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EVALUATION OF A RAPID HEADSPACE ANALYSIS METHOD FOR ANALYSIS OF VOLATILE CONSTITUENTS IN SOILS AND SEDIMENTS (U)

by

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EVALUATION OF A RAPID HEADSPACE ANALYSIS METHOD FOR ANALYSIS OF VOLATILE CONSTITUENTS IN SOILS AND SEDIMENTS

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ABSTRACT

Contamination of the subsurface by volatile organic solvents is a common and significant environmental problem. A critical component of developing an accurate assessment of a site contaminated by these solvents is the acquisition of closely spaced, high quality contaminant concentration data. Many volatile organics are relatively mobile in the subsurface, requiring characterization of both horizontal and vertical contaminant migration. The volatile nature of these analytes, combined with the cost and effort typically required to perform quantitative analysis, has often compromised the number and quality of analyses used in characterization studies. A headspace analysis method was developed by Savannah River Laboratory to facilitate accurate and rapid delineation of the vertical and horizontal extent of volatile organic contamination in the subsurface. The method was designed to reduce sample handling, laboratory preparation, and analytical complexity. The headspace analysis method consists of four steps: 1) subsample the split spoon core immediately after opening the barrel using a small tube/plunger system, 2) place the subsample into a 22.5 mL headspace vial, 3) add 5 mL of distilled water and cap with a teflon lined septum, and 4) analyze on a gas chromatograph. This method was developed and modified as a result of multiple site investigations and has been applied to over 1500 samples.

To evaluate the headspace analysis method, we collected over 100 samples from four borings at depths ranging from 5 to 140 feet. Samples were analyzed using the headspace method and the results were compared to adjacent samples analyzed onsite using EPA methods that were modified to minimize losses of volatile constituents. The modified EPA method consisted of pentane extraction in a sealed vial after collection, weighing, and transfer in an onsite laboratory. The comparison analyses were performed by an independent organization. Despite the precautions incorporated into the modified EPA method, the analytical results indicate that sample transfers in the field and laboratory resulted in volatilization of most of the volatile solvents in the sediment samples. The headspace method appears to provide more representative data on the samples. One limitation of the headspace method is that the sample can not be diluted; thus, very high concentrations are truncated by an upper limit of detection. In most cases, this truncation may not be of practical significance because it occurs at relatively high concentrations (e.g., 100,000 ng/g). The results indicate that the headspace method minimized loss of volatiles associated with sample handling and provided large amounts of closely spaced data in a cost effective manner. The headspace results can be generated rapidly and transferred to the field such that informed decisions can be made during site characterization.

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INTRODUCTION

Detection and delineation of volatile organic solvent contamination at a hazardous waste site can be a complex problem. The number and quality of analyses used in characterization studies has often been compromised by the difficulties and costs associated with quantitative analysis of these volatile analytes. A headspace analysis method was developed by the Westinghouse Savannah River Laboratory to facilitate the accurate and rapid delineation of the vertical and horizontal extent of volatile organic contamination in the subsurface, and to reduce the sample handling, laboratory preparation, and analytical complexity generally associated with the use of several United States Environmental Protection Agency Analysis Methods.

To evaluate the headspace method, over 100 subsurface sediment samples were collected from 4 sediment borings drilled at the Savannah River Site (Figure 1). The sediment samples were analyzed using the headspace method and the results were compared to adjacent samples collected and analyzed by an independent subcontractor. The subcontractor used EPA methods that were modified to minimize losses of volatile constituents. A comparative study of the sample collection procedures, laboratory procedures, and analytical results of the headspace method and the subcontractor modified EPA method is presented in this paper.

SAMPLING AND ANALYTICAL METHODS

Sample Collection Procedure

The sediment borings were drilled at four sites adjacent to a solvent tank farm located west of a fuel and target tube manufacturing facility in M-Area at the Savannah River Site (Figure 2). The boring locations were selected based on results from a shallow soil gas survey and a documented solvent spill. In October 1975, over 1200 gallons of tetrachloroethylene (PCE) leaked from a cracked ceramic pump seal connected to one of the solvent tanks. The solvents were used during the late 1950's to the early 1980's to degrease the fuel and target tubes prior to shipment to the nuclear reactors.

