Composite Sampling for Soil VOC Analysis

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Introduction

The goal of all sampling efforts should be to collect samples that are representative of the site in question. The degree of representativeness of the collected sample is affected by both temporal and spatial variability. Spatial variability of volatile organic compounds (VOCs) in soils can be large with more than an order of magnitude difference among samples within distances as little as 15 cm apart (Schumacher and Minnich, 2000; West *et al.*, 1995).

To overcome the influence of spatial variability in soils, one approach generally used to optimize sample representativeness has been to increase the number of samples collected at the site. However, this approach results in greatly increased project costs. Composite sampling has been suggested as an alternative means to obtain data which are representative of the overall site characteristics. Composite sampling consists of taking a number of field samples, adequate to represent the population in question, and combining the samples to form a single sample. Two principle advantages of sample compositing include: (a) reducing the inter-sample variance (*i.e.*, improving the precision of the mean estimate while reducing the probability of making an incorrect decision, and (b) reducing the sampling and analytical costs (ASTM, 2003). The principle limitations of sample compositing include: (a) loss of discrete information about the sample, and (b) the potential for dilution of the contaminants in a sample with uncontaminated material.

While sample compositing methods have been defined and tested for soils contaminated with non-volatile elements and compounds (*e.g.*, heavy metals, PCBs, pesticides, and PAHs), nearly all these methods state that they are inappropriate for samples contaminated with VOCs. The objective of this study was to demonstrate a procedure for collecting composite samples for soils contaminated with VOCs and to determine the efficacy of the composite sample to accurately represent the grand mean of the individual samples from which it was created.

Figure 1. Soil Core Collection in Grants, NM

Figure 2. Soil Core ready for Subsampling.

Methods

To explore the feasibility of composite sampling for soil VOC analysis, samples were collected from multiple plots at two hazardous waste sites. At each plot, five cores were collected, each to a vertical depth of 1 m (Figs. 1 and 2). The five cores were collected within a 1 m^2 area to help minimize lateral variability among the cores (Fig. 3). Each core was cut into sections (through both the liner and soil) at 20, 30, 40, 50, 60, 70 and 80 cm below the ground surface (Fig. 4). After each cut, approximately 5 g of soil was removed from the newly exposed surface (top end of the cut) using a truncated syringe, placed in a preweighed 40-mL septum-sealed vial containing 5 mL of methanol. A second 5 g subsample was removed from each core at the 20, 40, 60, and 80 cm intervals and combined in a preweighed 40-mL septum-sealed vial containing 20 mL of methanol to represent the composite sample.

All samples were stored chilled (4 ^{o}C) and analyzed within 8 days of field sample collection and within 3 days of the methanol aliquot removal procedure. A 100-uL aliquot of methanol from each sample was extracted using the low-level soil procedure from SW-846 Method 5035A followed by quantification using the gas chromatography/mass spectrometry technique described in SW-846 Method 8260B (USEPA, 1997).

Figure 3. Location of Cores within Plot.

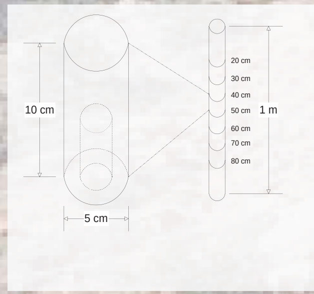

Figure 4. Sampling Scheme within a Core.

Results and Discussion

Soils at the Grants Site were contaminated with tetrachloroethene (Table 1). In one of the cores (core B), m,p-xylene was also identified. Tetrachloroethene (PCE) concentrations ranged from 0.74 to 3.90 mg/kg while the xylene concentrations ranged from non-detectable to 3.80 mg/kg.

Differences between the means of the seven individual samples making up the core and the composite sample associated with the core were relatively low ranging from -23% to 24%. The %D within the core (*i.e.*, representing the vertical VOC distribution) met the data quality objective (DQO) of %D < 30 set for this research effort. Similarly, when the grand mean, which represents the entire sampling area both laterally and vertically, and the means of the composite samples are compared, the %D was 6% for PCE.

