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Comparison of Four Volatile Organic Compounds in Frozen and Unfrozen Silt

Susan Taylor, Patricia Schumacher and Larry Perry

April 1990

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Special Report 90-13

U.S. Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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PREFACE

This report was prepared by Susan Taylor, Research Physical Scientist, Geological Sciences Branch, and Patricia Schumacher and Larry Perry, Research Technicians, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

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Comparison of Four Volatile Organic Compounds in Frozen and Unfrozen Silt

SUSAN TAYLOR, PATRICIA SCHUMACHER AND LARRY PERRY

INTRODUCTION

The purpose of this experiment was to study the effects of freezing on the distribution and movement of four volatile organic compounds (VOCs) in a silty soil. While studies of this nature have been conducted before,* they all used large Plexiglas cells that contained much more material than could be analyzed. The present study used small test containers, making it possible to analyze the entire sample—a distinct advantage for characterizing the concentration and distribution of the organics in soil, a heterogeneous and complicated medium. Knowledge of the effects of freezing on the distribution of volatile organics in contaminated soils is necessary for choosing among waste disposal and clean-up options.

EXPERIMENTAL DESIGN

Three hundred grams of Moulton Pit silt was spiked with an aqueous solution of chloroform, benzene, toluene, and tetrachloroethylene (C_2Cl_4) in concentrations of 990, 590, 230, and 210 mg/L, respectively. The soil was classified as an inorganic silt based upon a series of sieve and hydrometer analyses and the Unified Soil Classification System (group symbol ML) (see Appendix A for a summary of the physical characteristics). The initial water content of the soil prior to spiking was 13% (water wt/dry soil wt). Enough spike solution was added to increase the water content to 40%. The silt and solution were mixed using a large electric dough mixer. Eight polycarbonate test tubes, 11 cm long and 2 cm in diameter, were filled with the spiked soil. To determine the amount of VOCs lost during the time it took to spike, homogenize, and pack the soil into tubes, soil samples were taken from the batch after the volatiles were mixed into the soil (sample 0059) and after the tubes were packed (sample 0060).

Four of the eight tubes were left at room temperature as a control group and were labelled 'U' (unfrozen). The remaining test tubes, 'F' (frozen), were placed in an aluminum block set on a cold plate. All tubes were sealed with Parafilm. Insulation board was used to make an enclosed space around the cold plate and the samples. A glycol cooling bath was maintained at –6°C (21°F), the plate temperature was –1.5°C (29°F), and the air temperature in the box was about +5°C (41°F). These samples were frozen about half way up the tube, from the bottom upwards, at a rate of 2–3 cm a day (the rate of freezing was not constant). It took two days to freeze the saturated soil half way up the tube (about 5 cm).

After freezing was completed, the tubes were cut with a band saw into 4 sections labelled A, B, C, and D (A was the sample from the bottom of the test tube, D was the sample adjacent to the mouth of the tube), and each section was placed into a tared vial containing 10 mL of methanol and 5 µL of deuterobenzene. The deuterobenzene was added to check for losses in the volatile organics during the analytical phase of the experiment. If, for instance, the screw top on one of the vials was not tight, loss of the deuterobenzene would indicate loss of the other volatiles. The vials were reweighed, vortexed to expose all the soil particles to the methanol, and centrifuged.

All analyses were performed using a Hewlett Packard 5992 GC/MS System with a Hewlett Packard 7675A Purge and Trap Sampler and followed EPA Method 624. One of the advantages of using small test tubes instead of the large Plexiglas test cells used in on-going experiments is that, because the samples are small, the whole sample can be (and was) analyzed. Thus one source of error, estimating sample variability, was removed. The reproducibility of the GC/MS was checked by run-ning analytical replicates on randomly chosen samples.

The information needed to calculate concentration from the normalized peak area, obtained from the instrument, is shown in Appendix B. All of the input parameters are known except the moisture content. To estimate the moisture content at each level within our samples, two tubes (one frozen

*Personal communication with F. Ayorinde, CRREL, 1989.

half way up the tube, one at room temperature) were run alongside the test samples. At the end of the experiment, these tubes were sectioned in the same way as the test samples, and the moisture content of each section was determined.

