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REPRESENTATIVE SAMPLING AND ANALYSIS OF HETEROGENEOUS SOILS

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INTRODUCTION

Sampling and analysis presents specific problems with heterogeneous soils. These problems have been carefully evaluated in several projects for the Risk Reduction Engineering Laboratory (RREL), specifically Superfund Innovative Technology Evaluation (SITE) demonstrations. Of particular concern is the inability of standard analytical methods to account for heterogeneous samples. While a typical analytical method may normally accommodate only 2 grams (g) of sample (and therefore requires that "oversized material" be removed from a sample before analysis, potentially biasing analytical results), a representative sample aliquot from a heterogeneous site may require a sample size that is orders of magnitude greater than this. The inability to analyze representative samples may be the result of various factors, including the presence of oversized material (such as rocks or other debris); highly concentrated contaminants (such as lead chunks or tar balls), which may preclude taking large laboratory samples that would overwhelm instrument capabilities; or volatile contaminants which cannot be mixed to

create a more homogeneous aliquot because of the volatility of the contaminant being investigated. This paper contains several case studies that present the problems associated with sampling and analyzing heterogeneous soils; approaches to specific problems encountered in each of the projects discussed; and the relative success of these approaches.

Approaches previously recommended for selected RREL projects include the following: (1) screening pre-treated soil and then treating and analyzing the screened fraction; (2) grinding large amounts of material, followed by homogenization and analysis of a representative aliquot; (3) screening, sieving, and then analyzing separate portions of a sample; (4) removing oversized material from a sample, analyzing the sample portion that remains, and correcting for the percentage of oversized material in the sample; and (5) analyzing larger sample sizes. While one approach may be valid for a particular site or type of contamination, the case studies presented below emphasize how particular approaches were tailored to the perceived problems. For example, heterogeneous soils may include large rocks, (which are usually relatively free of contamination) or tar balls, which are highly concentrated forms of organic contamination. Excluding either of these materials may bias sample results. Typical laboratory glassware or the unavailability of concentrated laboratory spikes can also present problems particularly when analyzing larger sample sizes. Grinding and sieving samples may lead to loss of contaminants through volatilization or may release contamination from the inside of the oversized material, thereby producing biased results. In addition, there may be physical limitations to sampling based on the sample type. For example, oily samples or samples containing metallic lead may not mix, sieve, or grind well.

Data comparability is also an important consideration when sampling. Therefore, it may be more important to use a consistent approach from one event to the next, rather than to use a more accurate technique at a subsequent event. Another consideration, when sampling, is project cost limitations which may prevent the analysis of numerous samples necessary to fully characterize the contamination at a specific site. The examples presented below illustrate approaches used by RREL investigators to alleviate specific sampling and analysis problems associated with heterogeneous soils.

METHODOLOGY

A variety of sources were used during the preparation of this paper. A literature search was performed and previously published documents were reviewed. In addition, individuals considered knowledgeable in the area of sampling were contacted to provide further information. Quality Assurance Project Plans for RREL projects were also surveyed from the last five years to identify projects for the accompanying case studies.

The case studies below are structured as follows. First, a brief project description is presented with a discussion of site characteristics, the technology, the nature of the problem, the options considered, and the option chosen. The results of the chosen option are then presented, with the last section of each case study presenting the lessons learned for that particular site.

CASE STUDY 1 - RADIO FREQUENCY (RF) HEATING

The RF Heating technology uses electromagnetic energy in the RF band to heat contaminated soil. The soil is heated by providing power to an array of antennae located in drilled bore holes within the soil. Petroleum hydrocarbon, volatile, and semivolatile contaminants present are volatilized, collected, and treated. Soil moisture is also volatilized to provide a steam sweep inside the treatment zone. The organic vapors and moisture are recovered by applying a vacuum to vapor extraction wells near the antennae.

Particle size distribution (PSD) results indicated that the top 4.9 meters (m) of soil consisted of 25 to 48 percent gravel by weight, and that between 5.5 m and 9.1 m below the ground surface, the soil consisted primarily of gravel (64%-86%).

Due to the large amount of gravel, considerations were given to the manner in which a representative sample might be analyzed. The options considered included: (1) grinding and homogenizing; (2) screening and analyzing the different portions; and (3) removing the rocks and analyzing the portion that remained, with subsequent correction of the results based on PSD results for each sample. The third option was chosen. The analytical results were evaluated both with correction and without. This comparison indicated that the chosen method did not change the site evaluation.

CASE STUDY 2 - BIOGENESIS SOIL WASHING TECHNOLOGY

The BioGenesis soil washing technology uses a proprietary solution to transfer organic contaminants from a soil matrix to a liquid phase. The technology uses a specially designed wash unit that can treat contaminated soil at rates of up to 10 metric tons per hour. After washing, soil is stored in containers, and the liquid waste stream is either treated or recycled. The combination of the surfactant that remains on the soil and the water left over from washing enhances microbial activity, which biodegrades any residual contamination.