The sediment borings were drilled with a Speedstar Quickdrill 275 utilizing 4-1/4-inch inside diameter hollow-stem augers. A standard 2-inch inside diameter split-spoon sampler was advanced vertically according to Standard Penetration Test procedures (ASTM D1586) at five foot intervals, beginning immediately below ground surface to a depth of approximately 140 feet or top of the water table. After each advance, the split spoon sampler was opened and two adjacent samples of sediment were collected. One sediment sample was collected for headspace analysis and the other collected by an independent subcontractor for analysis by a modified EPA Method. The remaining sediment left in the split-spoon was field screened with an HNu photoionization organic vapor meter and a Ludlum G.M. radiation detector and visually classified.

Headspace Sampling Procedure

The headspace sediment subsample (3-5 grams) was collected immediately from the open spilt-spoon using an open-ended plastic disposable syringe and extruded into a 22.5 mL borosilicate vial. Five mL of distilled water were added to the subsample using a pipet and the vial was sealed by crimping an aluminium cap around a teflon-lined butyl rubber septum. The sample vial was labeled and placed in an ice chest cooled to approximately 4°

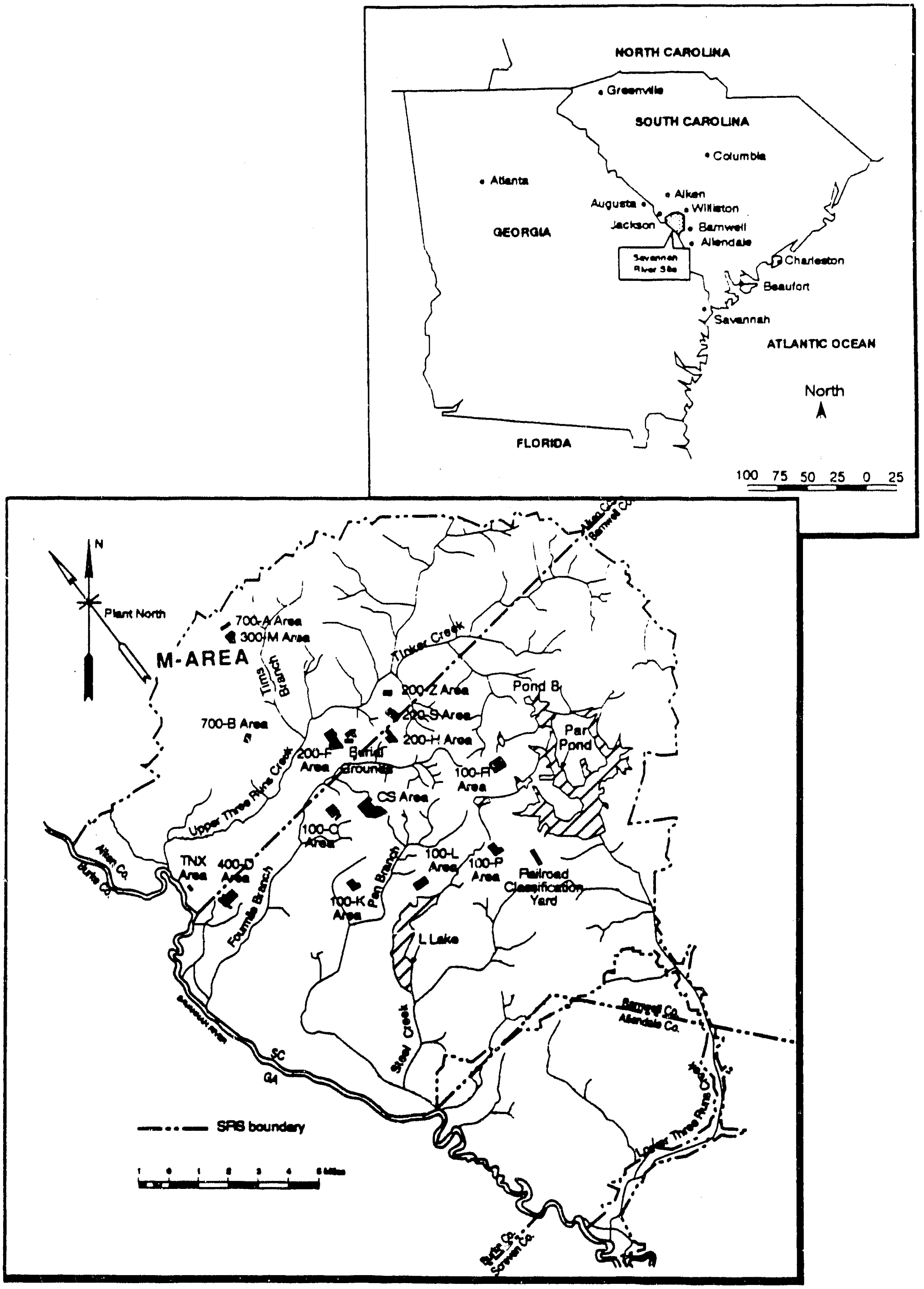


Figure 1. Map showing the location of the solvent spill site at the Savannah River Site

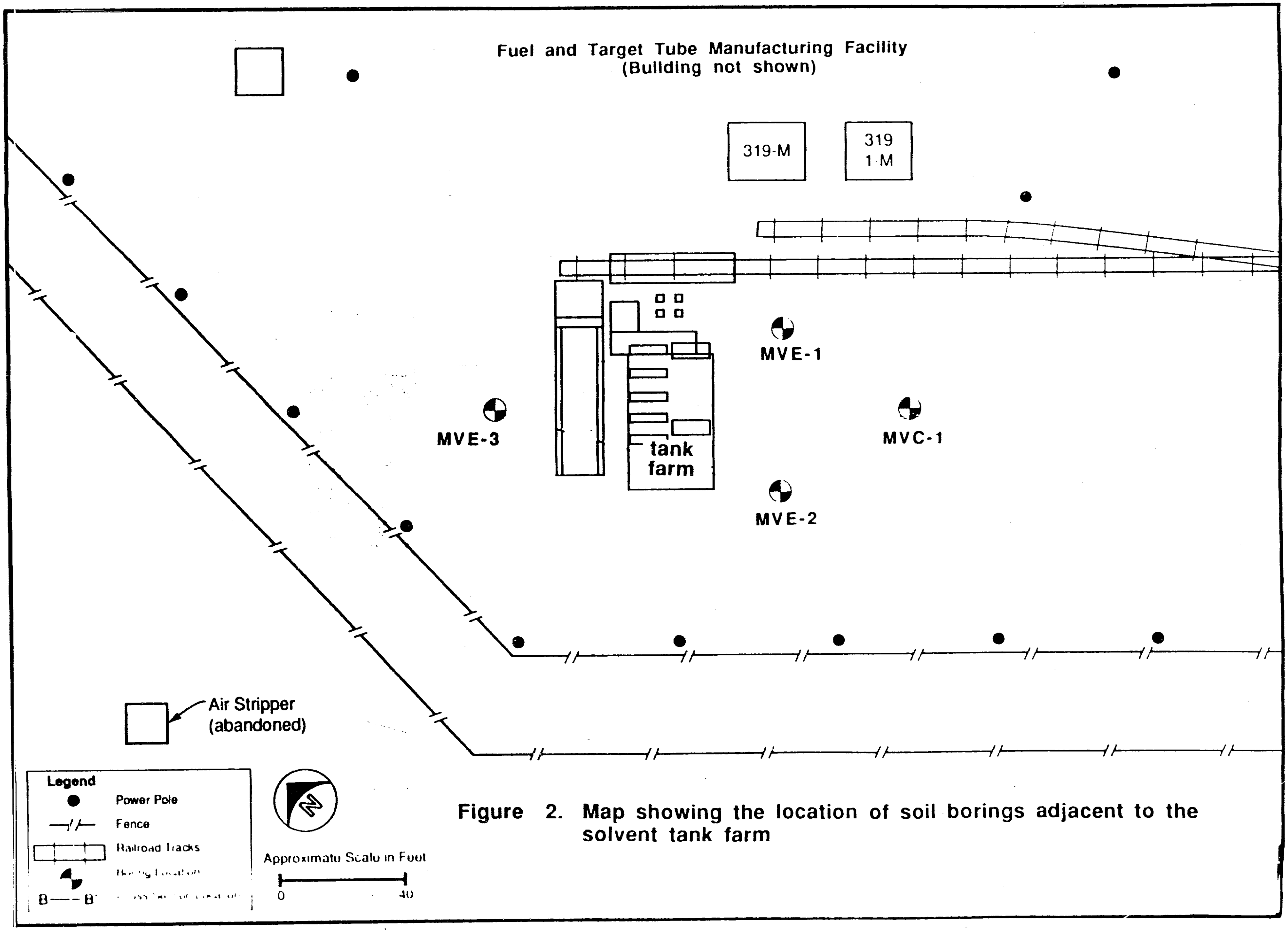


Figure 2. Map showing the location of soil borings adjacent to the solvent tank farm

C for later analysis at an onsite laboratory. The subsample corer (syringe) was decontaminated between sampling events by brushing and rinsing with isopropanol followed by a distilled water wash.