The results presented here used the moisture contents determined from each of the four layers in these separate samples. We know that the moisture content within our samples, although originally 40%, changed during the course of the experiment. In the frozen samples, the top, unfrozen portions were desiccated relative to the area adjacent to the freezing front. In the unfrozen samples, settling of the silt caused water to pool on the sample's surface.

This experiment was flawed by the fact that the freezing rate could not be controlled adequately and errors in estimating the moisture content could significantly alter the final concentrations. Future experiments should accurately determine the moisture content for each sample.

RESULTS

Table 1 shows the concentrations, in μg/g (dry soil), of the VOCs in the silt. The initial experimental conditions are listed at the beginning of the table. A soil blank (unspiked Moulton silt) was analyzed to determine the initial concentration of toluene, benzene, chloroform, and tetrachloroethylene in the soil. Three soil samples, two from different areas in the batch taken directly after spiking and mixing of the silt (sample 0059) and a sample taken after the tubes had been packed (sample 0060), give an estimate of the amount of volatiles lost during sample packing.

Analyses of the partially frozen samples, denoted with F and a letter indicating the tube location of the sample (A to D), are listed after the initial conditions in Table 1, followed by those samples not subjected to freezing (denoted as "U-A–D"). The first four columns are the concentrations of the volatile organics tested. The fifth column is the amount of deuterobenzene recovered from the samples; this value is a measure of the amount of volatiles lost from the vials. The deuterobenzene value, had none been lost, would be approximately 8.5 μg/g. The "corrected" values listed in Table 2 are the concentrations in μg/g of the four organics in each sample normalized to deuterobenzene.

Table 3 groups the corrected data by organic substance and by the position of the sample in the tube. Approximately half the chloroform and benzene in the unfrozen samples had been lost relative to the partially frozen samples. The proportion was even larger for toluene and tetrachloroethylene, which have higher values for Henry's constant.* When the measured concentration for each organic is divided by its initial concentration in the solution, the fractional decrease experienced by each volatile, independent of its original concentration, is obtained (Table 4). The higher the Henry's constant (a measure of the air–water partition coefficient of the substance, tetrachloroethylene > toluene > benzene > chloroform), the lower the fractional concentration found in the samples.

A two-way analysis of variance was performed on these data using sample location and freezing as the variables that affect the concentration. The F ratio (the treatment mean square/error mean square) from this analysis was used as a measure of the statistical significance of each variable on the concentration. For each of the four volatiles, whether the sample had been frozen or not was found to be statistically significant at the 95% confidence level (Table 5). Figures 1, 2, 3, and 4 show a clear distinction between the four frozen samples (plotted as F) and the four unfrozen samples (plotted as U). The sample location (either A, B, C, or D) was also found to be significant at the 95% level for the samples that were frozen half way up the tube, but not for the unfrozen samples. A least-significant-difference test applied to the unfrozen samples showed that only the sample adjacent to the tube top was different from samples from the other three tube positions.

CONCLUSIONS

We found that freezing a water-saturated silt spiked with chloroform, benzene, toluene, and tetrachloroethylene did not move the organics ahead of the freezing front but rather that it retarded the volatilization of each organic in the frozen soil relative to unfrozen soil. Hence, the air–water partition coefficient of the organic affected the magnitude of the final concentration in the soil. For the frozen samples, the final concentrations were relatively high in the frozen sections and about 30 to 50% lower in the unfrozen sections. For the unfrozen samples, the concentration of each organic was lower than that found in the frozen samples, but the concentration was uniform with tube position, except for the sample adjacent to the tube opening. Here the concentration was about 50% lower.

*Personal communication with D. Leggett, CRREL, 1989.

Table 1. VOC concentration in soil (μg/g).