The critical parameter measured in soil samples was petroleum hydrocarbons. To determine the removal efficiency of petroleum hydrocarbons, multiple waste streams were sampled and analyzed, including feed soils and treated soils. The presence of large rocks and tar balls prompted questions about the homogeneity of the soils and the representativeness of the sampling process. As a result, the sampling staff began subjectively excluding both rocks and tar balls from pre- and post-treatment samples. In addition, the means for excluding tar balls differed between pre- and post-treatment samples, which introduced further sampling bias.

To address the above concerns, the first samples were recollected by sampling large amounts of soil (346 kilograms). This entire amount of soil was screened through a 12.7 millimeter (mm) diameter screen; separated by hand into soil, tar ball, and rock fractions; and weighed to determine the percent composition of each. An aliquot from each fraction was analyzed. For rocks, 100 g to 200 g aliquots were obtained before rinsing the rocks with solvent. A 1 g aliquot of the tar ball material was also obtained and dissolved in freon. The solvent extract from both matrices was analyzed separately for petroleum hydrocarbons. The analytical data was then mathematically recombined to yield sample results. Results showed that the presence of rocks and tar balls were offsetting factors and did not affect the petroleum hydrocarbon data during the demonstration.

CASE STUDY 3 - TORONTO HARBOUR SOIL RECYCLING DEMONSTRATION

The Toronto Harbour demonstration is a three-phase operation consisting of a soil washer (used to separate the soil into different sized sample streams), a chelating process (for removal of metals), and a bioslurry process (to treat organics remaining in the fine material). SVOCs, metals, and oil and grease were the critical parameters for this project.

Two concerns, discovered in the field, were associated with representative sampling. First, the feed material consisted of a significant amount of rock and contained high concentrations of organics. Secondly, the oversize sample stream from the soil washer consisted of rocks ranging from about 6 mm to 25 mm in diameter.

To address these concerns, the feed material sample size was increased to 100 g to improve representativeness. Samples were then split by the laboratory into soil and rock fractions using a 9.5 mm sieve, and analyzed separately. This allowed the soil fraction to be homogenized and analyzed by SW-846 Method 3540 (soxhlet extraction) using 2 g aliquots. The rock fraction obtained from the 100 g aliquot was also analyzed by Method 3540 to ensure soil clinging to the outside of the rocks would be fully included.

For the oversize sample stream, the original plan was to grind and homogenize the samples. This was rejected as the grinding of these samples would expose surfaces of the rock that would not otherwise be exposed for extraction thus creating a non-representative sample. It was decided that a 200 g aliquot would be obtained for the laboratory and the entire sample would be extracted and analyzed for organics. Any organic contaminants on the surface of the rocks could then easily be extracted by using a solvent wash. This allowed large quantities to be extracted without the usual limitations associated with laboratory glassware. For both the oversized fraction and the feed material, several sample aliquots had similar analytical results indicating samples were representative.

CASE STUDY 4 - BESCORP SOIL WASHING PROCESS

The Bescorp process uses a combination of soil washing, size segregation, and density separation to remove heavy metals from soils. This demonstration was carried out at a previous lead-acid battery reclamation site. Native soil consisted of approximately 50% gravel (>6.4 mm), 40% sand (6.4 mm to 0.1 mm), and 10% fines (<0.1 mm). Lead tended to be most concentrated in the fine fraction, but the coarser fractions also contained significant fractions of lead as battery posts, lead plates, and lead materials attached to battery casings.

This project represented a serious sampling and analytical challenge in that it required sampling a heterogeneous soil for lead that was present both as lead chunks and as fines. The primary challenge was measuring total lead in the coarse fractions. The standard laboratory digestion procedure digests only a 1 g aliquot, which is unsuitable for samples containing pieces of rock and lead that can weigh several grams each.

For this project, a 1 kilogram (kg) sample was first dried and then screened into four weighed fractions: 64 mm to 6.4 mm, 6.4 mm to 2 mm, 2 mm to 0.1 mm, and < 0.1 mm. Each fraction was examined visually for pieces of lead, which were removed and weighed. The two larger fractions were then placed in a polyethylene bottle and digested with 6% HNO_3 overnight on a rotating apparatus, while 2 g aliquots of the two smaller fractions were placed in beakers and digested with SW-846 Method 3550 and analyzed. The masses measured were then combined to arrive at an average concentration for the entire sample.

The approach described above was satisfactory for the sand and fine fractions, but marginal for the larger fractions due to the intermittent occurrence of lead chunks. A larger initial sample size (e.g., 50 to 100 kg) could have alleviated this problem.

CASE STUDY 5 - THE COGNIS INC. (COGNIS) TERRAMET^{TM} LEAD EXTRACTION PROCESS

The COGNIS Inc. TerraMet^{TM} lead extraction process uses chemical leaching to remove metals bound to sands and fines (including silts and clays). Sands and fines are separated before leaching, and particulate lead is collected for recycling by density separation. Lead present in the liquid phase is precipitated for recovery, and the leaching solution is recycled.