Modified E.P.A. Sampling Procedure

Adjacent to the headspace subsample collection point, a subcontractor immediately collected an aliquot of sediment from the open split-spoon using a stainless steel spatula and packed it into a 2-ounce borosilicate jar with a teflon-lined screw cap. The jar was labeled and placed in an ice chest cooled to approximately 4° C for later analysis by the Close Support Laboratory (CSL). The stainless steel spatula was decontaminated between sampling events by wiping with a disposable moist Towelette.

Laboratory Analysis Procedure

The two separate laboratories utilized in the study to analyze the sediment subsamples were an onsite laboratory operated by Savannah River Laboratory personnel and a CSL operated by independent subcontract personnel. The onsite laboratory analyzed the headspace sediment subsamples and the CSL analyzed the sediment subsamples collected by the independent subcontractor. Both laboratories used standard Chain of Custody procedures and collected Quality Assurance/Quality Control (QA/QC) sediment subsamples to comply with the Savannah River Site Quality Assurance Requirements. These requirements included the analysis of duplicate samples, matrix spikes, and trip blanks at a minimum of ten percent of the total number of samples. All analyses were performed within the required holding time.

Headspace Analysis Procedure

The onsite laboratory consisted of a headspace analyzer connected to a Hewlett Packard 5890A Gas Chromatograph (GC). The headspace analysis procedure used is given below.

Step 1. Prior to field sampling, determine the average weight of a sealed headspace vial containing 5 mL of water. Upon receipt of the headspace sample vials from the field, weigh the capped vial containing the sediment sample. Subtract the weight of the vial without the sediment from the vial containing the sediment to determine the amount of sediment in the sample vial.

Step 2. Placed vial with the sediment subsample in the headspace analyzer for analysis. Download the GC results from each sample analyzed into a computer for interpretation.

A previous study was conducted by Savannah River Laboratory personnel in order to evaluate the effects of adding a sodium sulfate/phosphoric acid solution instead of distilled water to the headspace sediment sample. The results of this study indicated that there was a significant statistical difference between the VOC analysis using distilled water versus the sodium sulfate/phosphoric acid solution. The use of distilled water in the headspace vial increased the volatilization and measured concentration of VOC. Additional work was conducted to determine whether sonication of the sample increased the measured VOC concentration. The results indicated that there was not a significant statistical difference between the samples that were sonicated for 15 minutes and the samples that were not sonicated.

Subcontractor Modified EPA 3550 Analysis Procedure

The CSL consisted of a travel camper outfitted with a Hewlett Packard 5890A gas chromatograph, electron capture detector, and an ultrasonic sonicator. Additional equipment included a balance, an oven for drying samples, a computer with printer and laboratory/safety supplies. The CSL was operated on a daily basis during the sediment boring investigation to provide analytical results on a real-time basis. The results were used to determine screen intervals for the vapor extraction wells installed as part of a vadose zone remediation program in M-Area.

The CSL analytical method used pentane in conjunction with sonication to extract the target constituents (predominantly PCE) from the sediment matrix. The method was based on EPA Method 3550, Sonication Extraction, found in EPA SW 846, "Test Methods for Evaluating Solid Wastes", 3rd ed., November 1986. The modified EPA Method 3550 procedure for sample preparation and extraction is included below.

Step 1. In a labeled VOA vial (40 mL), volumetrically pipet 5 mL of pentane and record the volume added. Place the vial on the top loading balance and record its tare weight. Add an aliquot of sediment from the 2-ounce jar subsample (approximately 5 to 10 grams) to the vial and accurately record the sample weight to the nearest 0.01 grams.

Step 2. If the sample is wet or highly consolidated (i.e. clay), add approximately 2 grams of sodium sulfate and mix.