Sample ID no.	*Sample location*	*Chloro-form*	*Benzene*	C_2Cl_4	*Toluene*	C_6D_6 *recovered*
Silt blank		0.18	0.39	B.D.	0.60	17.13
0059		89.29	45.21	7.41	15.24	16.03
0059		91.97	45.07	6.34	15.44	15.85
0060		55.81	28.25	4.90	9.71	16.13
Silt blank		0.04	0.08	B.D.	B.D.	8.53
0061	F-A	49.30	18.05	3.89	9.25	4.59
0062[s]	F-B	68.06	27.99	4.14	11.03	5.89
0063[s]	F-B	84.81	41.58	4.32	11.74	8.06
0064	F-C	50.08	24.80	2.91	7.41	6.54
0065	F-D	33.67	14.39	1.99	4.89	6.54
0066[a]	F-A	50.63	19.67	3.97	9.17	4.50
0066[a]	F-A	53.63	20.89	4.37	9.77	4.81
0067	F-B	70.19	35.48	3.77	9.58	6.92
0068	F-C	55.72	28.36	3.10	7.86	7.51
0069	F-D	25.33	10.61	1.53	4.01	5.72
Silt blank		0.04	0.10	B.D.	B.D.	9.49
0070	F-A	38.58	14.60	3.64	8.24	4.30
0071	F-B	63.16	37.34	3.51	8.25	8.25
0072	F-C	40.73	24.80	2.78	5.97	8.05
0073	F-D	32.95	16.62	1.64	4.00	7.96
9974	F-A	64.56	41.85	5.27	10.62	8.08
0075[a]	F-B	63.08	33.32	3.42	8.42	7.27
0075[a]	F-B	56.60	30.53	3.03	7.60	6.69
0076	F-C	45.26	27.58	2.28	5.60	8.20
0077[s]	F-D	42.71	20.10	3.12	6.72	6.72
0078[s]	F-D	37.48	16.02	1.36	4.03	8.45
Silt blank		0.08	0.10	B.D.	B.D.	9.25
0079	U-A	49.91	20.75	1.15	3.91	6.96
0080[a]	U-B	53.22	23.66	1.08	4.12	7.96
0080[a]	U-B	52.29	22.29	1.13	3.80	7.65
0081	U-C	47.39	21.16	1.21	3.88	7.59
0082	U-D	33.28	14.31	0.74	2.74	7.95
0083	U-A	47.28	21.01	0.82	3.66	8.01
0084	U-B	41.86	18.95	0.79	3.45	7.54
0085[s]	U-C	42.98	17.90	B.D.	3.55	7.96
0086[s]	U-C	44.13	18.46	B.D.	3.41	8.55
0087	U-D	19.83	9.38	0.53	2.09	6.90
Silt blank		0.08	0.09	B.D.	B.D.	8.83
0088[s]	U-A	38.16	17.70	0.99	4.39	8.34
0089[s]	U-A	32.88	14.71	0.89	3.88	7.75
0090	U-B	36.57	17.89	1.03	3.84	8.41
0091	U-C	23.11	8.06	0.82	3.07	4.87
0092	U-D	19.70	8.61	0.58	2.06	7.36
0093[a]	U-A	32.09	13.21	0.95	3.64	6.93
0093[a]	U-A	31.86	12.39	0.79	3.18	6.96
0094	U-B	23.76	8.76	0.75	3.08	5.16
0095	U-C	30.94	14.50	0.96	3.51	8.02
0096	U-D	15.82	6.78	0.40	1.61	7.48

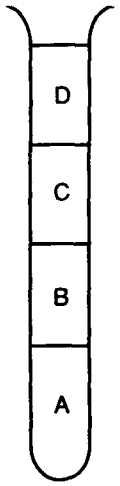
s Sample duplicates
a Analytical duplicates
B.D. Below detection limit

Table 2. VOC concentration in soil (μg/g) corrected for volatile loss.

