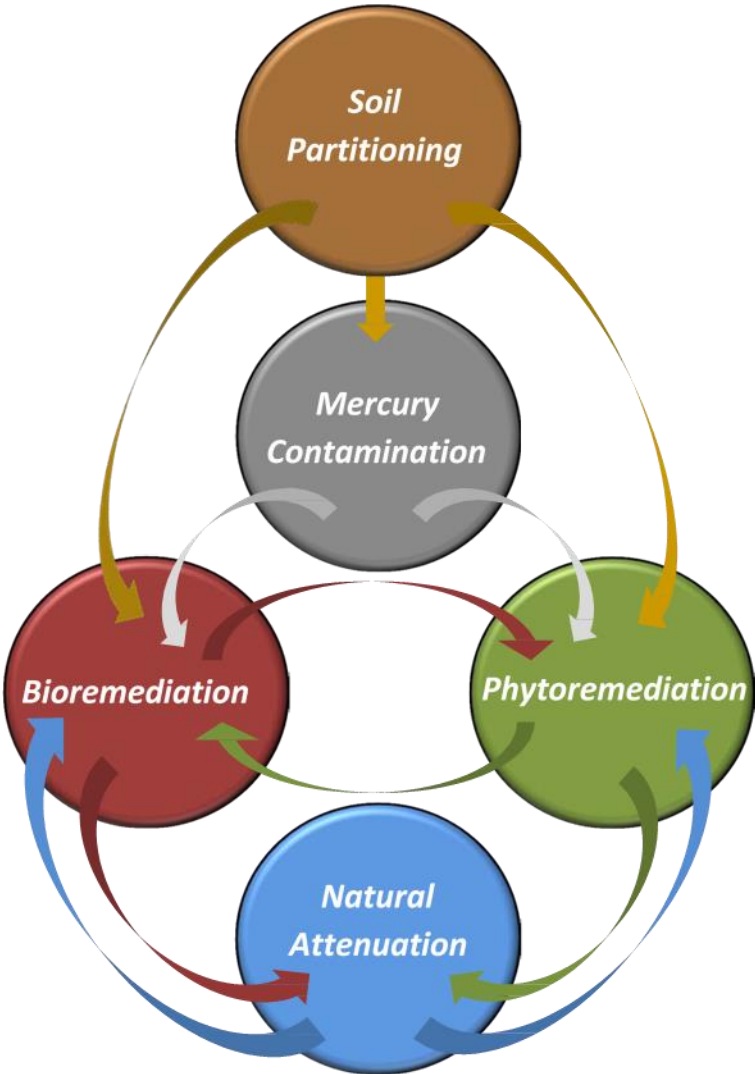


**Soil Treatability Studies  
Area IV Santa Susana Field Laboratory  
Ventura County, California**



September 2015

# **Soil Treatability Studies Summary Report Area IV Santa Susana Field Laboratory Ventura County, California**

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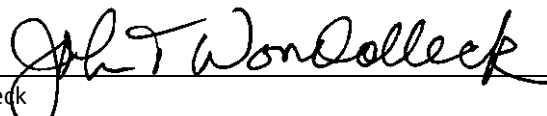
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## Acronyms

AOC	Administrative Order of Consent
Cal Poly	California Polytechnic State University
COIs	contaminants of interest
dioxins	polychlorinated dibenzo dioxins
DOE	U.S. Department of Energy
DTSC	Department of Toxic Substances Control
EDTA	ethylenediaminetetraacetic acid
EFHs	Extractable Fuel Hydrocarbons
ft bgs	feet below ground surface
LUT	Look-up Table
mg/kg	milligrams per kilogram
mm	millimeters
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
Sandia	Sandia National Laboratories
SSFL	Santa Susana Field Laboratory
TPH	total petroleum hydrocarbons
UCR	University of California-Riverside





# Section 1

## Introduction

In accordance with the Administrative Order of Consent (AOC) signed by the U.S. Department of Energy (DOE) with the California Department of Toxic Substances Control (DTSC), DOE conducted a series of soil treatability studies using soil from Area IV of the Santa Susana Field Laboratory (SSFL). The objective of the soil treatability studies was to evaluate onsite soil treatment technologies that could reduce the volume of contaminated soil that otherwise would need to be excavated and transported from Area IV.

DOE's first step in conducting the soil treatability studies was engaging Sandia National Laboratories (Sandia) to review literature and inquire with practicing remediation professionals on soil treatability studies conducted throughout the world to determine which soil treatment technologies may be applicable to contaminants in soil at Area IV. The contaminants of interest (COIs) investigated by the treatability studies were, generally, metals (primarily mercury, silver, lead), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo dioxins (dioxins), and total petroleum hydrocarbons (TPH).

