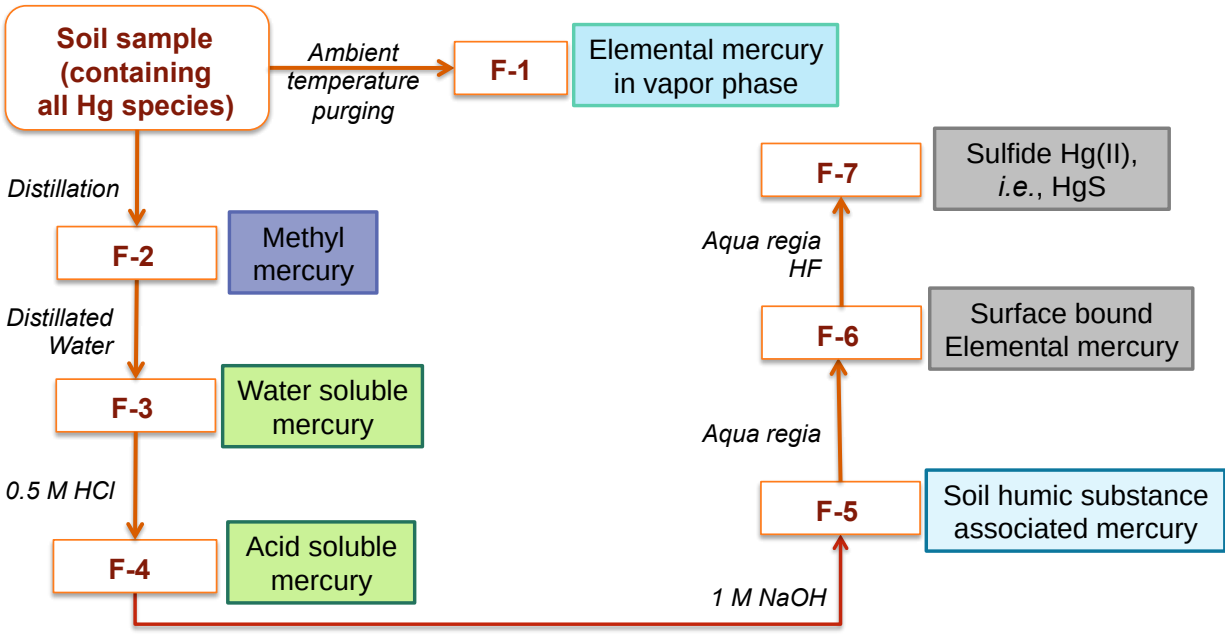

Figure 3: Sequential extraction procedures to analyze different speciation of mercury in soil sample.

The mobility of each fraction of mercury species, their associate mobility in soil and the potential for bioremediation and phytoremediation are listed in Table 2. The check symbol in the table represents how easily each fraction can be mobile or is bioavailable. The greater the number of checks, the more mobile or bioavailable the fraction is. Three is the maximum number of checks and one is the minimum. The (x) symbol means that the particular fraction is not mobile or bioavailable.

Table 2: The relative mobility and bioavailability of each mercury species fraction

Fraction	Mercury speciation	Mobility in soil	Bioavailability
F-1	Elemental mercury (vapor phase)	✔✔✔	✗
F-2	Methyl mercury	✔✔✔	✔✔
F-3	Water soluble mercury	✔✔✔	✔✔✔
F-4	Acid soluble mercury	✔✔	✔✔
F-5	Soil humic substance associated mercury	✔	✔
F-6	Elemental mercury (surface bound)	✗	✗
F-7	Mercury sulfide	✗	✗

Elemental mercury in the vapor phase in soil (Fraction F-1) is extremely mobile. Therefore, it receives three checks for its mobility. The F-1 fraction is not available for bacterial or plant uptake.

Methyl mercury (Fraction F-2) is organo mercury whose mobility depends upon its complexation. Generally, it can be taken up by plants or bacteria.

Water soluble mercury (Fraction F-3) is basically a dissolved form of mercury, normally existing as mercury chloride or mercury sulfate. This fraction of mercury can be easily washed away by rain and actively taken up by plants and bacteria. Therefore, Fraction F-3 receives three checks for both mobility and bioavailability potentials.

Acid soluble mercury (Fraction F-4) is mostly composed of inorganic mercury minerals that can be dissolved under acidic conditions, including mercury carbonate and hydroxide minerals. The dissolution of these minerals can take place when plant roots or bacterial cells exude organic acids capable of dissolving the minerals. Therefore, this fraction receives two checks for its mobility and bioavailability.

Soil humic substance associated mercury (Fraction F-5) is not very mobile in soil. Humic substances are part of the organic soil fraction. Therefore, the mercury sorbed to humic substances may not be very mobile unless there is a breakdown of the humic acids. This fraction receives one check for its mobility and bioavailability.

Fraction F-6 is surface bound elemental mercury (mostly as amalgamated mercury). This form of elemental mercury can only be extracted from soil with very strong acids. Therefore, this fraction is essentially immobile in the soil and receives symbols of (x) for its mobility and bioavailability.

Finally, Fraction F-7 represents sulfide mercury (e.g., HgS). This fraction of mercury is tightly bound in a mineral lattice, and is among the least bioavailable mercury complex fractions.