Sample ID no.	*Sample location*	*Chloro-form*	*Benzene*	C_2Cl_4	*Toluene*
0061	F-A	91.24	33.40	7.21	17.12
0062[s]	F-B	98.21	40.39	5.97	15.91
0063[s]	F-B	89.44	43.85	4.56	12.38
0064	F-C	65.08	32.23	3.78	9.62
0065	F-D	43.77	18.71	2.58	6.36
0066[a]	F-A	95.55	37.12	7.48	17.31
0066[a]	F-A	94.70	36.88	7.72	17.24
0067	F-B	86.22	43.58	4.63	11.77
0068	F-C	63.09	32.11	3.52	8.90
0069	F-D	37.62	15.75	2.27	5.95
0070	F-A	76.34	28.88	7.20	16.30
0071	F-B	65.08	38.48	3.62	8.50
0072	F-C	43.01	26.19	2.93	6.30
0073	F-D	35.16	17.73	1.76	4.27
0074	F-A	67.90	44.02	5.55	11.17
0075[a]	F-B	73.75	38.96	4.00	9.84
0075[a]	F-B	71.96	38.82	3.85	9.66
0076	F-C	46.92	28.59	2.36	5.81
0077[s]	F-D	54.01	25.43	3.95	8.50
0078[s]	F-D	37.71	16.12	1.37	4.05
0079	U-A	60.99	25.35	1.41	4.77
0080[a]	U-B	56.85	25.27	1.16	4.40
0080[a]	U-B	58.13	24.78	1.25	4.22
0081	U-C	53.10	23.71	1.36	4.35
0082	U-D	35.57	15.29	0.79	2.93
0083	U-A	50.20	22.31	0.87	3.88
0084	U-B	47.20	21.36	0.89	3.89
0085[s]	U-C	45.90	19.11	B.D.	3.79
0086[s]	U-C	43.88	18.35	B.D.	3.39
0087	U-D	24.43	11.55	0.65	2.57
0088[s]	U-A	38.88	18.04	1.01	4.48
0089[s]	U-A	36.06	16.13	0.98	4.26
0090	U-B	36.95	18.08	1.04	3.88
0091	U-C	40.33	14.06	1.42	5.36
0092	U-D	22.76	9.95	0.67	2.38
0093[a]	U-A	39.38	16.22	1.17	4.46
0093[a]	U-A	38.89	15.13	0.97	3.88
0094	U-B	39.13	14.44	1.23	5.07
0095	U-C	32.77	15.36	1.01	3.72
0096	U-D	17.98	7.71	0.46	1.83

s Sample duplicates
a Analytical duplicates
B.D. Below detection limit

Table 3. Normalized concentration data grouped by organic compound and sample's position in tube.



		Frozen samples tube position					*Unfrozen samples tube position*			
Volatile		*A*	*B*	*C*	*D*		*A*	*B*	*C*	*D*
		91.24	98.21	65.08	43.77		60.99	57.49	53.10	35.57
Chloroform			89.44				50.20	47.20	45.90	24.43
		95.13	86.22	63.09	37.62				43.80	
		76.34	65.08	43.01	35.16		38.88	36.95	40.33	22.76
		69.90	72.86	46.92	54.01		36.06			
					37.71		39.14	39.13	32.77	17.98
	Average	83.15	82.36	54.52	41.65	Average	45.05	45.19	43.20	25.18
		33.40	40.39	32.23	18.71		25.35	25.03	23.71	15.29
Benzene			43.85				22.31	21.36	19.11	11.55
		37.00	43.58	32.11	15.75					18.35
		28.88	38.48	26.19	17.73		18.04	18.08	14.06	9.95
		44.02	38.89	28.59	25.43		16.13			
					16.12		15.67	14.44	15.36	7.71
	Average	35.82	41.04	29.78	18.75	Average	19.50	19.73	18.12	11.12
		7.21	5.97	3.78	2.58		1.41	1.21	1.36	0.79
C_2Cl_4			4.56				0.87	0.89	B.D.	0.65
		7.60	4.63	3.52	2.27					B.D.
		7.20	3.62	2.93	1.76		1.01	1.04	1.42	0.67
		5.55	3.93	2.36	3.95		0.98			
					1.37		1.07	1.23	1.01	0.46
	Average	6.89	4.54	3.15	2.64	Average	1.07	1.09	1.26	0.64
		17.12	15.91	9.62	6.36		4.77	4.31	4.35	2.93
Toluene			12.38				3.88	3.89	3.79	2.57
		17.28	11.77	8.90	5.95				3.39	
		16.30	*8.50*	*6.30*	4.27		4.48	3.88	5.36	2.38
		11.17	9.75	5.81	8.50		4.26			
					4.05		4.17	5.07	3.72	1.83
	Average	15.47	11.66	7.66	5.83	Average	4.31	4.29	4.12	2.43

Table 4. Fraction of VOCs remaining relative to the original concentration of the solution.

	Frozen samples Tube position				*Unfrozen samples Tube position*			
Volatile	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*
Chloroform	0.84	0.83	0.55	0.42	0.46	0.46	0.44	0.25
Benzene	0.61	0.70	0.50	0.32	0.33	0.33	0.31	0.19
Toluene	0.67	0.51	0.33	0.25	0.19	0.19	0.18	0.11
C_2Cl_4	0.33	0.22	0.15	0.13	0.05	0.05	0.06	0.03

Table 5. Results of analysis of variance test performed on normalized concentrations.