Based on Sandia's literature review and inquiry with professionals, Sandia recommended that DOE consider six soil study options (Sandia 2012) for the COIs:

- Mercury valence state determination
- Soil partitioning
- Bioremediation
- Phytoremediation
- Natural attenuation
- Thermal treatment



## Section 2

### Background

Mercury has unique chemical properties that allow it to exist in the environment in different chemical states (also termed valence states) – as a liquid metal, as a salt, or as a complex with other compounds. The chemical state of mercury in soil is important to know for soil treatment considerations because as a metal it can be removed from soil through thermal treatment, as a soluble salt it can be absorbed in soil by microbes and plant roots, and as an insoluble complex only soil washing may be effective in removing mercury from soil.

Soil partitioning evaluates within which of the various particle size ranges the contaminants may be found. Soil is composed of particles ranging in size from a fraction of a millimeter (clay, silt, and fine sand) to coarse sand and gravel sizes. Typically soil contaminants preferentially adsorb to the smaller soil particles (termed "fines"). If this is the case, it may be possible to separate larger soil particles from the smaller particles through the use of sieves. If the contaminants are primarily found on the smaller soil particles, then the separation can reduce the volume of soil to be transported from Area IV. The Area IV soil is primarily of sandstone origin so it consists of predominantly larger soil particle sizes. The types and sizes of soil particles that contaminants are adsorbed to is also important for biological remediation considerations. In order for microbes and plant roots to absorb contaminants, the contaminants must be soluble or found in soil moisture. If the contaminants are strongly adsorbed to smaller soil particles, the contaminants may not be soluble and thus are not available to microbes and plant roots. Soil partitioning is also the first step in evaluating whether soil washing (removing contaminants from soil particles using chemicals and mechanical mixing) would be an effective treatment technology.

Bioremediation employs microorganisms (e.g., bacteria) and fungi to use the contaminants as an energy source or to chemically convert the contaminants to less toxic forms. How the microorganisms can convert the contaminants is highly dependent on the amount of oxygen and types of bacteria/fungi in the soil. Some microorganisms can only live in soil with oxygen, while others can only live in the absence of oxygen. And, as indicated in the paragraph below, there can be a symbiotic relationship between microorganisms and plant roots.

Phytoremediation is the use of plants to uptake (remove from soil) and/or degrade contaminants. The contaminants either are metabolized (converted to carbon dioxide, water, and salts) by the plants, incorporated into plant tissue, or volatilized from the plants into the atmosphere. In order for the contaminants to be absorbed into plant roots, the contaminants must be biologically available, usually meaning the contaminants must be in a soluble form. In some instances, a symbiotic relationship between plants and microbes exists; microorganisms in the soil can make some contaminants more available to plant roots, and the roots can release compounds making chemicals more available to microorganisms.

Natural attenuation is the use of physical, chemical, and biological processes to reduce concentrations of contaminants in soil. All organic compounds (meaning compounds with carbon as a basis) will eventually degrade into basic elements such as carbon dioxide, water, and mineral

salts. However, the rate of chemical degradation can vary greatly depending on contaminant properties (e.g., volatility, solubility, and degree of chlorination) and soil type and conditions. Degradation rates can range from months to years depending upon the aforementioned variables. Knowing rates of degradation is important not only for site monitoring considerations, but also for understanding the feasibility of enhancing degradation of contaminants in soil.

Thermal treatment is the practice of either heating soil to drive off volatile chemicals (fuels, solvents, mercury) or incinerating soil to destroy highly stable chlorinated chemicals. Thermal treatment can involve placement of thermal probes into the soil to heat it, or excavation of the soil for placement in incinerators for burning.

## Section 3

### Treatability Studies Discussion

Based on the recommendations made by Sandia, DOE elected to conduct five soil treatability studies:

- Mercury chemical (valence) state determination
- Soil partitioning
- Bioremediation
- Phytoremediation
- Natural attenuation

Thermal treatment was not chosen to be studied at this time.

The selected soil treatment technologies are interrelated and provide supporting information for each other. For example, knowing the mercury chemical state is necessary to determine whether mercury is amenable to soil washing, bioremediation, phytoremediation, and/or thermal treatment. The soil partitioning study results indicate whether contaminants could be available to plants, microorganisms, or fungi for bioremediation and phytoremediation studies. All of the studies are related to the biological, chemical, and/or physical aspects of natural attenuation. Therefore, the findings of each study determine the natural attenuation processes present at Area IV and their rates of COI reductions.

At the suggestion of the community, DOE contracted two local universities to conduct the soil treatability studies. Researchers at California Polytechnic State University (Cal Poly) conducted the bioremediation, phytoremediation, and natural attenuation studies; researchers from the University of California-Riverside (UCR) conducted the mercury and soil partitioning study. The goal of the studies conducted by the universities was to determine whether any of the technologies could reduce soil concentrations to meet cleanup levels identified in the AOC soil Look-up Table (LUT), or could reduce the volume of contaminated soil requiring excavation and transportation from Area IV.