Step 3. Tightly cap the VOA vial and sonicate at an output setting of 30 percent for approximately 5 minutes. The resulting sonicated sample should be dispersed throughout the pentane solvent and have a grain-like appearance. If not, then add an additional 1 gram of sodium sulfate and sonicate. Repetitions of this process may be needed to complete the extraction from some samples.

Step 4. After sonication, let the VOA vial stand until the solids have settled. Using a pasteur pipet, transfer a suitable aliquot of the pentane solvent (extract) from the vial in a labeled GC auto-sampler vial and cap immediately with septum crimp seals. Refrigerate the sample extracts until analyzed.

Step 5. After the sample was prepared, the extract was injected into a Hewlett Packard 5890A GC with an electron capture device for analysis.

DISCUSSION

The results of the laboratory analyses for the headspace method and the subcontractor modified EPA 3550 Method are presented in Tables 1 and 2. A total of 92 sediment subsamples were analyzed for this study. In addition, 16 duplicate headspace sediment subsamples were collected to determine reproducibility of the analytical data. The concentrations of TCE and PCE in the headspace sediment subsamples ranged from less than 1 ng/g (presented as 1 on the Table 1 and 2), up to 14,583 and 91,670 ng/g respectively. The concentrations of TCE and PCE in the sediment subsamples utilizing the subcontractor modified analytical method ranged from less than 1 ng/g up to 1,016 and 2,620,000 ng/g respectively. The duplicate samples, trip blanks, matrix spikes, and matrix

Table 1

SOIL BORING MVE-1

		Trichloroethylene (ng/g)			Tetrachloroethylene (ng/g)		
Sample Collection Depth (ft)		Headspace Results	Modified EPA 3550 (EPA SW 846)	Headspace Greater Than Modified?	Headspace Results	Modified EPA 3550 (EPA SW 846)	Headspace Greater Than Modified?
6		1	1	SR	10331	216	Y
11		1	1	SR	14240	600	Y
16		4	1	Y	43765	84694	N
20		50	1	Y	28271	970000	N
21		8320	1	Y	91670	2620000	N
26		9318	1	Y	82874	75000	Y
31		706	1	Y	81126	420000	N
36		538	199	Y	19643	1300	Y
41		247	1	Y	8132	95	Y
46		754	17	Y	10339	323	Y
51		1135	11	Y	12036	11	Y
56	S	1	1	SR	4	1	Y
57	S	4	1	Y	7080	1	Y
61		607	1	Y	7804	1	Y
64		6	1	Y	4610	1	Y
66		2	1	Y	14	1	Y
71		1	1	SR	6	1	Y
76		2	1	Y	24	1	Y
81		7	1	Y	21	1	Y
86		2	1	Y	17	1	Y
91		3	1	Y	11	1	Y
96		1670	1	Y	7007	1	Y
100.5	S	3	1	Y	9	1	Y
101.5	S	16	1	Y	3135	1	Y
106		8	1	Y	14	1	Y
111.5		1	1	SR	2	1	Y
116		15	1	Y	29	1	Y
121		3	1	Y	7	1	Y
126		24	1	Y	59	40	Y
131		3	1	Y	9	1	Y
135.5	S	14583	1	Y	20638	1	Y
136	S	5	1	Y	8	1	Y
141		10119	4100	Y	14864	5700	Y

SOIL BORING MVE-3*

21	3	2	Y	3	1	Y
31	327	9	Y	7726	1	Y
36	204	7	Y	27	15	Y
46	444	3	Y	2684	10	Y
51	290	33	Y	2079	45	Y
56	2147	3	Y	3694	11	Y

Y = Yes
N = No
SR = Same Result
* = Soil Boring Partially Sampled
D = Average of Duplicate Headspace Analyses
S = Two Subsamples Collected From One Split-Spoon Core

