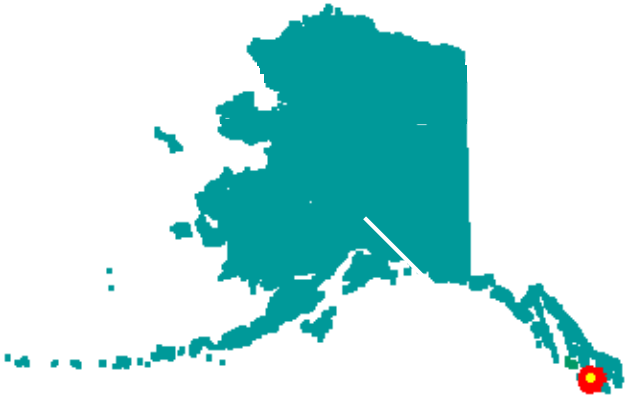
CASE STUDY
Petroleum-Contaminated Soil Stockpile Multi-Increment Sampling
Prince of Wales Island – Southern Southeast Alaska
August 2007

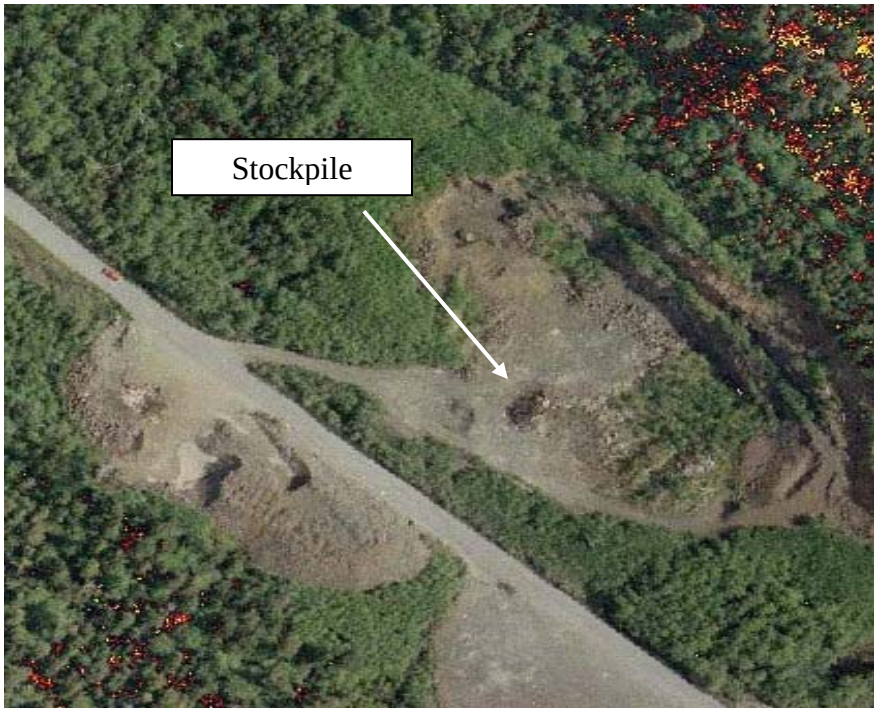
Purpose

The purpose of this project was to test the protocols in the department's draft Multi-Increment Sampling Guidance.

Location

A small soil stockpile in a rock quarry on Prince of Wales Island near Craig was sampled. Craig is located on a small island off the west coast of Prince of Wales Island and is connected by a short causeway. It is 56 air miles northwest of Ketchikan and 220 miles south of Juneau.





Synopsis

During the 2006 excavation and removal of an underground heating oil tank, discrete samples were collected which documented diesel range organics (DRO) between 300 – 900 mg/kg. Stockpile tilling and fertilizing were conducted by the responsible person several times after the soil was moved from its original location in May 2006.