To describe the relationships, background, and purposes of the studies, DOE developed a Master Work Plan (CDM Smith, 2013). Cal Poly developed separate work plans for the bioremediation study (Nelson et al., 2015a), phytoremediation study (Nelson et al., 2015d), and natural attenuation study (Nelson et al., 2014 and 2015c). UCR developed separate work plans for the mercury study (Liu, 2015) and soil partitioning study (Matsumoto and Martin, 2015).

The treatability studies determined that attaining the AOC soil cleanup levels (LUT values) would require significant time and effort, if the LUT values could be achieved at all, through the identified treatment options. This determination is due in part to the combination of the highly weathered state of the contaminants (i.e., the more easily degradable contaminants have already been degraded), contaminant chemical state (e.g., mercury valence state), and the nature of the AOC cleanup levels. The results of the five individual treatability studies are summarized below.

More detailed descriptions of each study's purpose, design and methodology, results, and conclusions can be found in the individual treatability study work plans and study reports (see References Section for full citations).

### 3.1 Mercury Contamination Study Conclusions

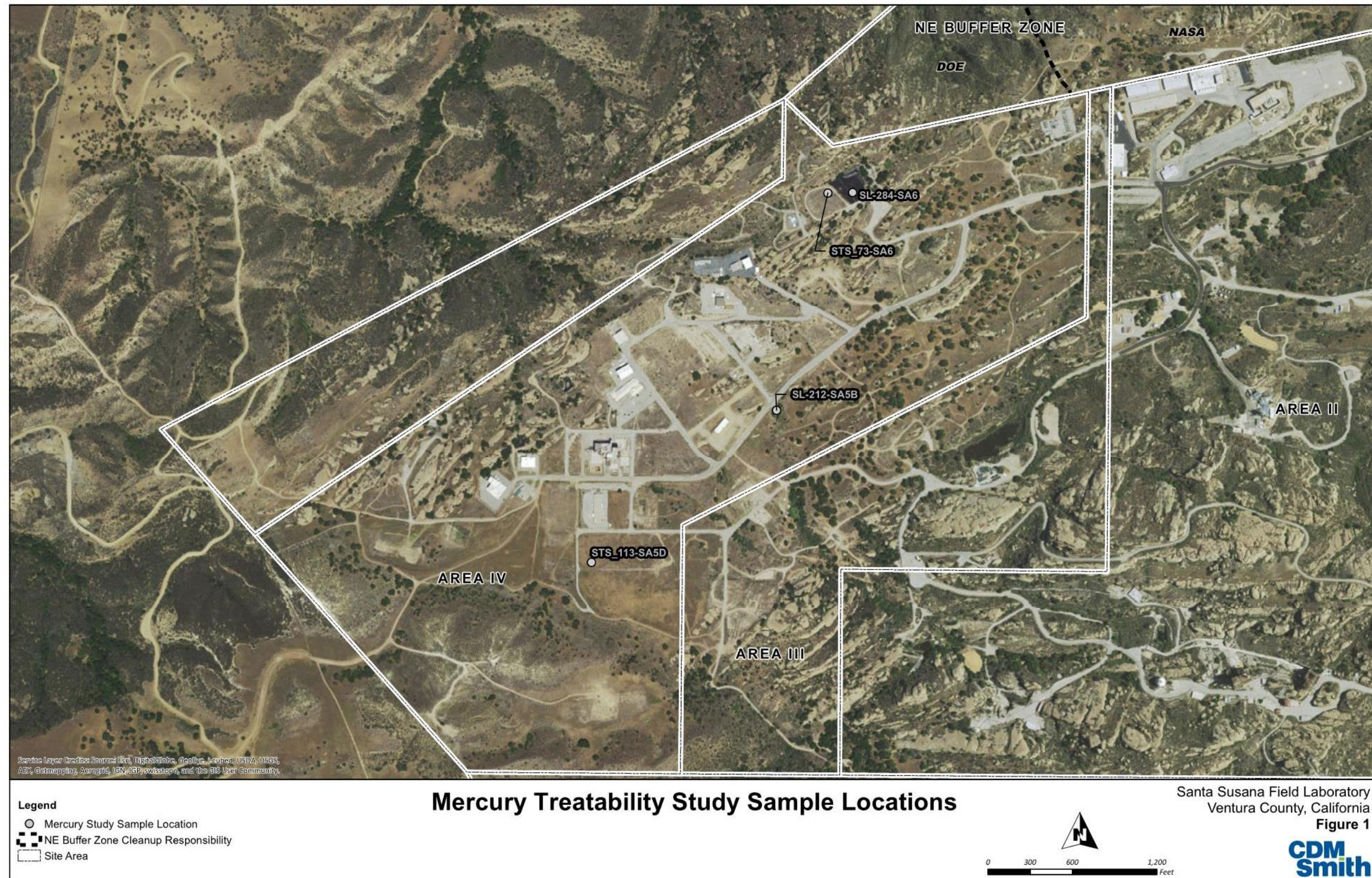
The mercury contamination treatability study was designed to determine the current valence states and spatial distribution of mercury in Area IV soils, and assess potential mercury remediation technologies. The results are reported in Liu (2015). Soil samples were collected from four locations within Area IV, and these samples were then analyzed to determine the concentration of each mercury valence state. Mercury concentration information from previous soil sampling events was also reviewed to aid in the interpretation of the spatial distribution of total mercury at Area IV.