		Toluene		*Benzene*		*Chloroform*		C_2Cl_4	
	DF	*MS*	*F*	*MS*	*F*	*MS*	*F*	*MS*	*F*
Tube position	3	49	19	377	23	1725	17	9	30
Frozen/unfrozen	1	303	119	1551	96	4722	46	84	280
Interaction	3	27.5	11	70	4	311	3	7	23
Error	24	2.5		16		102		0.3	

Statistically significant at the 95% level if F is greater than 3.01 for 3 degrees of freedom and 4.26 for 1 degree of freedom.
DF = Degrees of freedom
MS = Mean square
F = Treatment mean square/error mean square

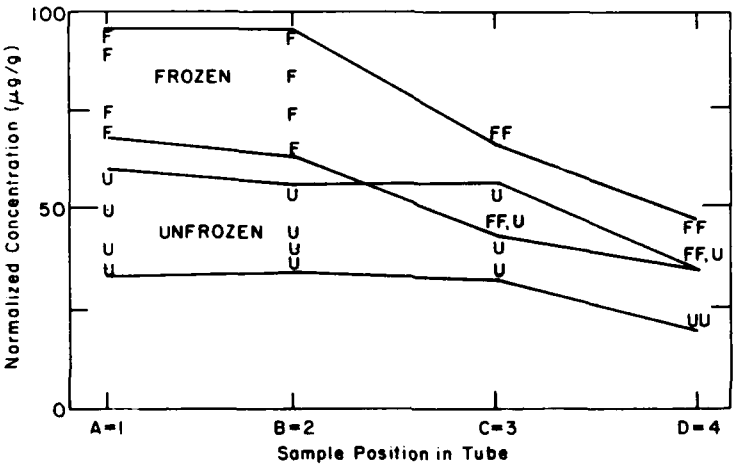


Figure 1. Frozen and unfrozen samples of chloroform.

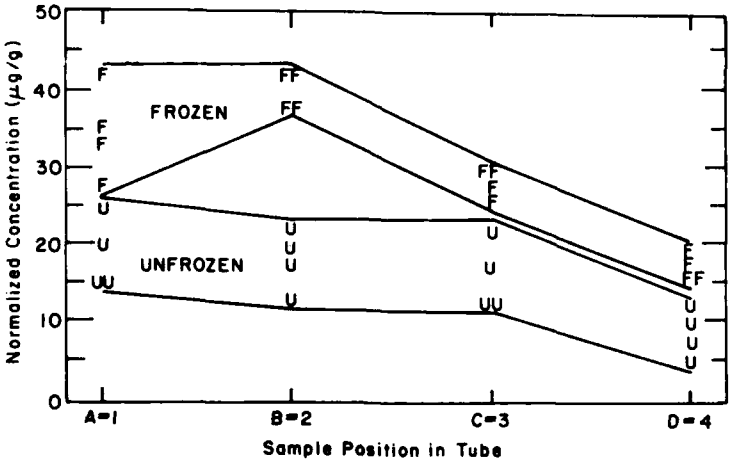


Figure 2. Frozen and unfrozen samples of benzene.

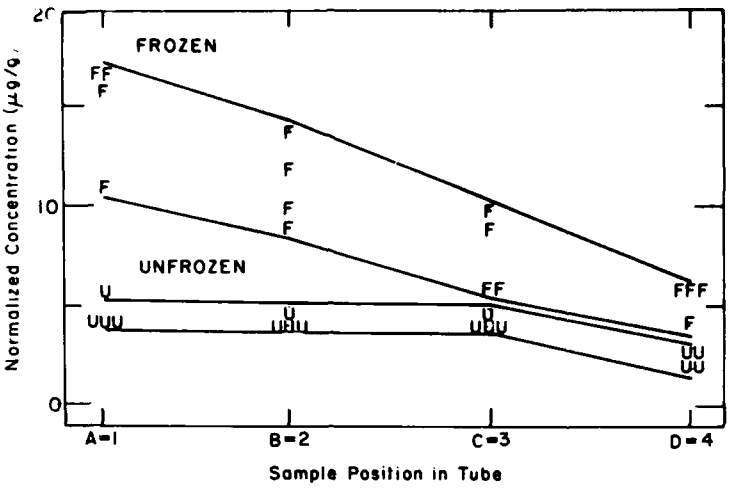


Figure 3. Frozen and unfrozen samples of toluene.