Table 2

SOIL BORING MVC-1

Sample Collection Depth (ft)		Trichloroethylene (ng/g) Headspace Results	Trichloroethylene (ng/g) Modified EPA 3550 (EPA SW 846)	Headspace Greater Than Modified?	Tetrachloroethylene (ng/g) Headspace Results	Tetrachloroethylene (ng/g) Modified EPA 3550 (EPA SW 846)	Headspace Greater Than Modified?
6		1	1	SR	1	1	SR
11		1	1	SR	1	1	SR
16		1	1	SR	14	1	Y
21		1	1	SR	2	1	Y
26		1	1	SR	3	1	Y
36		10	1	Y	19	1	Y
41		149	1	Y	5376	1	Y
46		14	1	Y	31	1	Y
51		1	1	SR	1	1	SR
56		1	1	SR	1	1	SR
65	S	1	1	SR	1	1	SR
66	S	2	1	Y	5	1	Y
71		1	1	SR	2	1	Y
76		1	1	SR	1	1	SR
81		1	1	SR	3	1	Y
86		3	1	Y	8	1	Y
91		16	1	Y	62	1	Y
100		6621	33	Y	13892	35	Y
101		8	1	Y	17	1	Y
105	S	544	1	Y	5170	1	Y
106	S	1	1	SR	2	1	Y
111		1513	362	Y	8569	119	Y
116		4920	1	Y	8768	87	Y
121		4	1	Y	6	1	Y
126		13	1	Y	20	9	Y
131		15	1	Y	28	1	Y
SOIL BORING MVE-2							
6		2	1	Y	9	16	N
11		2	1	Y	9	9	SR
16		3	1	Y	30	1	Y
21	D	2	1	Y	2594	11	Y
26		80	3	Y	4667	31	Y
31	D	27	2	Y	3135	14	Y
36		32	5	Y	3312	33	Y
41	D	35	2	Y	3531	12	Y
46	D	68	5	Y	3332	36	Y
51		206	5	Y	4321	33	Y
56	D	5	7	N	5	34	N
61	D	266	5	Y	5189	27	Y
66		2	2	SR	4	10	N
71	D	10	1	Y	13	1	Y
76		1	1	SR	1	1	SR
81	D	1	2	N	1	12	N
86		1	1	SR	3	1	[illegible]
91	D	1	1	SR	3	1	Y
96		4	558	N	3397	668	Y
101	D	7	2	Y	16	8	Y
106	D	21	3	Y	1711	17	Y
111	D	1	2	N	2	11	N
116	D	9	14	N	19	44	N
121		1	6	N	4	20	N
126	D	2	14	N	3	41	N
131	D	3	79	N	5	92	N
136	D	7551	1016	Y	9361	706	Y

Y = Yes
N = No
SR = Same Result

S = Two Subsamples Collected From One Split-Spoon Core
D = Average of Duplicate Headspace Analyses

spike duplicates performed for the methods indicated that both methods could adequately measure the contaminants at concentrations down to the detection limit and that both methods generated reproducible results.

In general, the headspace analysis method resulted in a higher value for the measured concentration of both TCE and PCE (Table 3). The primary exceptions to this general trend are: 1) samples with very high concentrations of contaminants, and 2) samples where both methods were below detection. For example, in soil boring MVE-1, there are five instances where the two methods are the same for TCE -- all of these instances result from below detection results from both methods. Similarly, in this core, the results from the modified EPA method are greater four out of thirty-three times -- all four instances result from truncation of very high concentrations inherent in the headspace method. These same trends may be observed in all of the other cores. The paired data used to generate Table 3 were ranked and ordered for statistical analysis. In this form, a Wilcoxon Signed Rank Test was applied to determine if the two methods yield statistically different results. This test is used when the shape of the underlying distribution is unknown to test the hypothesis that two population distributions are identical. At the 99% confidence interval, this hypothesis was rejected signifying that the two populations are different. Thus, the statistical test indicated that there is greater than a 99% probability that the two methods are statistically different (i.e., the headspace method generates higher values).

Table 4 provides detailed information on depth, PCE concentrations, and lithology for MVE-1. Results from this core illustrate the relationship between concentration and lithology, and reinforce the general conclusions discussed above. The headspace method indicated the presence of contamination in each of the silty, clayey and poorly graded layers throughout the core. The modified EPA method generated below detection results for most of these zones. The headspace method truncated a series of very high concentrations in the upper part of the core. Figure 3 is a graphical representation of the data. The headspace method indicates low (but measurable) concentrations in the well graded sands, while the modified EPA method indicates below detection results in almost all of these layers.