5. Study Findings

5.1 Total Mercury Distribution with Soil Depth

The mercury depth data were analyzed for each of the four treatability study sample locations. Since sampling at these locations took place in both 2011 and 2014, the depth analysis is based on an assumption that the mercury did not mobilize over that three year period.

Site SL-284-SA6: This location is the primary mercury spill site. The different bar colors on Figure 4 indicate the different sampling dates. The dark blue color represents samples taken on November 30, 2011, and the light blue color represents samples taken on May 19, 2014. The sampling data show that the total mercury concentration was the highest at the top soil layer, and its concentration dropped with soil depth. The red dashed line represents the mercury LUT value, which is 0.10 mg mercury per kilogram of soil.

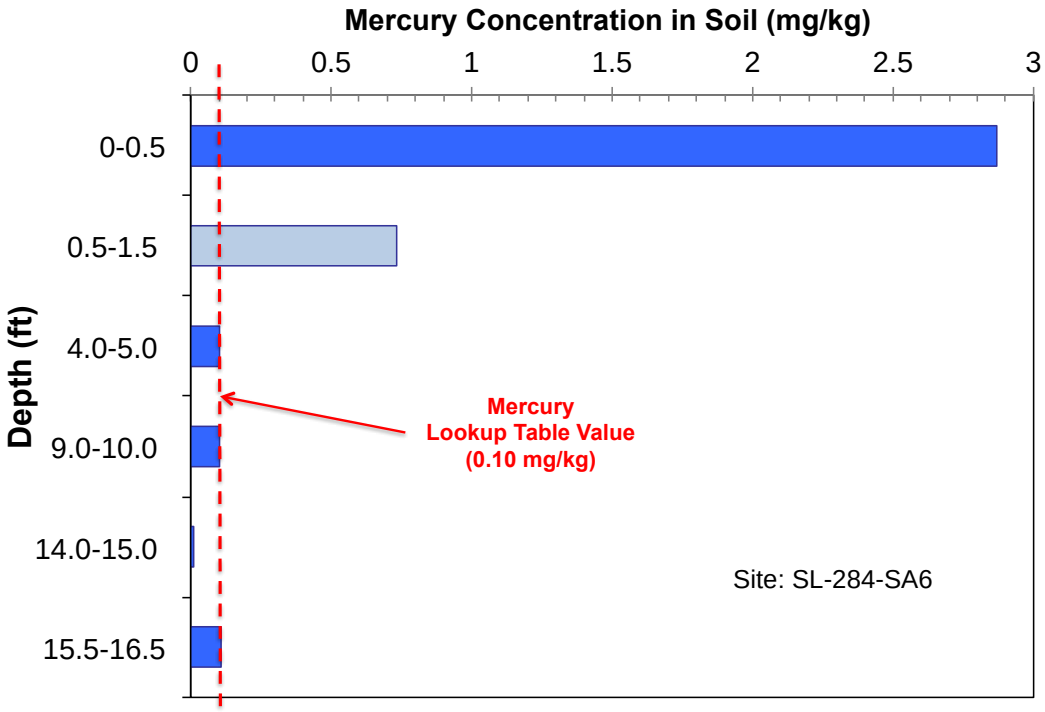

Figure 4: Soil depth profile of total mercury at SL-284-SA6

The total mercury concentration was approximately 2.8 mg/Kg in the surface soil layer between 0 and 0.5 ft below ground surface (bgs), and decreased to below the LUT value at a soil depth of 4 ft bgs. This depth profile trend indicates that the mercury at this location was released to the top layer of the soil.

Site SL-73-SA6: This location is the open field site next to the primary mercury spill site. The different bar colors on Figure 5 indicate the different sampling dates. The dark purple color represents samples taken on July 21, 2011, and the light purple color represents samples taken on May 19, 2014. At this location, the total mercury concentration was actually lowest in the surface soil layer, and higher concentrations were detected deeper in the soil. This concentration profile is a result of the original surface soil layer being excavated and hauled away from this location, resulting in a low total mercury concentration (approximately the Look-up Table Value) in the surface soil. However, the soil depths more than 3 ft had not been excavated and the total mercury concentration remains elevated in these deeper soils.

Site SL-212-SA5B: This site is located in subarea 5B near the 17th street pond and drainage area. The soil sample depths at this location varied between 0 ft and 4 ft. The different bar colors on Figure 6 indicate different sampling dates. The dark orange color represents samples taken on December 20, 2010, and the light orange color represents samples taken on May 19, 2014. The sampling data show that the total mercury concentration was the highest at the surface soil layer, and the mercury concentration dropped with increasing soil depth. The total mercury concentration was approximately 24 mg/Kg in the surface soil layer between 0 and 0.5 ft, and then decreased to below the detection limit (non-detect, "N.D." on the graph) at a soil depth of 0.5-1.5 ft).