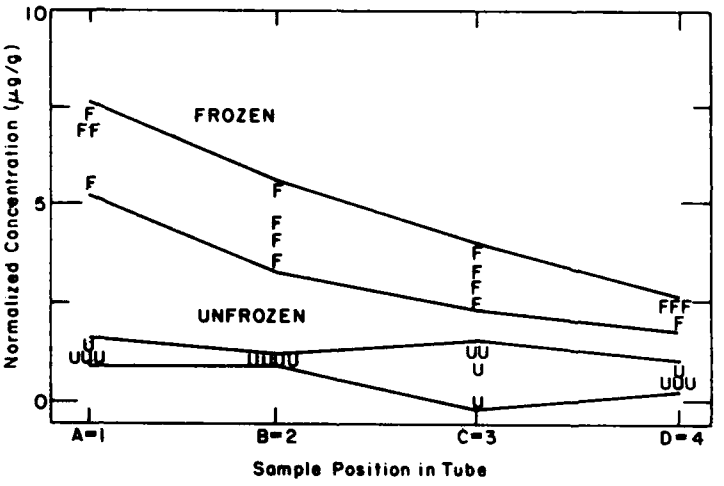
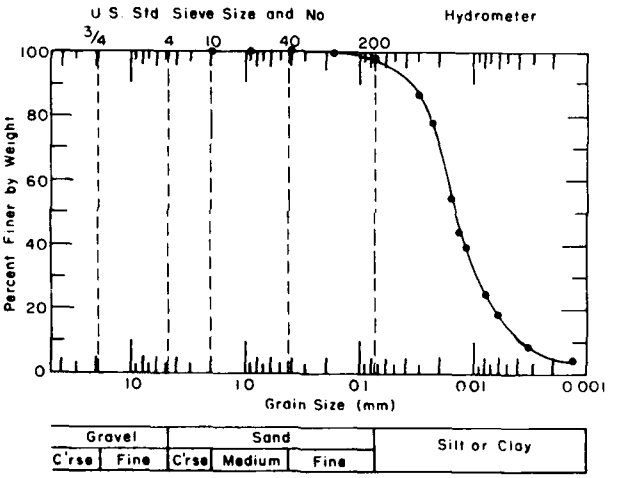


Figure 4. Frozen and unfrozen samples of tetrachloroethylene.

APPENDIX A: SOIL CHARACTERISTICS

MOULTON PIT SILT

Soil classification	ML
Specific gravity	2.79
pH	ND
Percent gravel	0.00
sand	1.80
silt or clay	98.20
Uniformity coefficient	4.85
Coefficient of curvature	1.34
Total organic carbon (%)	ND
Liquid limit	0
Plastic limit	0
Plasticity index	0



APPENDIX B: FORMULA TO CALCULATE CONCENTRATION FROM PEAK AREAS MEASURED BY HPLC

To determine the concentration of benzene, tetrachloroethylene, toluene, and chloroform the following calculation was performed for each analysis:

$$\mu g/g = \frac{\dfrac{\text{total sample volume } (\mu L)}{\text{injection volume } (\mu L)}}{\text{dry wt of sample } (g) \times 1000 \times \text{response factor}} \times \text{normalized area measured from sample}$$

$$\text{Response factor} = \frac{\text{normalized area of standard}}{\text{concentration of standard } (mg/\mu L) \times \text{injection volume } (\mu L)}$$

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12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

The effect of freezing on the distribution and movement of four volatile organic compounds was studied in a silty soil. Eight polycarbonate test tubes were filled with spiked saturated soil. The soil was frozen half way up in four of the tubes; the other four were controls and were not frozen. We found that freezing a water-saturated silt spiked with chloroform, benzene, toluene, or tetrachloroethylene did not move the organics ahead of the freezing front, but rather that freezing retarded the volatilization of each organic in the frozen soil relative to the unfrozen soil.

14. SUBJECT TERMS				15. NUMBER OF PAGES
	Benezene,	Silty soil,	Volatile organics,	15
	Chloroform,	Tetrachloroethylene,		16. PRICE CODE
	Freezing,	Toluene,		

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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