From an analytical standpoint, there are several advantages of the headspace method over the subcontractor modified EPA Method. Some of these advantages include:
1) reduced sample handling effort and time in the field, 2) no solvent extraction required (the Henry's Law mass transfer in the headspace vial requires no operator effort), and
3) elimination of multiple sample transfers and minimization of the opportunities for volatilization of analyte. The headspace sediment sample is sealed in its final form ready for analysis within a few seconds of collection and is never directly handled again during weighings or transfers. Once in the laboratory, approximately 50 samples can be analyzed in a normal working day on a single instrument. This allows data to be rapidly transmitted back to the field for incorporation into decisions about the drilling and characterization operations.

CONCLUSION

Despite the precautions incorporated into the modified EPA method, the analytical results indicate that sample transfers in the field and laboratory resulted in volatilization of most of the volatile solvents in the sediment samples. The headspace method appears to provide more representative data on the samples. One limitation of the headspace method is that the sample can not be diluted; thus, very high concentrations are truncated by an upper limit of detection. In most cases, this truncation may not be of practical significance because it

Table 3

DATA SUMMARY

Method Comparison From Tables 1 and 2 For Trichloroethylene and Tetrachloroethylene	Trichloroethylene					Tetrachloroethylene				
	Soil Boring MVE-1	Soil Boring MVE-2	Soil Boring MVE-3	Soil Boring MVC-1	Total	Soil Boring MVE-1	Soil Boring MVE-2	Soil Boring MVE-3	Soil Boring MVC-1	Total
Number of Headspace Analytical Results Greater Than The Subcontractor Modified Method Analytical Results [Y]	28	15	6	14	63	29	16	6	20	71
Number of Subcontractor Modified Method Analytical Results Greater Than The Analytical Results of The Headspace Method [N]	0	8	0	0	8	4	9	0	0	13
Number of Identical Results [SR]	5	4	0	12	21	0	2	0	6	8