Department of Environmental Conservation (DEC) personnel sampled the stockpile on May 24-25, 2007. Multi-increment bulk samples were collected from 90 different locations in the 12-15 cubic yard stockpile. Sub-samples were sieved to 2 mm and placed in sample jars for laboratory analysis. Fundamental error, relative standard deviation, and the 95% UCL of the mean were determined following receipt of analytical results; all calculations were within acceptable parameters. The average DRO concentration was below the method 2 migration to groundwater cleanup level (230 mg/kg).

Field Sampling Procedures

Tools and Materials

- Internet random number generator
- Garden shovel
- 20-penny galvanized nails
- Hand spade
- Stainless steel spoons
- 2-gallon zip-lock bags
- Colored nylon twine
- 50-foot flexible tape
- 12-foot tape
- Stainless steel ruler
- Hand calculator
- Leather gloves
- Disposable latex sampling gloves
- Field notebook
- Digital camera

Although the edges of the stockpile were not clearly delineated, the stockpile dimensions measured approximately 33’ x 13’ x 1’ deep. A 30-cell grid (10 cells long and 3 cells wide) was constructed using 20-penny nails for stakes and colored twine to form the grid pattern. Each cell measured approximately 40 inches in length by 52 inches in width.

Random planar and depth coordinates were determined after the cell dimensions were established using an on-line random number generator. Thirty length coordinates were determined by setting the minimum and maximum numbers in the random number generator between 0 and 40. Thirty width coordinates were determined by setting the minimum and maximum numbers between 0 and 52. Thirty depth coordinates were determined by setting the minimum and maximum numbers between 6 and 12. This

ensured that the top six inches of soil would not be sampled, as dictated by the MI Guidance.

21	22	23	24	25	26	27	28	29	30
11	12	13	14	15	16	17	18	19	20
1	2	3	4	5	6	7	8	9	10

North

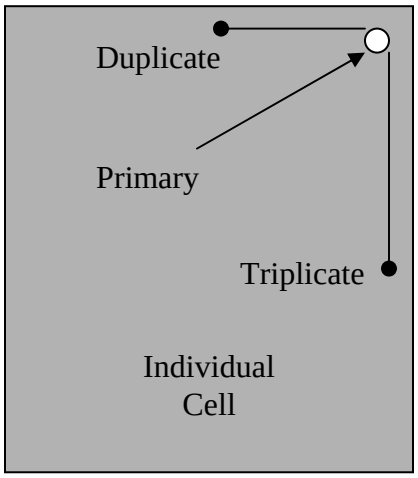
Overall dimensions: 33’ x 13’
Individual cell dimensions: 40” x 52”
Depth: 12”

Sampling locations were determined by assigning X and Y axes to the grid. Length was measured along the X axis beginning at the southwest corner of the cell, followed by a Y axis, or perpendicular measurement, to determine the width coordinate. A 20-penny nail was pushed into the soil at each coordinate to establish the primary sampling location. For example, the random coordinates for cell # 2 were 33 inches along the length (X axis), and then 18 inches to the north (Y axis). Beginning at the southwest corner of each cell, this process was repeated until the 30 primary sampling locations were established.

A garden shovel was used to dig the holes to the approximate depth once all planar coordinates were determined. A small hand spade and 12” ruler were used to obtain the exact depth at each location and to clean away any soil that may have sloughed from the sidewalls.

Using a stainless steel spoon, three tablespoons of soil (which equates to about 60 grams per increment) were collected from the proper depth at each location and placed in Zip-lock bags. If the hole was over-excavated the sample was taken from the sidewall at the proper depth. This process was repeated until all thirty primary bulk sample increments were collected.

Duplicate and triplicate bulk samples were collected at the same depth as the primary sample within each cell using the procedures described above. Sample locations were determined by stepping out approximately ½ the distance of the cell length and width from the primary sample hole. The step-out direction varied depending on the location of the primary sample hole within the cell. For example, if the primary hole was near the far corner, as shown by the figure to the right, step-out directions were to the left (duplicate) and down (triplicate). This method ensured an independent and systematic random approach within each cell.