In three of the four locations sampled specifically for this study, mercury concentrations were highest in surface soils (0 and 1.5 feet below ground surface [ft bgs]) and decreased with increasing soil depth. Total mercury exceeded its AOC LUT value at these locations. The sample location not exhibiting the trend of mercury concentration decreasing with depth (STS-73-SA6) had been excavated as part of a soil removal action prior to the commissioning of these soil treatability studies.

No elemental vapor phase mercury was detected in any of the samples. Methyl mercury was detected only in trace amounts at two locations. Approximately 12 percent of all mercury found in the soil samples was in a chemical form that is soluble (mobile) and thus potentially bioavailable. This would suggest that soil washing, bioremediation, and phytoremediation, theoretically, could be viable treatment options to remove the mobile fractions of mercury from these surface soils. However, the immobile fraction of mercury at the same locations is still above the mercury LUT value. This means that bioremediation and phytoremediation alone would likely not be able to achieve mercury LUT values for Area IV soil. The phytoremediation study saw no increase of mercury in plant tissue samples under controlled greenhouse conditions.

In deeper soils, the 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 for these immobile fractions.

**Figure 1** presents the location of the samples collected for the Mercury Contamination Study.



## 3.2 Soil Partitioning Study Conclusions

The soil partitioning study was designed to determine the soil particle size range(s) where contaminants are found. The results are reported in Matsumoto and Martin (2015). Surface soil samples (0.0 to 0.5 or 0.5 to 1.5 ft bgs) were collected from four Area IV locations. At one location, three distinct depth intervals were sampled (0.0 to 0.5, 0.5 to 1.5, and 2.0 to 3.0 ft bgs). Each sample was subsequently separated into one of four particle size ranges (greater than 2.0 millimeters [mm], 0.425 to 2.0 mm, 0.075 to 0.425 mm, and less than 0.075 mm) via mechanical sieving. Each size fraction and an aliquot of the whole un-sieved soil for each sample were then analyzed for the COIs to determine if the COIs were preferentially found in a certain soil particle size range.

The soil partitioning study concluded that it may be possible to reduce the removal depth of contaminated soil for offsite disposal or onsite treatment, as the COI concentrations generally decreased with increasing depth in the soil column (suggesting that downward migration through the soil of the contaminants is a slow process). However, the potential for reducing the volume of contaminated soil requiring treatment or disposal via particle size separation is minimal. COI concentrations were found to exceed the LUT values in many of the soil size fractions. *Ex-situ* soil washing is a potentially applicable remedial technology due to dominance of coarse material and sands in Area IV soils, but further laboratory testing would be required to determine the strength of the chemical washing agents (solvents, surfactants, acids, etc.) required for COI removal, to determine the agent's effects on the soil, and to determine proper waste disposal procedures for any generated waste stream. It is likely that multiple washing agents would be required for COI removal, resulting in sterilization of the soil. This sterilization would likely require the addition of significant soil amendments to restore the soil biological function.

**Figure 2** presents the location of the samples collected for the Soil Partitioning Study.





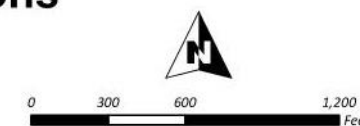
Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, AeroGRID, USDA, USGS, AeroGRID, IGN, IGP, swisstopo, and the GIS User Community.

**Legend**

- Soil Partitioning Study Sample Location
- NE Buffer Zone Cleanup Responsibility
- Site Area

**Soil Partitioning Treatability Study Sample Locations**

Santa Susana Field Laboratory  
Ventura County, California  
**Figure 2**



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### 3.3 Bioremediation Study Conclusions

The bioremediation treatability study was conducted in two phases. Both phases are reported in Nelson et al. (2015a). Phase 1 involved the collection of soil samples from across Area IV that had a range of COI concentrations. These samples were then cultured and/or analyzed to determine if the microbial organisms already present in Area IV soils are capable of degrading the COIs.

Phase 2 involved collecting Area IV soils for use in controlled laboratory microcosms to measure biodegradation rates under typical site conditions and to estimate the effectiveness of biostimulation (e.g., adding fertilizers) and bioaugmentation (e.g., adding organisms) for increasing COI degradation rates.