Table 4

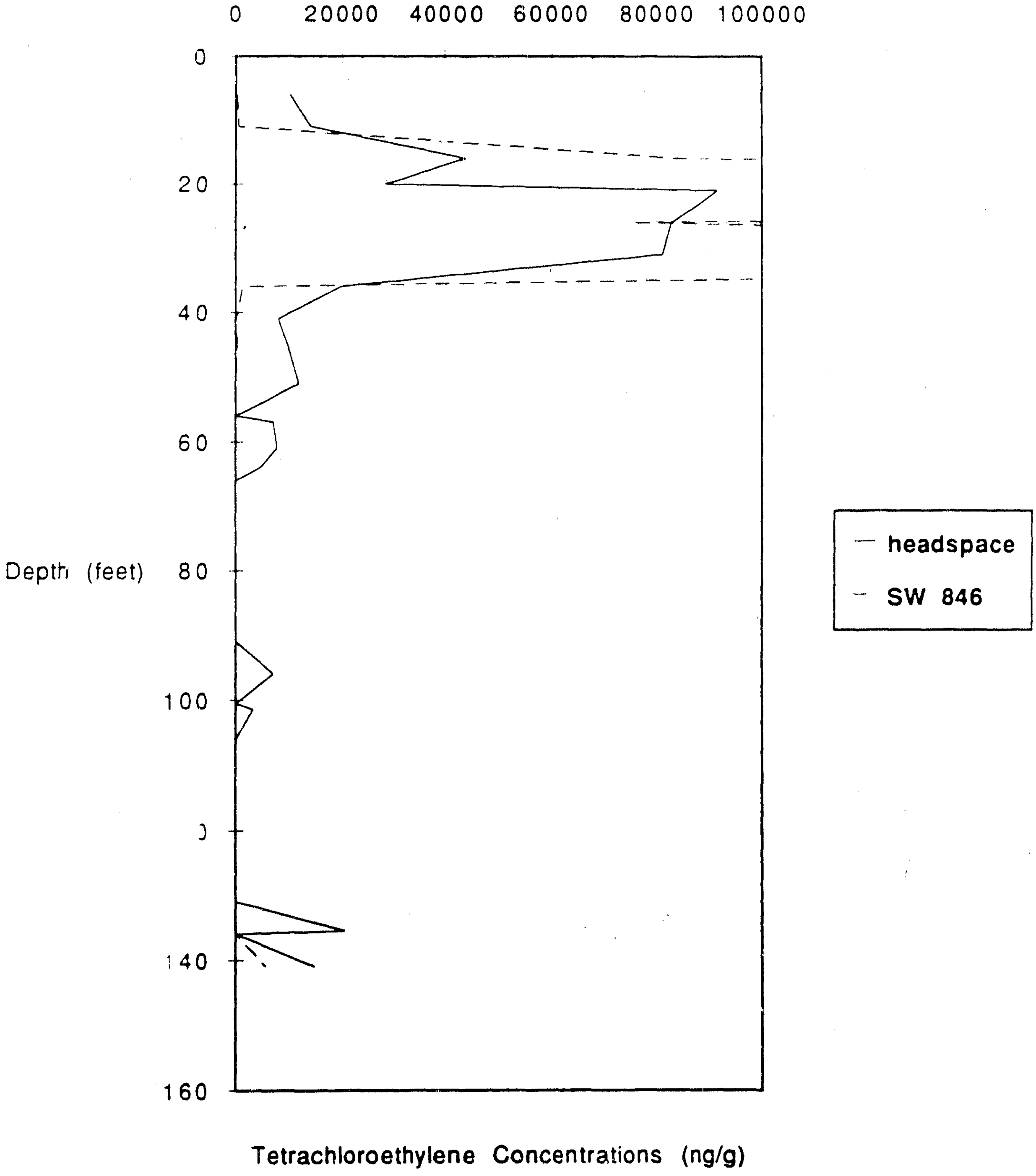
PCE CONCENTRATIONS VERSUS LITHOLOGY IN SOIL BORING MVE-1

		Tetrachloroethylene (ng/g)		
Sample Collection Depth (ft)		Headspace Results	Modified EPA 3550 (EPA SW 846)	Abbreviated Field Lithologic Description of the Split Spoon Core
6		10331	216	SANDY SILT (ML), dense, 5% clay
11		14240	600	SANDY SILT (ML), dense, 5% clay
16		43765	84694	SILTY SAND (SM), very dense,10-15% clay
20	S	28271	970000	SILTY SAND (SM), very dense,10-15% clay
21	S	91670	2620000	SILTY SAND (SM), very dense,10-15% clay
26		82874	75000	SILTY SAND (SM), very dense,10-15% clay, clayey lenses
31		81126	420000	CLAYEY SAND (SC)
36		19643	1300	POORLY GRADED SAND WITH SILT (SP-SM)
41		8132	95	POORLY GRADED SAND WITH SILT (SP-SM)
46		10339	323	SILTY SAND (SM)
51		12036	11	SILTY SAND (SM)
56	S	4	1	WELL GRADED SAND (SW)
57	S	7080	1	POORLY GRADED SAND (SP)
61		7804	1	POORLY GRADED SAND (SP), clay lenses
64	S	4610	1	SILTY SAND (SM), clay lenses
66	S	14	1	WELL GRADED SAND (SW)
71		6	1	WELL GRADED SAND (SW)
76		24	1	WELL GRADED SAND (SW)
81		21	1	WELL GRADED SAND (SW)
86		17	1	WELL GRADED SAND (SW)
91		11	1	WELL GRADED SAND (SW)
96		7007	1	WELL GRADED SAND WITH CLAY (SW-SC)
100.5	S	9	1	WELL GRADED SAND (SW)
101.5	S	3135	1	WELL GRADED SAND WITH CLAY (SW-SC)
106		14	1	WELL GRADED SAND (SW)
111.5		2	1	WELL GRADED SAND (SW), thin clay stringers (white)
116		29	1	WELL GRADED SAND (SW), thin clay stringers (white)
121		7	1	WELL GRADED SAND (SW)
126		59	40	WELL GRADED SAND (SW),some gravel
131		9	1	WELL GRADED SAND (SW),some gravel
135.5	S	20638	1	POORLY GRADED SAND WITH CLAY (SP-SC), 2 mm clay lns.
136	S	8	1	WELL GRADED SAND (SW)
141		14864	5700	WELL GRADED SAND (SW), Moist, Top of the Water Table

S = Two Subsamples Collected From One Split-Spoon Core

Figure 3.

VERTICAL PROFILE OF PCE CONCENTRATIONS FROM THE TWO ANALYTICAL METHODS



occurs at relatively high concentrations (e.g., 100,000 ng/g). The results indicate that the headspace method minimized loss of volatiles associated with sample handling and provided large amounts of closely spaced data in a cost effective manner. The headspace results can be generated rapidly and transferred to the field such that informed decisions can be made during site characterization.

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BIOGRAPHICAL SKETCHES

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