Technical Documents

EFFECTIVENESS OF PURGE-AND-TRAP FOR MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS IN AGED SOILS

Minoo D.F. Askari[1], Mike P. Maskarinec[2], Stacey M. Smith[2], Paul M. Beam[3], Curtis C. Travis[1]

[1]Health Sciences Research Division, Oak Ridge National Laboratories. Oak Ridge, TN 37831. [2]Chemical and Analytical Sciences Division, Oak Ridge National Laboratories. [3]EM-451, 1000 Independence Ave. U.S. Department of Energy, Washington D.C. 20585

Correspondence to: Curtis C. Travis, Health Sciences Research Division, Oak Ridge National Laboratory, 1060 Commerce Park, Oak Ridge, TN 37830

OPTIONAL FORM 99 (7-90)

FAX TRANSMITTAL

To	TIM MICHEAL	# of pages ►	10
Dept./Agency		From	Paul Beam
Fax #		Phone #	301 903 8133
		Fax #	

NSN 7540-01-317-7368 5099-101 GENERAL SERVICES ADMINISTRATION

"THE SUBMITTED MANUSCRIPT HAS BEEN AUTHORED BY A CONTRACTOR OF THE U.S. GOVERNMENT UNDER CONTRACT No. DE-AC05-84OR21400. ACCORDINGLY, THE U.S. GOVERNMENT RETAINS A NONEXCLUSIVE, ROYALTY-FREE LICENSE TO PUBLISH OR REPRODUCE THE PUBLISHED FORM OF THIS CONTRIBUTION, OR ALLOW OTHERS TO DO SO, FOR U.S. GOVERNMENT PURPOSES."

Managed by Lockheed Martin Energy Systems, Inc., under contract number DE-AC05-84OR21400 with the U.S. Department of Energy

9671

Effectiveness of purge-and-trap for measurement of volatile organic compounds in aged soils

Introduction

A critical requirement in the cleanup of contaminated soil sites is an accurate determination of the nature and extent of soil contamination. The EPA recommended method (EPA/SW-846-5030A & 8260A) for measurement of volatile organic compounds (VOCs) in soils is purge-and-trap (1). Under this protocol, organic-free water containing internal standards and surrogates is mixed with a soil sample and heated to 40°C. An inert gas is bubbled through the solution at ambient temperature and the vapor passed through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column (1). Use of purge-and-trap to measure VOCs in soil is based on the assumption that soil VOCs rapidly equilibrate with soil water. Recent studies(2-5), however, strongly question this assumption and indicate that soil desorption is a biphasic process with an initial rapid surface desorption followed by a much slower, diffusion-limited, desorptive phase from the interior of the soil matrix(2-4,6-11).

The biphasic nature of desorption casts doubt on the widely-used, USEPA-recommended purge-and-trap method. When soil has been in contact with VOCs for a long time period (aged soils), VOCs diffuse into soil micropores, where they are unavailable for purge-and-trap measurement. Except for a single study (8) involving 1,2-dibromoethane (EDB), the impact of soil aging on the effectiveness of VOC measurement techniques is largely unexplored. The present study focuses on the effectiveness of three commonly used techniques for measuring VOC concentrations in aged soils: purge-and-trap, methanol immersion, and hot methanol extraction. Since vapor extraction is a currently popular technique for removal of VOCs from soils, we subjected one soil sample to air stripping to evaluate the effect of vapor extraction on the extraction efficiency of purge-and-trap measurements.

Experimental Procedure

Soils. Soil samples were obtained from three geographically distributed sites with a 10- to 20- year history of VOC contamination. The Kentucky soil had high clay content with 100 ppb of trichloroethylene. The Louisiana soil was a silty loam with 3000 ppb of Cis-1,1-dichloroethylene and 6000 ppb of Trichloroethylene. The Florida soil was silty, fine to very fine sand containing methylene chloride at 240 ppb, benzene at 2 ppb, toluene at 190 ppb, and chloroform at 2 ppb.

Sample collection. Soil samples were extracted with a hollow-stem auger and split-spoon sampler. Undisturbed soil cores were sealed in glass jars with minimum headspace and stored at 4°C on arrival. At the start of each experiment, the sample core was plugged and subdivided to obtain three 5-gram subsamples. Subsamples were extruded directly into VOA vials (Dynatech, Baton Rouge, LA) and mixed with 5 ml of water containing internal standards and surrogates before capping.

Measurements of VOCs. Contaminants were extracted from soil samples by methods of purge-and-trap, methanol immersion, and hot methanol extraction. Contaminant concentrations were expressed as microgram per kilogram of soil.