Phase 1 results identified 21 unique microorganism species in Area IV soils, including 14 bacteria and 7 fungi. These isolated microorganisms included three strains of the fungi *Phanerochaete chrysosporium*; bacterial species *Arthrobacter*, *Streptomyces*, *Micromonospora*, and *Variovorax*; and six strains of the bacteria *Pseudomonas*. Ten of the bacteria and three of the fungi that were isolated are known to be degraders of the COIs or come from a genus that contains known COI degraders.

Phase 2 results suggested slow biodegradation rates for the organic COIs. Slight decreases in organic COI concentrations were observed over the 8-month laboratory microcosm incubation period, but decreases were not statistically significant at 95% confidence. Biostimulation with fertilizer and bulking agents was not effective at increasing organic COI degradation rates, and biostimulation with surfactants had limited effect. Bioaugmentation with the white-rot fungi *Phanerochaete chrysosporium* was determined to have potential for degradation of dioxins.

The Phase 2 conclusions also suggested that the organic COIs at Area IV are highly weathered and strongly adsorbed to soil particles. Most of the readily biodegradable compounds have likely already biodegraded or volatilized, and the remaining compounds are likely to be sequestered in the soil, reducing their bioavailability. Therefore, if bioremediation were considered as a remedial technology, it would primarily be for those areas with low COI concentrations, low risk of COI exposure to humans, and where significant time for degradation could be allowed.

**Figure 3** presents the location of the samples collected for the Bioremediation Study.



### 3.4 Phytoremediation Study Conclusions

The phytoremediation study was conducted in two phases. Phase 1 involved the collection of plant roots, above ground stems and foliage, and associated soils to determine which plant species presently growing in Area IV may contribute to the phytoremediation of the COIs. Nine species of plants were sampled during Phase 1. Phase 2 involved growing three candidate plant species identified during Phase 1 in greenhouse microcosms to measure COI uptake/degradation rates and test the effects of additives (e.g., chelating agents, fertilizer) on uptake/degradation rates. Both phases are reported in Nelson et al. (2015d).

Phase 1 results showed that Extractable Fuel Hydrocarbons (EFHs) were observed in the roots and foliage of all plant species. However, the EFHs observed in plant tissues appeared to be phytogenic (i.e., produced by plants). PAHs were also detected in the roots of most plant species but, similar to EFHs, the PAHs detected in some species appeared to be phytogenic.

PCB uptake was not observed for any Phase 1 plant species; however, PCBs were not detected in the soils associated with Palmer's Goldenbush or Purple Needlegrass specimens. Chlorinated dioxins were found in Blue Elderberry, Palmer's Goldenbush, Yerba Santa, and Purple Needlegrass tissues.

Mercury uptake was not observed for any species; however, mercury was below the detection limits in soil associated with Palmer's Goldenbush, Narrowleaf Milkweed, and Purple Needlegrass. Silver was observed in the roots of all plant species except for Palmer's Goldenbush and Purple Needlegrass. Summer Mustard was the only species that showed uptake of silver into the foliage. This uptake of silver into the foliage was at much lower concentrations than the silver concentration present in the soil.

For the Phase 2 greenhouse microcosms, Coyote Brush (*Baccharis pilularis*) and Mule Fat (*Baccharis salicifolia*) were selected for study as they both showed uptake of most of the COIs during Phase 1. A grass species had to be selected without field screening due to growing-season constraints, and Purple needlegrass (*Nassella pulchra*) was chosen because it is native to Area IV and known for its resilience.

A comparison of Phase 2 planted and unplanted microcosm results indicated that EFH degradation rates via rhizostimulation of soil microbes are slow over the first 85 days. Final EFH concentrations at 211 days were inconclusive because of an apparent anomaly in EFH measurement between different contract analytical laboratories used for the 85-day test analysis and 211-day analysis. Therefore, 12-month samples were sent to the first analytical laboratory (same as the 85-day test). The resulting petroleum hydrocarbon concentrations fell in a similar concentration range as the initial and second analyses.