Tricholorethene (TCE) and cis-1,2-dichloroethene (DCE) were consistently found in all cores and at all depths at the Boarhead Farms site (Table 2). Concentrations ranged from 0.07 to 1.31 and 0.06 to 2.22 mg/kg for TCE and cis-1,2-DCE, respectively, showing high variability (absolute concentration differences of >15-fold) within the sample cores and across the plot. Trace quantities of 1,1,1-trichloroethene were also found but their distribution was erratic (*i.e.*, not found in all cores or all depths within a core) and their concentrations were very low or non-detectable.

The %D between the mean of the seven individual samples and their related composite sample ranged from -117% to 52%. The wide spread in percent differences at this site are associated with the high variability identified in absolute VOC concentrations within a given soil core. At this site, the composite samples met our DQO only 60% of the time. However, when comparing the grand means and the means of the composite samples, the DQO was met with the %D for cis-1,2-DCE and TCE of 28% to -20%, respectively.

Table 1. Core Means, Composite Sample, and Grand Means for VOCs found at the Grants Site*

	Individual Samples	Composite Sample	%D†
PCE - Core A	1.77	2.22	-23
PCE - Core B	1.90	1.74	9
PCE - Core C	1.93	1.80	7
PCE - Core D	2.30	1.81	24
PCE - Core E	1.53	1.33	14
m,p-Xylene - Core B	1.65	1.54	7
Grand Means‡	1.90	1.78	6¶

* - units are mg/kg for all compounds.
† - %D = % difference between the mean of the 7 individual samples and the composite sample.
‡ - mean of all data from given plot site.
¶ - %D = % difference between mean of all samples and the mean of the composite samples.

Table 2. Core Means, Composite Sample, and Grand Means for VOCs found at the Boarhead Farms Site*.

	Individual Samples	Composite Sample	%D†
cis 1,2-DCE - Core A	0.98	0.83	-16
cis 1,2-DCE - Core B	0.68	0.45	-42
cis 1,2-DCE - Core C	0.30	0.08	-117
cis 1,2-DCE - Core D	0.66	0.49	-30
cis 1,2-DCE - Core E	0.30	0.35	17
TCE - Core A	0.60	0.50	-18
TCE - Core B	0.49	0.84	52
TCE - Core C	0.20	0.31	42
TCE - Core D	0.23	0.20	-15
TCE - Core E	0.45	0.57	24
Grand Means‡ - *cis* 1,2-DCE	0.58	0.44	28¶
Grand Means‡ - TCE	0.39	0.48	-20¶

* - units are mg/kg for all compounds.
† - %D = % difference between the mean of the 7 individual samples and the composite sample.
‡ - mean of all data from given plot site.
¶ - %D = % difference between mean of all samples and the mean of the composite samples.

Summary And Conclusions

Composite sampling provides a means for reducing inter-sample variability and reducing costs associated with sampling and analysis at hazardous waste sites. This study was conducted to test a procedure for collecting composite samples for soil VOCs and to determine the efficacy of the composite sample to accurately represent the grand mean of the individual samples from which it was created.

At each site, 5 core samples within a 1 m^2 area were collected, approximately 5 grams removed at each of 7 intervals, and placed in 5 mL of methanol. A composite sample was collected simultaneously by placing approximately 5 g of soil from the 20, 40, 60, and 80 cm segments into a single vial containing 20 mL of methanol. The concentration differences between the mean of the individual 7 samples and its associated composite sample ranged from -23 to 24 %D at the Grants site and from 52 to -117 %D at the Boarhead Farms site. The distinctly wider range at the Boarhead Farms site is directly related to the greater VOC concentration variability within a given soil core.

When the grand mean of the plot was compared to the mean of the associated composite samples, the DQO (%D < 30) was met for all VOCs at both sites. This result indicates that the technique used for compositing VOC-contaminated soils is capable of producing accurate, representative samples that can be used for site characterization. Further, a reduction in the number of samples analyzed from 7 to 1 to assess vertical heterogeneity and from 35 to 5 to assess both vertical and lateral heterogeneity (*i.e.*, within the plot) would be seen leading to a marked savings in analytical costs.

References

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Notice

This work has been funded by the United States Environmental Protection Agency. It has been subjected to the Agency's peer review and approved for publication.

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