Samples were collected from the feed soil and several sand and fine streams before and after leaching. Obtaining representative samples of some of the coarse-grained soil streams became an issue due to the presence of lead shards in the samples. Grinding soil samples prior to analysis was determined to be the most appropriate method of obtaining representative samples. Originally, soils were to be ground finely enough to pass through a 0.11 mm sieve. However, based on time and cost evaluations, it was decided that this approach would not be applicable in this situation. Samples from the Cognis demonstration are presently being analyzed to determine the most appropriate methods of sample preparation and analyses.

CASE STUDY 6 - BIOVENTING FOR ENHANCED BIODEGRADATION

The Bioventing process is an in-situ biological process that increases aerobic degradation of organic materials in soil. Specifically, several wells are drilled into the contaminated soil plot and air is pumped into the wells for a period of several years to increase aerobic activity and thereby stimulate biodegradation. In-situ soil samples are taken at pre- and post-demonstration periods to determine removal efficiency for the process.

While at the site, it was observed that soil cores contained what appeared to be a significant number of rocks and creosol balls, which were later referred to as cinder chunks. The rocks and cinder chunks were separated from the soil and saved. The soil samples that remained were then homogenized in the field and sent to the laboratory for analysis as per standard procedures. The total volume of the rocks and cinder chunks was determined for the entire site. A ratio was then calculated for the volume of rocks and cinders in comparison to the total soil volume at the site. This was based upon estimations of soil core volumes and the number of soil cores collected. A representative sample of the rocks and cinder chunks was then analyzed by the laboratory. It was determined that no significant bias existed by excluding these materials in the analyses. Thus, the analysis of a rock/cinder sample was necessary, but the number of analyses was minimized, with the results obtained from the soil analyses verified as being representative of the entire site.

CONCLUSIONS

RREL investigators perform a variety of research projects and frequently encounter unusual sampling situations. The following conclusions have been drawn from heterogeneous soil sampling efforts associated with RREL projects:

- No single approach for sampling and analyzing heterogeneous soils will be applicable for all sites or technologies.
- Multiple approaches for sampling and analyzing heterogeneous soils may need to be used at different sampling locations for a specific technology.
- New approaches for sampling and analyzing heterogeneous material must continue to be developed.
- The risk of collecting unusable data is reduced by developing an adequate sampling approach *before* an actual sampling episode. Before selecting an approach, investigators should review the site characteristics, the technology, the nature of the problem, and the approaches available. Once an approach is selected, investigators should review its success and document the outcome.

In light of the above conclusions, RREL will continue to handle the sampling of heterogeneous soils on a case-by-case basis, while drawing on the knowledge base it has developed. RREL anticipates maintaining a database of heterogeneous sampling approaches, and their results, so that RREL investigators can improve their future planning decisions.

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BIOREMEDIATION OF TRINITROTOLULENE BY A RUMINAL MICROORGANISM

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INTRODUCTION

2,4,6-trinitrotoluene (TNT) has been widely used for the production of explosives because of its low boiling point, high stability, low impact sensitivity, and safe manufacture. TNT is known to produce adverse health effects from occupational exposure including increased incidences of aplastic anemia, liver damage, dermatitis, ocular disorders, and gastrointestinal distress. In addition, TNT is of ecological concern based on its toxicity to certain aquatic organisms. More than 1,100 military facilities, each potentially contaminated with munitions waste, are expected to require treatment of more than one million cubic yards of contaminated soils. The cost associated with remediation of these sites has been estimated to be in excess of $1.5 billion.

Recently, researchers have studied ruminal microorganisms in relation to their ability to degrade xenobiotic compounds. Many of these organisms are strict anaerobes with optimal redox potentials as low as -420 mV . Ruminal organisms have been shown capable of destroying some pesticides, such as parathion, p-nitrophenol, and biphenyl-type compounds; thiono isomers, (8, 33); and nitrogen-containing heterocyclic plant toxins such as the pyrrolizidine alkaloids (5). Many of these compounds have structures similar to TNT.

A TNT-degrading ruminal microorganism has been isolated from goat rumen fluid with successive enrichments on triaminotoluene (TAT) and TNT. The isolate, designated *G.8,* utilizes nitrate and lactate as the primary energy source. *G.8* was able to tolerate and metabolite levels of TNT up to the saturation point of 125 mg/l.

Objectives

Based upon the results of previous studies, the present research was directed at understanding the process of TNT degradation by the denitrifying ruminal microorganism *G.8* (5). The objectives of this study were: 1) to identify specific metabolites and define TNT destruction pathways and 2) to understand TNT and the metabolites transformation mechanisms on the different primary electron acceptors.

METHODOLOGY

Growth Medium

The media used to incubate the isolate in serum bottles consisted of (mg/l) $CH_3CHOHCOONa$ (500), $MnSO_4.H_2O$ (8.5) $FeSO_4.7H_2O$ (10), KNO_3 (2000), $ZnSO_4.7H_2O$ (5), $CaCl_2.2H_20$ (24), $Na_2HPO_4.H_2O$ (2550), H_3BO_3 (1.5), $NaMo_4.2H_2O$ (1.5), $NaH_2PO_4.H_2O$ (975), $CoCl_2.6H_2O$ (0.6),