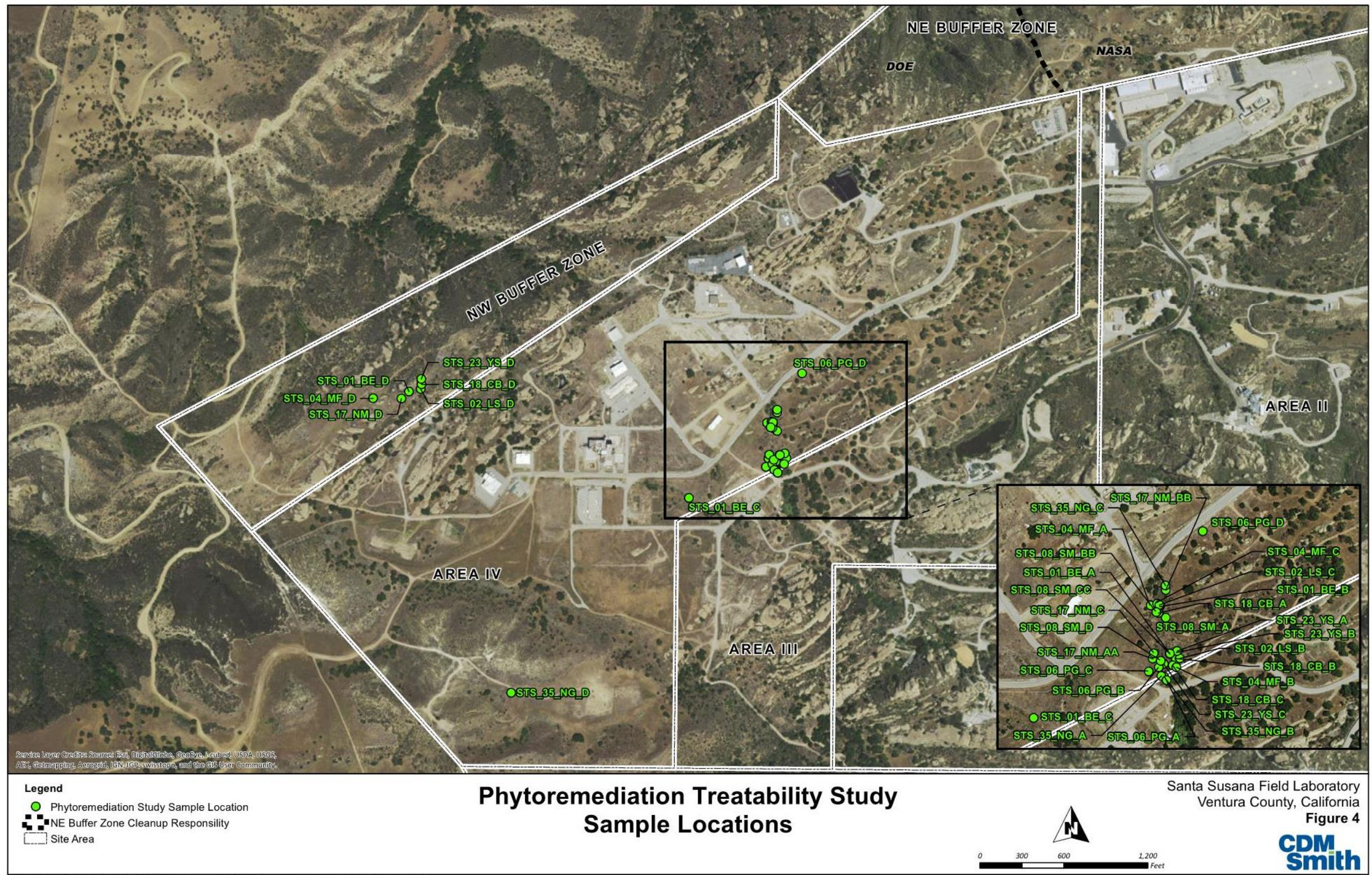
As a follow-up effort to these treatability efforts, university researchers investigated, in part, the inherent difficulties of accurately measuring petroleum hydrocarbons at low concentrations (Nelson et al., 2015b). The study's authors observed that it is difficult to accurately quantify petroleum hydrocarbons at the concentrations that were present in their Area IV soil samples (100 to 300 milligrams per kilogram [mg/kg]). As such, the study's authors concluded that reliable hydrocarbon measurement near the 5 mg/kg LUT value for TPH would be nearly impossible to achieve for Area IV. Hydrocarbon concentrations are calculated by integrating the area under numerous overlapping gas chromatograph data peaks, and thus a baseline has to be drawn underneath the peaks for the integration. The study author's stated that drifting baselines, non-zero signal at the end of the elution time, and non-zero blanks all can make the concentration calculation inaccurate at low hydrocarbon concentrations.

No significant reductions of PAH, silver, or mercury soil concentrations were observed for any of the Phase 2 microcosms. Amending the soil by adding the chelation agent ethylenediaminetetraacetic acid (EDTA) did not improve mercury uptake.

Soil PCB concentrations decreased by 13 to 15 percent (with significant variability of observed PCB concentrations) over 7 months for soil microcosms planted with purple needlegrass and coyote brush, relative to sterile controls. Since no PCBs were observed in the plant tissue of these microcosms, the mechanism for this PCB reduction appears to be stimulation of soil bacteria. Soil dioxin concentrations decreased by 18 to 20 percent over 7 months for soil microcosms planted with coyote brush. Rhizostimulation again appears to be the operative mechanism.

As with bioremediation, phytoremediation could be useful in conjunction with site restoration in areas with low COI concentrations, low risk of COI exposure to humans, and where significant time for degradation could be allowed.