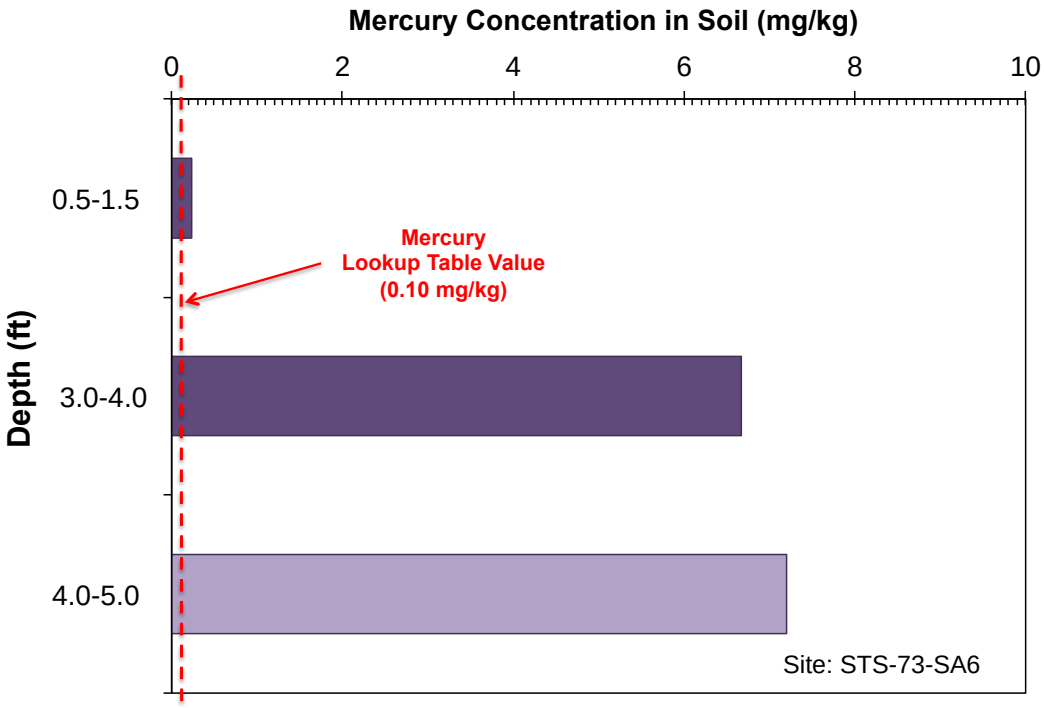

Figure 5: Soil depth profile of total mercury at STS-73-SA6

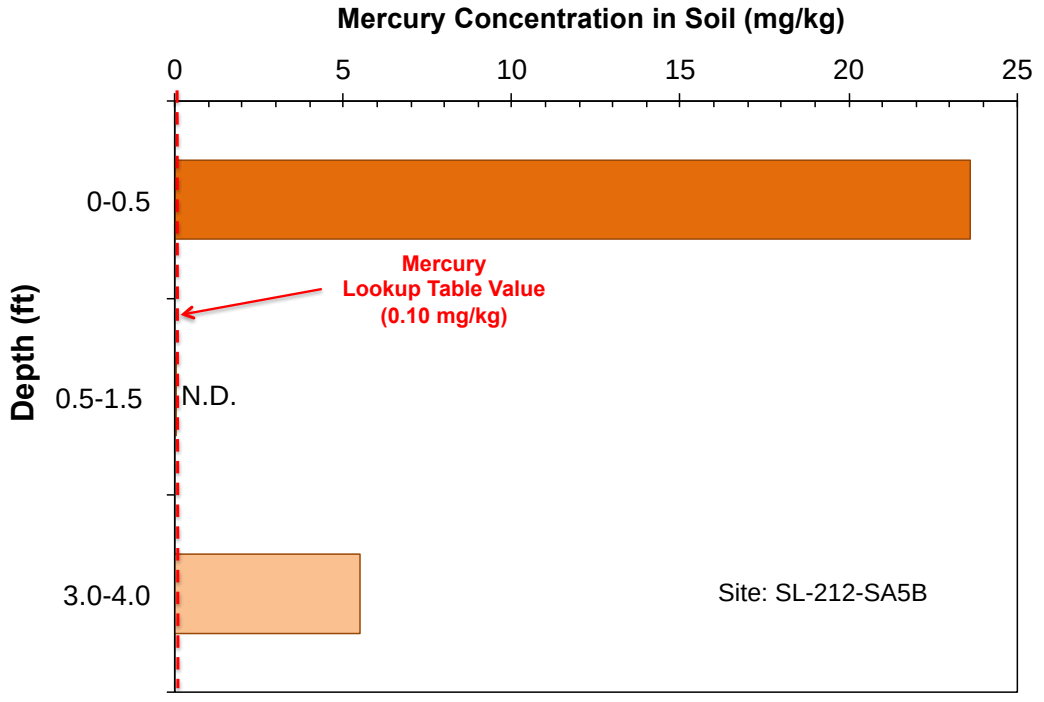

Figure 6: Soil depth profile of total mercury at SL-212-SA5B

Site STS-113-SA5ND: This site is located in subarea 5D North. Initial sampling was conducted on June 10, 2011 with two soil depth intervals collected: 0 to 0.5 ft and 4 to 5 ft (shown in the light green color in Figure 7). The treatability study sampling was conducted on May 19, 2014 at a soil depth of 3 to 4 ft. The sampling data show that the total mercury concentration was the highest at the surface soil layer, and the mercury concentration dropped with increasing soil depth. The total mercury concentration was approximately 54 mg/Kg in the surface soil layer between 0 and 0.5 ft below the surface, and decreased to below the detection limit (N.D.) at a soil depth below 3 ft.