Bulk soil samples, weighing approximately 1.8 kilograms each, were doubled bagged, sealed and taped for shipment. Samples were not cooled because transit time back to Juneau was minimal. After the samples arrived in Juneau they were refrigerated until the time of sub-sampling.

Sub-Sampling Procedures

Tools and Materials

- # 10 sieve
- Stainless steel trays lined with aluminum foil
- Stainless steel spatula
- 4-ounce amber sample jars
- Bench scale
- Wire brush
- Liquid soap
- 12” ruler
- Disposable latex sampling gloves
- Notebook and digital camera

Sub-sampling was conducted in the Department of Transportation and Public Facilities Materials Lab in Juneau. Six sub-samples were collected, including a duplicate for each of the three sub-samples for an additional comparative metric.

Bulk samples were sieved to 2 mm using a #10 sieve. Following an initial attempt at sieving the wet soil (sample HWL 1-1), the bulk samples were placed on trays and dried at room temperature for 30 hours prior to sub-sampling.

Before sieving, the bulk soil samples each weighed approximately 1.8 kilograms. Less than one half of the bulk sample was removed during the sieving process, leaving approximately 1000 grams of soil for use during sub-sampling.

Sieved soil was spread onto a foil-lined tray with dimensions of about 7” x 10” x 3/8” thick. The soil was then evenly divided into a thirty-square grid. About 1.5 grams were collected from a minimum of two locations in each square using a small spatula to ensure that fine particles were not missed.

The 30 sub-sample increments, weighing approximately 45 grams total, were placed in a labeled, wide-mouth sample jar placed on a bench scale. The process was repeated for

the remaining two bulk samples and their duplicates; the spatula was cleaned with soap and water between each bulk sub-sampling event.

Results

Table 1 **Laboratory Results (DRO by AK 102)**			
#1 Samples		**#2 Samples**	
HWL 1-1	130 mg/kg	HWL 1-2	87 mg/kg
HWL 2-1	160 mg/kg	HWL 2-2	140 mg/kg
HWL 3-1	110 mg/kg	HWL 3-2	110 mg/kg
Mean	**133.33 mg/kg**	**Mean**	**112.33 mg/kg**
Standard Deviation	**25.17**	**Standard Deviation**	**26.58**

Table 2
Fundamental Error (based on mass analyzed by the lab)

$$FE = \sqrt{\frac{20(d^3)}{m}}$$

d = particle size (0.2 cm for all samples)
m = sample mass

Sample 1-1	**Sample 1-2**	**Sample 2-1**	**Sample 2-2**	**Sample 3-1**	**Sample 3-2**
m = 29.98 g	m = 30.04 g	m = 30.05 g	m = 30.01 g	m= 30.03 g	m = 30.02 g
FE = 0.07	**FE = 0.07**	**FE = 0.07**	**FE = 0.07**	**FE = 0.07**	**FE = 0.07**

Table 3 Relative Standard Deviation	
$RSD = \frac{100s}{\bar{x}}$	
#1 Samples	**#2 Samples**
$RSD = \frac{100(25.17)}{133.33}$	$RSD = \frac{100(26.58)}{112.33}$
$RSD = 18.9\%$	$RSD = 23.7\%$

Table 4 95% Upper Confidence Limit	
$95\%UCL = \bar{x} + \frac{ts}{\sqrt{n}}$	
#1 Samples	**#2 Samples**
$95\%UCL = 133.33 + \frac{(2.92)(25.17)}{\sqrt{3}}$	$95\%UCL = 112.33 + \frac{(2.92)(26.58)}{\sqrt{3}}$
$95\%UCL = 176$	$95\%UCL = 157$

Quality Control Review

1. Field QC protocols were violated because samples were not cooled for shipping.

2. Sub-sampling inconsistency occurred because one sub-sample was collected wet and the other five sub-samples were collected dry.