**Figure 4** presents the location of the samples collected for the Phytoremediation Study.



### 3.5 Natural Attenuation Study Conclusions

The natural attenuation study was conducted in two phases. Phase 1 primarily consisted of a literature review of natural attenuation processes to determine which Area IV COIs are amenable to natural degradation processes. The literature review results were then used to estimate the time that would be required for natural attenuation of these COIs to reach LUT values, based on current Area IV soil COI concentrations. Phase 1 also examined soil COI concentrations from locations resampled over a period of time in order to estimate site-specific natural attenuation rates. All of these results were presented in a Phase 1 natural attenuation study report (Nelson et al., 2014).

**Figure 5** presents the location of the samples collected for the Natural Attenuation Study.

Phase 2 involved using findings from the companion bioremediation and phytoremediation treatability studies to further develop site-specific COI degradation rates under typical site conditions. The Phase 1 natural attenuation study report was then updated with the findings from Phase 2 (Nelson et al., 2015c).

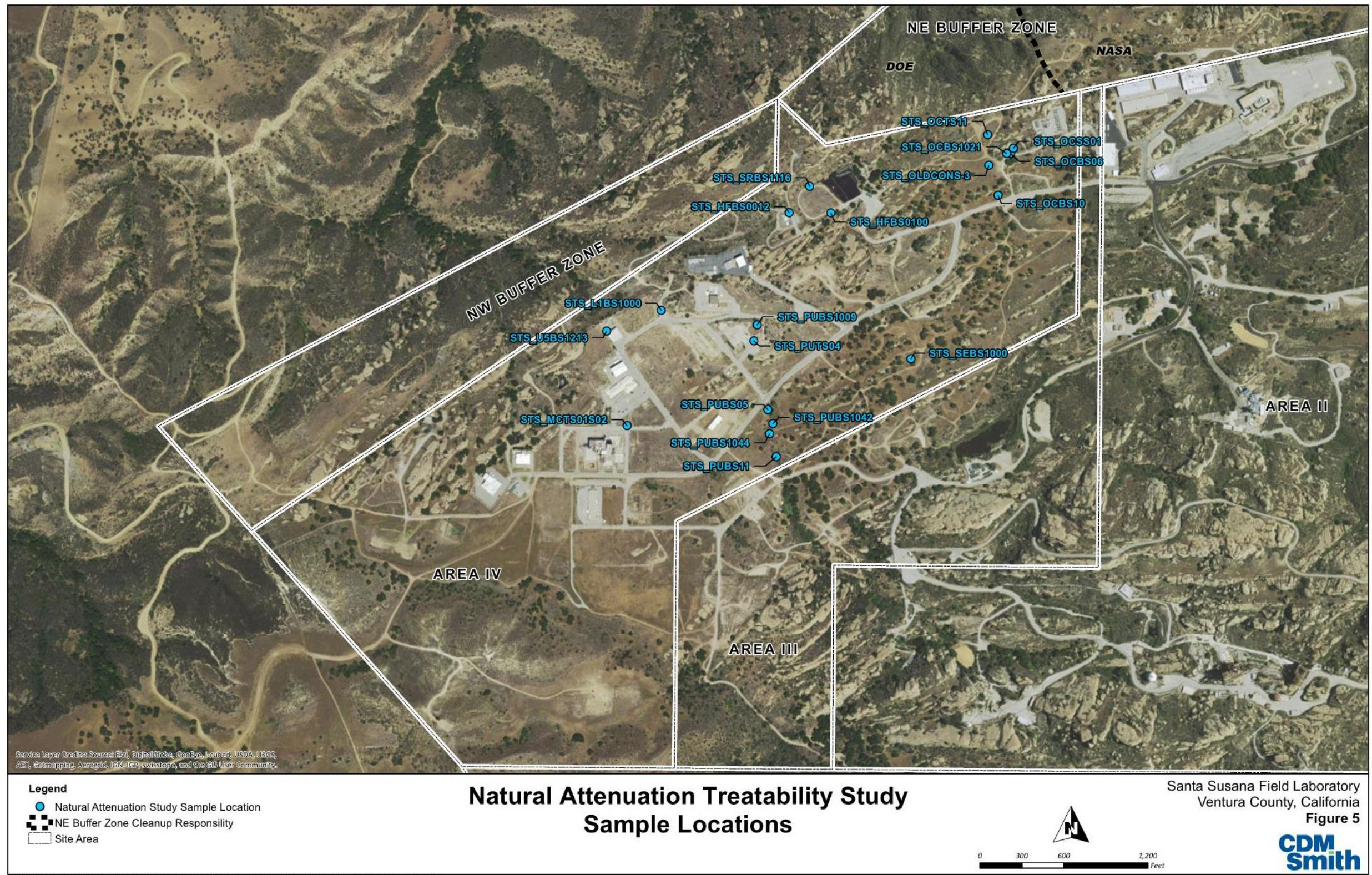
The findings of the Phase 1 literature review (Nelson et al., 2014) suggest all organic COIs in Area IV soils will eventually biodegrade, but some COIs will degrade slowly. Predicted times for Area IV soil COI concentrations to reach LUT values, as determined by the natural attenuation study Phase 1 literature review, are as follows:

- Petroleum hydrocarbons: 0.42 to 69 years
- PAHs: 5 to 15 years
- PCBs: Undetermined (half-life = 40 years)
- Chlorinated dioxin/furans: 1 to 50 years

The broad range of predicted natural attenuation rates were attributed to the variances in the initial concentrations and biodegradation rates reported in the literature.