Summary of Total Mercury Analysis with Soil Depths

Based on the sampling data from the four treatability study sample locations, the general trend for the mercury concentration profile is that total mercury decreases with soil depth (Figure 8), with the exception of STS-73-SA6. STS-73-SA6 had mercury surface soil concentrations below the LUT values due to a previous excavation of contaminated surface soils. Below the depth of this excavation, mercury was elevated above the LUT values.

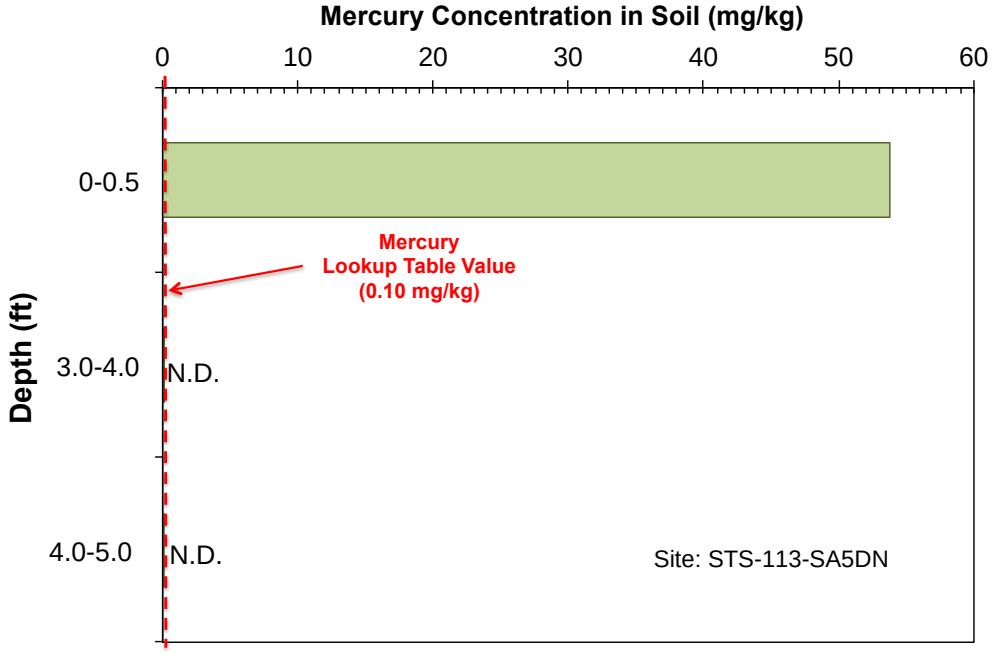

Figure 7: Soil depth profile of total mercury at STS-113-SA5DN

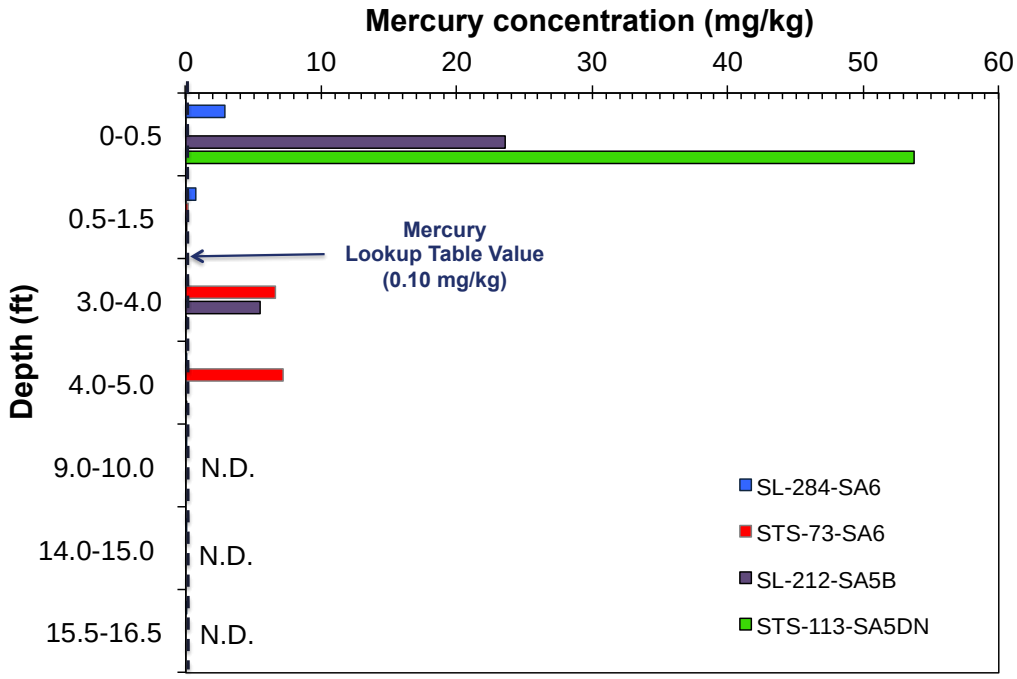

Figure 8: Overall trend of soil depth profile of total mercury of all sampling sites