3. Laboratory samples were prepared and analyzed for DRO according to Method AK102. The Laboratory Data Review Checklist was completed for the lab data. All data requirements were met except the 14-day hold time; sample temperatures were thus exceeded due to sub-sampling challenges and shipping problems.[1]

[1] Samples were temporarily misplaced in Seattle, returned to Juneau and then re-packaged and sent to the Analytica lab in Colorado.

Discussion

Although the stockpile was shallow it was compacted and difficult to excavate by hand. Field sampling was therefore labor intensive, requiring approximately 15 person hours to complete.

Data quality may have been affected by three factors.

1. Bulk samples were not cooled for shipping; possible hydrocarbon degradation due to an increase in microbial activity may have occurred.

2. The initial attempt at sub-sampling was challenging due to high soil moisture content which caused clumping and clogged the #10 sieve. The next five sub-samples were collected after first air drying the remaining bulk samples. However, data comparability is assumed because of the requirement to report on a dry weight basis.

3. The 14-day holding time and sample temperatures were exceeded. Again, increased microbial activity due to elevated temperatures may have biased sample results low.

Fundamental Error (FE) is a result of not representing proportional concentrations of all particles in the population. Adequate mass (30 grams) and a maximum particle size of 2 millimeters control fundamental error. As expected, the FE for each of the samples was well below the required 15% since the particle size was $\leq$ 2 mm and the sample masses were > 30 g.

Relative Standard Deviation (RSD) is a measure of data precision and is used as a quality control measure to assess the MI sampling procedure and the mean concentration of the decision unit. The RSD calculations were 18.9% for Samples #1 and 23.7% for Samples #2. The RSD limit for a normal distribution is about 30%; therefore we can be confident that the MI sampling results are representative.

The 95% Upper Confidence Limit (UCL) for Samples #1 was 176 and for Samples #2 was 157, indicating that the DRO cleanup level of 230 mg/kg has been met..

Conclusions and Recommendations

1. Quality control problems could cause DEC to reject the data under some circumstances, such as closing a site to a human health-based threshold.

2. The random number generator worked well to establish three-dimensional, independent sampling coordinates. A simpler method, and equally effective, would be to generate a random location for the first cell and apply that coordinate to all other cells.

3. Even though the stockpile was shallow and had been periodically mixed, the MI Guidance was strictly followed to ensure that the top six inches was not sampled. This should be standard practice, even for shallow, well-tilled stockpiles.

4. While 20-penny galvanized nails worked to establish the field grid they pulled out too easily; wooden stakes would have performed better. For large decision units, cell corner stakes would be sufficient rather than delineating the entire grid with twine.

5. To minimize field time, QC for properly designed MI sampling could possibly be reduced for low-risk petroleum sites where concentrations are expected to be well below levels that may be a human health concern. Examples are direct contact and inhalation where migration to groundwater is not a concern or where groundwater is already being monitored. The merits of this recommendation will be evaluated at the end of the 2007 field season.

6. Proper sampling oversight can best be achieved by the third party contractor directly employed by the responsible person. For this reason, a contractor may wish to conduct sub-sampling in a controlled environment prior to shipment to the selected laboratory. The merits of this recommendation will be evaluated at the end of the 2007 field season. .

7. Sieving wet soil is problematic. Although holding times and temperatures should be maintained to the extent practicable, contaminants such as weathered diesel are not expected to significantly degrade. Air drying prior to sieving may therefore be justified for DRO and RRO in some cases, particularly at lower risk sites. If volatile contaminants are a concern, separate samples should be collected according to procedures in the guidance. The merits of air drying prior to sieving will be evaluated at the end of the 2007 field season.

8. At sites where the action level is human health direct contact or inhalation, where migration to groundwater is a significant issue, or where another exposure pathway is a potentially significant concern, splitting each increment sub-sample as an additional laboratory QC measure may be prudent. Fundamental error, relative standard deviation, and 95% UCL calculations can be independently performed on the two data sets; archived lab samples could be evaluated if there are significant differences. The merits of this recommendation will be evaluated at the end of the 2007 field season.