Phase 2 analyses of the companion bioremediation and phytoremediation studies suggested longer estimated remediation times than those predicted by the published literature. Conclusions regarding Area IV-specific natural attenuation rates, as determined by the review of the bioremediation and phytoremediation treatability study results, are provided further below.

This study ultimately concluded that natural attenuation at Area IV is expected to take on the order of decades to reach current AOC LUT values for the various COIs. These predicted remediation times are partially the result of the current clean-up goals to reach background COI levels and the result of COI weathering into the soil matrix, rendering the contaminants generally unavailable to biological or phytoremediation potential. The natural attenuation study also concluded that much shorter remediation times would be expected if clean-up goals were set similar to those set for typical past industrial sites (Nelson et al., 2015c).





### 3.5.1 EFH Natural Attenuation Conclusions

More than a 40 percent reduction in EFH concentrations in 126 days was observed for one of the three unamended bioremediation Phase 2 microcosms. However, little or no EFH was observed for the other two microcosms. These results indicate the variability in the efficacy of hydrocarbon bioremediation.

Naturally occurring organic matter could possibly be misinterpreted as petroleum hydrocarbons during chemical analyses. As stated above, Nelson et al. (2015b) determined that it is difficult to accurately quantify petroleum hydrocarbons at the concentrations that were present in their Area IV soil samples. The study also concluded that reliable hydrocarbon measurement near the 5 mg/kg LUT value would be nearly impossible to achieve.

### 3.5.2 PAH Natural Attenuation Conclusions

Phase 2 bioremediation microcosm experiments did not show significant PAH biodegradation for the unamended controls. Phytoremediation study results also indicated little or no PAH biodegradation in microcosm soils with plants. Together, these results suggest limited PAH degradation under natural conditions, and that the PAHs remaining in Area IV soils have low biodegradability. This limited PAH degradation may be a result of PAHs being weathered and sequestered in the soil matrix, limiting their availability to microorganisms.

### 3.5.3 PCB Natural Attenuation Conclusions

Bacterial PCB degradation requires anaerobic dechlorination, and anaerobic conditions were not observed in Area IV soils. This suggests that bacterial dechlorination of PCBs will not be a viable mechanism for PCB degradation. However, fungal biodegradation of PCBs is possible under aerobic conditions, and three strains of the white-rot fungi *Phanerochaete chrysosporium* reportedly capable of biodegrading PCBs were isolated from Area IV soils. PCB degradation via white-rot fungi may be a potential remedial measure.

PCB concentrations decreased over the bioremediation microcosm incubation period, but these decreases were not statistically significant at the 95% confidence level from the sterile controls. In the phytoremediation study, soil PCB concentrations also decreased for soil microcosms planted with purple needlegrass and coyote brush. No PCBs were observed in plant tissue, so the mechanism for PCB concentration reduction appears to be stimulation of microorganisms in the soil.

### 3.5.4 Dioxin Natural Attenuation Conclusions

Only small decreases in dioxin concentrations were observed in the unamended bioremediation soil microcosms, suggesting slow dioxin biodegradation under natural attenuation conditions. The bioremediation microcosms augmented with the fungi *Phanerochaete chrysosporium* exhibited decreases in chlorinated dioxin concentrations more than in unamended microcosms. Some decreases in soil dioxin concentrations were observed in the planted phytoremediation microcosms. This suggests some potential, albeit limited, for dioxin remediation via phytoremediation processes.



## Section 4

### Summarized Conclusions

Results from the Cal Poly and UCR soil treatability studies identified the following conclusions:

- The COIs present in Area IV soils appear to be highly weathered. The easily degraded COIs have likely already been degraded.
- Due to their state of weathering, the COIs are fairly recalcitrant and are not likely readily amenable to natural attenuation, bioremediation, or phytoremediation processes.
- It will take considerable time (possibly decades in some cases) to achieve current LUT values for organic COIs via natural attenuation, bioremediation, or phytoremediation processes.
- It is likely that bioremediation or phytoremediation processes cannot achieve current LUT values, regardless of duration, for mercury as the immobile fraction of mercury present in many samples is, by itself, above the mercury LUT value.
- The potential for reducing the volume of contaminated soil requiring disposal or treatment via size separation is minimal.
- *Ex-situ* soil washing is a potential remedial technology for Area IV soils; however, further study would be required to determine the required strength of the extraction fluid and its effects on the soil.
- University researchers determined that naturally occurring organic matter could possibly be misinterpreted as petroleum hydrocarbons during laboratory chemical analyses.



## Section 5

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