5.2 Mercury Speciation Data

To better understand the potential for *in situ* mercury remediation using bioremediation or phytoremediation, it is important to assess the mercury speciation and its associated mobility in the soil. To that end, sequential extraction procedures were applied to the soil samples collected for this study

The first observation from the analyses of these samples was that vapor phase elemental mercury was not detected. This means that very minimal risk to immediate mercury exposure is present at these locations. In addition, methyl mercury was only detected at trace amounts at two locations (SL-212-SA5B and SL-284-SA6). At these two locations, methyl mercury only accounted for 0.003% of total mercury, and was only detected at soil depths between 3.0 and 4.0 ft.

Mercury speciation with respect to its concentration is shown in Figure 9. For samples taken from the top layer of the soil columns (i.e., 0.5-1.5 ft), there is a reasonable portion of total mercury existing as either highly mobile or potentially mobile mercury species. These fractions could become bioavailable and theoretically could be cleaned up by bioremediation or phytoremediation. However, for samples taken from deeper in the soil columns (*i.e.*, 3.0-4.0 ft), total mercury exists predominantly as highly immobile amalgamated mercury. This form of mercury is tightly bound to the surface of the soil particles. It would be difficult for bacteria or plant roots to actively take up this immobile fraction. Meanwhile, the predominance of the immobile fraction suggests that this mercury will not be volatilized to the surface under natural soil conditions. This indicates that the risk for human exposure from these mercury species at these locations is minimal.

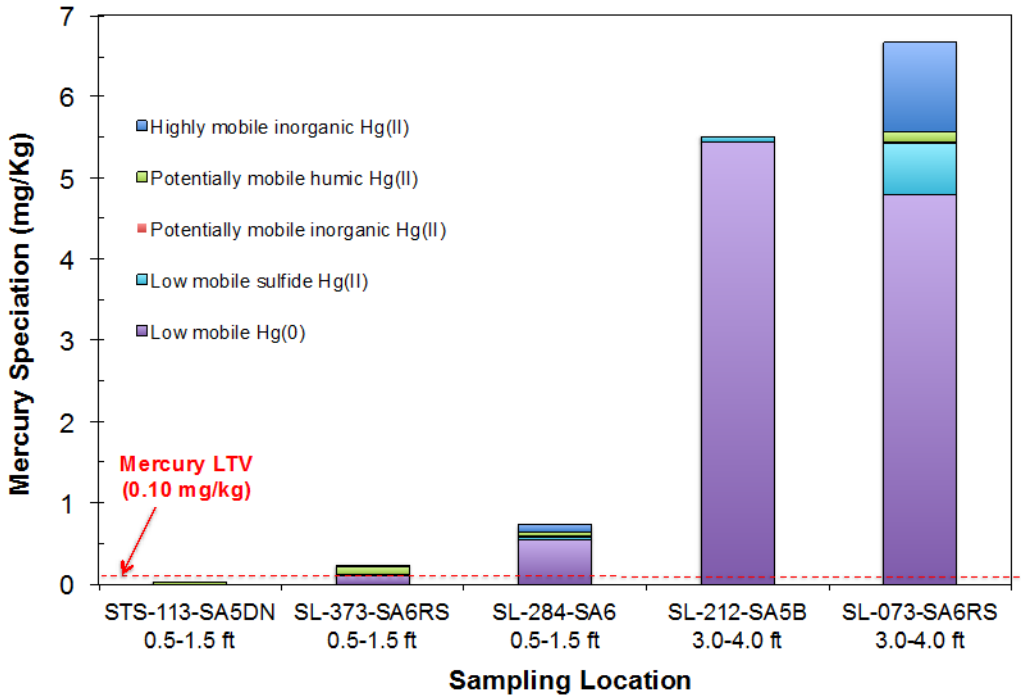

Figure 9: Mercury speciation with respect to its concentration at all sampling sites

The mobility of the mercury species at the sampling locations is illustrated in Figure 10 with respect to its concentration, and further visualized in Figure 11 with respect to its percentage. The total mercury is divided into three categories: mobile mercury (Fraction 3 from sequential extraction), potentially mobile mercury (Fractions 4 and 5) and immobile mercury (Fractions 6 and 7). The sample ID SL-73-SA6RS is a resample from the same site of SL-73-SA6 on May 19, 2014 for speciation analysis.

For the surface soils, the mercury mobility varies depending upon location. For mercury-containing deep soils, total mercury exists predominantly as highly immobile amalgamated mercury (Figure 11). This fraction of mercury is expected to remain stable for a significant time period, and is resistant to bioremediation or phytoremediation. Thermal treatment could be an alternative to remediate mercury in deep soil, but additional lab tests would be required to determine the feasibility of this technology.

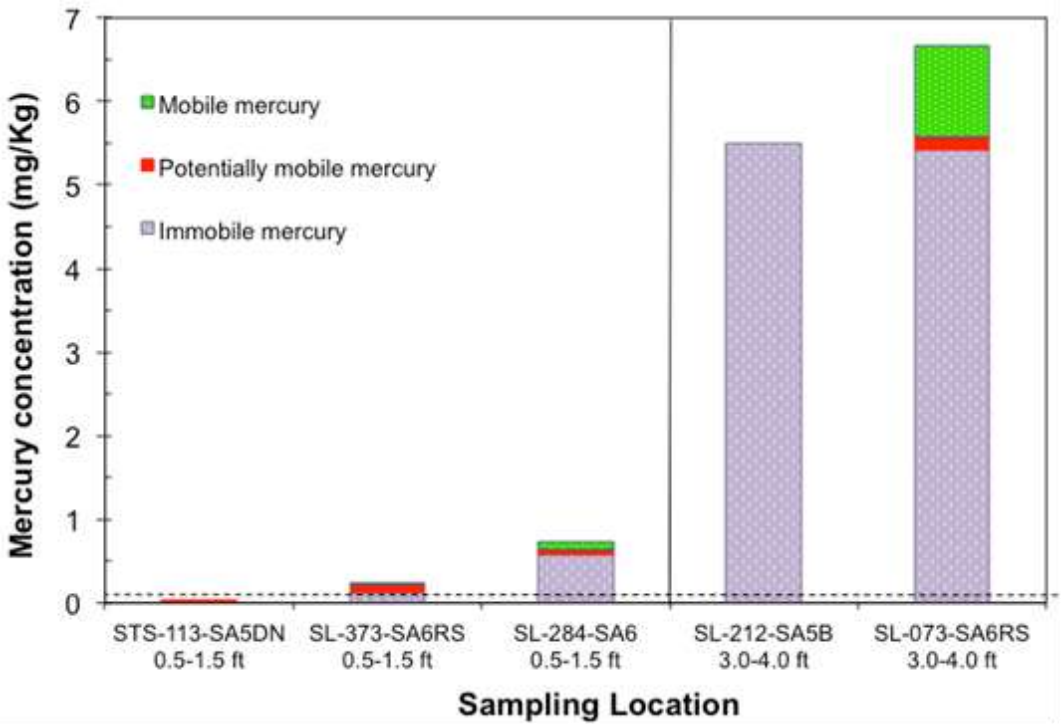

Figure 10: Mercury mobility with respect to its concentration at all sampling sites.

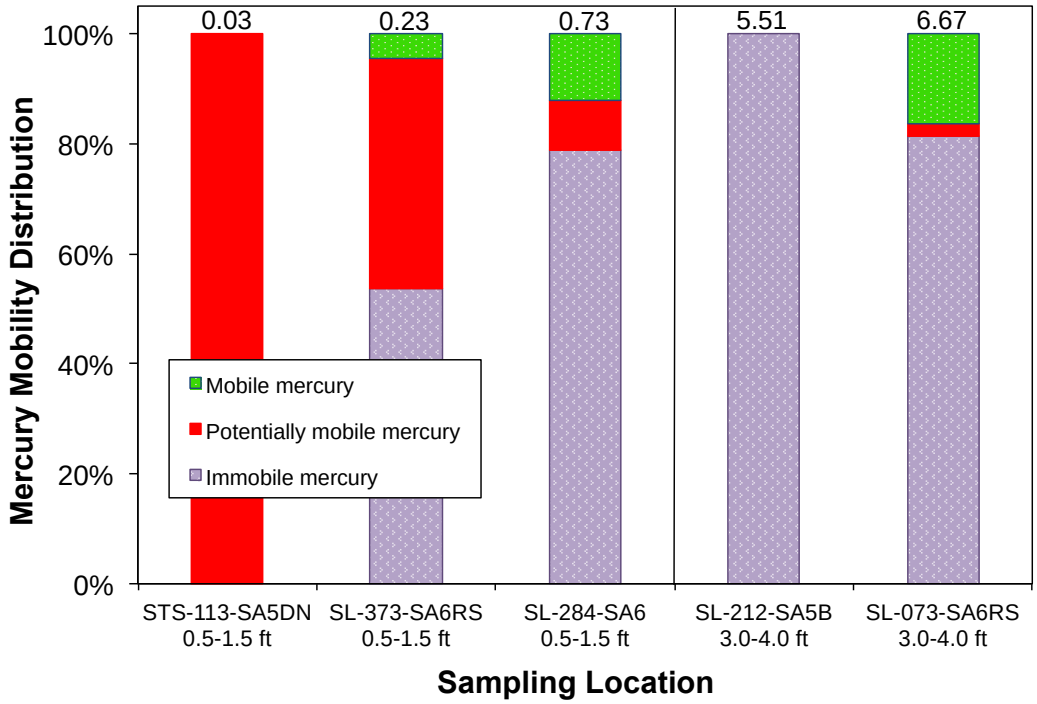

Figure 11: Mercury mobility with respect to its percentage of total mercury at all sampling sites.

Note for Figure 11: The numbers at the top of the bars show total mercury concentrations in the unit of mg/kg.

6. Conclusions

Conclusions from this mercury study are presented first, followed by recommendations for additional consideration.

6.1 Conclusions

- With respect to the soil depth profile, the majority of total mercury was distributed in surface soils with depths between 0 and 1.5 ft.
- In three sampling locations, mercury concentrations were highest in surface soils and decreased with soil depth. Total mercury exceeded Look-up Table Value (0.10 mg/kg) at these locations. STS-73-SA6 had the soil from 0 to 3 ft excavated and this sampling location did not match the trend present at the other three sampling locations.
- With respect to valence state, no elemental vapor phase mercury was detected in any of the samples. Elemental mercury tightly bound to soil particles was found mostly in deep soils. Methyl mercury was detected only in trace amounts at a few locations. Ionic mercury in a divalent state was widely observed in surface soils.
- In some surface soils with depths between 0.5 and 1.5 ft, a considerable fraction of mercury exists in chemical forms that are mobile or potentially bioavailable. This suggests that soil washing, bioremediation and phytoremediation, theoretically, could be viable treatment options to remove the mobile fractions of mercury in these surface soils. However, the immobile fraction of mercury (i.e., that fraction of mercury not susceptible to bioremediation or phytoremediation) at many of these same locations is still above the LUT values; therefore, bioremediation and phytoremediation will likely not be able to achieve LUT values for mercury at many locations.
- In deeper soils below 3 ft, a majority of mercury exists in the immobile elemental form that is tightly bound to soil particles. Additional testing of potential alternative cleanup approaches would be required to determine the feasibility of any treatment methods, especially at locations near the primary mercury spill site.

6.2 Recommendations

Based on the analytical results and conclusions, a number of recommendations are proposed.

- Phytoremediation, theoretically, could be a viable treatment for mercury remediation in surface soil layers. A large fraction of mercury is present in potentially mobile fractions (Fractions F-3, F-4 and F-5) that are associated with soluble salts and soil organic matter. These fractions can be solubilized by plant roots and bacteria, which then enhances the mobility of mercury and promotes its uptake by plants and bacteria from the soil. However, due to the concentrations of immobile mercury at these locations, it is unlikely that phytoremediation could achieve LUT values for mercury.
- Because a large fraction of mercury is present in potentially mobile fraction in surface soil layers, soil washing of the top soil layer is potentially applicable to remove the mobile mercury,

but this would require additional testing to determine the feasibility of this technology on Area IV soils.

- Bioremediation or phytoremediation is not likely to be effective for deep soil. The predominance of mercury in deeper soils is immobile mercury, and mostly in an elemental valence state and tightly bound to soil particles.
- Thermal treatment could be an alternative to remediate mercury in deep soils, but additional testing would be required to determine the feasibility of using this technology on deep Area IV soils.
- Soil size partitioning has the potential to reduce volume for thermal treatment. Additional testing on the distribution of mercury species within the soil particle sizes would be required to determine the feasibility of using this technology on Area IV soils.

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Appendix A
Analytical Method Reporting Limits

Analytical Method Reporting Limits

Analyte	Soils		Waters	
	Reporting Limit	Unit	Reporting Limit	Unit
Metals by EPA Method 6010C/6020A				
Aluminum	20000	mg/kg	0.2	mg/L
Antimony	8.7	mg/kg	0.001	mg/L
Arsenic	15	mg/kg	0.002	mg/L
Barium	140	mg/kg	0.002	mg/L
Beryllium	1.1	mg/kg	0.0005	mg/L
Boron	9.7	mg/kg	0.05	mg/L
Cadmium	1	mg/kg	0.0005	mg/L
Calcium	20	mg/kg	0.2	mg/L
Chromium	36.8	mg/kg	0.002	mg/L
Cobalt	21	mg/kg	0.0005	mg/L
Copper	29	mg/kg	0.002	mg/L
Iron	28000	mg/kg	0.2	mg/L
Lead	34	mg/kg	0.001	mg/L
Lithium	37	mg/kg	0.02	mg/L
Magnesium	10	mg/kg	0.1	mg/L
Manganese	495	mg/kg	0.005	mg/L
Molybdenum	5.3	mg/kg	0.0005	mg/L
Nickel	29	mg/kg	0.002	mg/L
Phosphorus	10	mg/kg	0.1	mg/L
Potassium	6400	mg/kg	0.5	mg/L
Selenium	0.655	mg/kg	0.002	mg/L
Silver	0.79	mg/kg	0.0005	mg/L
Sodium	110	mg/kg	1	mg/L
Strontium	0.495	mg/kg	0.005	mg/L
Thallium	0.46	mg/kg	0.0005	mg/L
Tin	10.9	mg/kg	0.02	mg/L
Titanium	0.995	mg/kg	0.01	mg/L
Vanadium	62	mg/kg	0.0005	mg/L
Zinc	110	mg/kg	0.015	mg/L
Zirconium	8.6	mg/kg	0.05	mg/L
Nitrogen by ASTM D5373				
Total Nitrogen	0.5	%	0.5	%
Organic Carbon by Standard Method (SM) 5310				
Organic Carbon	1	mg/kg	1	mg/L
Total Mercury by EPA Method 7471B/7470A/3200				
Mercury	0.09	mg/kg	0.0002	mg/L
Methyl Mercury by EPA Method 1630				
Methyl Mercury	0.12	pg/g	0.06	ng/L
Elemental Mercury by EPA Method 1613				
Elemental Mercury	2.00	ng/g	0.500	ng/L
Mercury Complexes by EPA Method 3200/1630/1631				
Mercury (Hg^0)	2.00	ng/g	0.500	ng/L
Mercury ($HgCl_2$ and $HgSO_4$) Fraction 1	3.12	ng/g	0.500	ng/L
Mercury (HgO) Fraction 2	3.12	ng/g	0.500	ng/L
Mercury (Hg_2Cl_2 Hg- Humics) Fraction 3	6.25	ng/g	0.500	ng/L
Mercury (mineral lattice, Hg_2) Fraction 4	15.6	ng/g	0.500	ng/L
Mercury (HgS, m-HgS, HgSe, HgAu) Fraction 5	1.00	ng/g	0.500	ng/L
Mercury (Hg in crystal lattice) Fraction 6	5.00	ng/g	0.500	ng/L
Anions by EPA Method 300.0/9056A				
Fluoride	6.7	mg/kg	0.1	mg/L
Nitrate	1.5	mg/kg	0.1	mg/L
Bromide	5	mg/kg	0.2	mg/L
Chloride	5	mg/kg	0.2	mg/L
Nitrite-NO_2	5	mg/kg	0.1	mg/L
Phosphate	21	mg/kg	0.2	mg/L
Sulfate	5.2	mg/kg	0.4	mg/L

Analytical Method Reporting Limits

Analyte	Soils		Waters	
	Reporting Limit	Unit	Reporting Limit	Unit
Miscellaneous Analyses				
Percent Moisture (D2216)	0.1	%	NA	NA
pH (9040C and 9045D)	8.86	pH	0.01	pH

EPA - United States Environmental Protection Agency
mg/kg - milligrams per kilogram
mg/L - milligrams per liter
ng/g - nanograms per gram
ng/L - nanograms per liter
pg/g - picogram per gram
pg/L - picogram per liter

Appendix B
Quality Control Objectives for Analytical Methods

Quality Control Objectives for Analytical Methods

Analytical Category	Method Number and Reference	MS/MSD or Surrogate Accuracy Criterion (% Recovery)		BS/LCS Accuracy Criterion (% Recovery)		Precision Criterion (Maximum RPD)	
		Soil	Water	Soil	Water	Soil	Water
pH	**EPA Method 9040C/9045D**						
pH		NA	NA	95-105	90-110	5	
Metals	**EPA Method 6010 C/6020A**						
Aluminum		75-125	75-125	—	80-120	20	
Antimony		75-125	75-125	—	80-120	20	
Arsenic		75-125	75-125	—	80-120	20	
Barium		75-125	75-125	—	80-120	20	
Beryllium		75-125	75-125	—	80-120	20	
Cadmium		75-125	75-125	—	80-120	20	
Calcium		75-125	75-125	—	80-120	20	
Chromium		75-125	75-125	—	80-120	20	
Cobalt		75-125	75-125	—	80-120	20	
Copper		75-125	75-125	—	80-120	20	
Iron		75-125	75-125	—	80-120	20	
Lead		75-125	75-125	—	80-120	20	
Magnesium		75-125	75-125	—	80-120	20	
Manganese		75-125	75-125	—	80-120	20	
Nickel		75-125	75-125	—	80-120	20	
Potassium		75-125	75-125	—	80-120	20	
Selenium		75-125	75-125	—	80-120	20	
Silver		75-125	75-125	—	80-120	20	
Sodium		75-125	75-125	—	80-120	20	
Thallium		75-125	75-125	—	80-120	20	
Vanadium		75-125	75-125	—	80-120	20	
Zinc		75-125	75-125	—	80-120	20	
Miscellaneous Analyses							
Percent Moisture	D2216	—	—	—	—	—	
Total Nitrogen	ASTM D5373	75-125	75-125	—	80-120	20	
Organic Carbon	Standard Method (SM) 5310	75-125	75-125	—	80-120	20	
Total Mercury	**EPA Method 7471B/7470A**						
Total Mercury		65-135	75-125	85-120	90-115	20	
Mercury	**EPA Method 3200/1630/1631**						
Mercury (Hg^0)		71-125	71-125	80-120	80-120	24	24
Mercury ($HgCl_2$ and $HgSO_4$) Fraction 1		75-125	75-125	80-120	80-120	25	25
Mercury (HgO) Fraction 2		75-125	75-125	80-120	80-120	25	25
Mercury (Hg_2Cl_2 Hg- Humics) Fraction 3		75-125	75-125	80-120	80-120	25	25
Mercury (mineral lattice, Hg_2) Fraction 4		75-125	75-125	80-120	80-120	25	25
Mercury (HgS, m-HgS, HgSe, HgAu) Fraction 5		75-125	75-125	80-120	80-120	25	25
Mercury (Hg in crystal lattice) Fraction 6		75-125	75-125	80-120	80-120	25	25

Acronyms and Abbreviations:

BS/LCS = Blank Spike/Laboratory Control Sample
EPA = U.S. Environmental Protection Agency
MS/MSD = Matrix Spike/Matrix Spike Duplicate
NA = not applicable
RPD = Relative Percent Difference
"—" = Laboratory-specific lower control limit-upper control limit or laboratory specific maximum RPD