Purge-and-trap. Sample aliquots were purged using a Dynatech PTA-30 auto sampler and a Tekmar (Cincinnati, OH) LSC-2 purge-and-trap device. The trap was desorbed and measurement performed with a Hewlett-Packard Model 5890/5971 GC/MS and EPA method 8260 (12,13).

Methanol immersion. Five ml of purge-and-trap grade methanol was added to sample aliquots. The vial was capped as previously described and vigorously shaken for 30 seconds to facilitate wetting of the soil surface. A 50 micro liter (ul) aliquot of the methanol was then removed and added to 5 micro liter (ml) of water containing internal standards and surrogates. The water was then subjected to purge-and-trap and analyzed for the concentration of chemicals by GC.

Hot methanol extraction. Hot methanol extraction was performed in the same manner as methanol immersion except that, prior to withdrawal of the aliquot of methanol, the VOA vial was placed in a 40°C ultrasonic water bath for 30 minutes. The methanol was drawn and analyzed as described above.

Extraction following air stripping. The Louisiana sample was mixed in a 7:3 ratio with calcium oxide to prevent solidification during air stripping. The sample was then placed in a buchner funnel with a vacuum running from the bottom of the funnel through a flask. Ambient air was passed through the sample using a vacuum of 450-675 mm of mercury for one week. Occasional mixing of the soil was performed throughout this time. The soil sample was divided into three subsamples and each was then subjected to one of the three methods as previously described.

Results

Measurement results from the three different sites--Kentucky, Louisiana, and Florida--are presented in Table 1. Trichloroethylene was the only contaminant detected in the

Kentucky soil (Table 1), with a purge-and-trap recovery only 42% as compared to hot methanol extraction. Both Cis-1,1-dichloroethylene and trichloroethene were detected in the Louisiana soil. Purge-and-trap recovery of these two contaminants was only 7.4% and 4.8%, respectively, when compared to hot methanol extraction method. Four compounds were identified in the Florida soil: methylene chloride, benzene, toluene, and chloroform, with purge-and-trap recovery 38.0% , 1.5%, 71.2%, 1.5%, respectively, in comparison to hot methanol extraction.

Table 1: Comparison of three methods for measuring VOCs in soils.

Soil Type & Component	Compounds	Purge-and-trap[1] (ug/kg)	Methanol immersion[1] (ug/kg)	Hot methanol extraction[1] (ug/kg)
Kentucky (clay)	Trichloroethylene	100	140	240
Louisiana (silty loam)	Cis-1,1-dichloroethylene	3070	2600	41700
	Trichloroethylene	5900	85000	121700
Florida (silty fine to very fine sand) a	Methylene chloride	240	530	630
	Benzene	2	110	150
	Toluene	190	240	270
	Chloroform	2	110	130

[1].Average of three soil sample measurements

Effect of air stripping. Contaminant concentrations for air-stripped Louisiana soil are presented in Table 2. Purge-and-trap detected levels of methylene chloride, Cis 1,1-dichloroethylene and TCE at 58%, 4.1%, and 5.6%, respectively, that of hot methanol extraction. Comparison of these results with those in Table 1 for Louisiana soils indicates that air stripping does not appear to affect the distribution of contaminants between the

accessible and inaccessible phases.

Table 2: Comparison of extraction methods for Louisiana soil after one week of air stripping.

Compound	Purge-and-trap (ug/kg)	Methanol immersion (ug/kg)	Hot methanol extraction (ug/kg)
Methylene chloride	94	150	160
Cis-1,1-dichloroethylene	86	390	2110
Trichloroethylene	310	5400	5500

Discussion

Purge-and-trap is the EPA-recommended method (EPA/SW-846-5030A) for measurement of VOCs in soils. Under the protocol, organic free water is mixed with a soil sample and heated to 40° C. An inert gas is bubbled through water and the concentration of chemicals in the gas is measured with a gas chromatograph. This method is only effective if VOCs in soils rapidly desorb from the soil surface into surrounding water. Recent studies (2-4,8,14,15) on the physical inaccessibility of contamination in soils suggest that this may not be the case, particularly in long-contaminated soils. It has been hypothesized that aging involves diffusion into soil micropores, partitioning into soil organic matter, strong surface adsorption, or a combination of these processes (2,14,16,17). Studies (6,18) indicate that 20-90% of contamination may be located in the interior of the soil matrix and thus inaccessible for purge-and-trap measurement. The purpose of the present study was to compare the effectiveness of three commonly used techniques for measuring VOCs in soils: purge-and-trap, methanol immersion, and hot methanol extraction. We found that purge-and-trap consistently underestimated the concentration of VOCs in aged soils by factors ranging from 2 to approximately

100. This consistent underestimation of soil concentrations undermines EPA s attempt to remediate contaminated soils to levels consistent with health-based cleanup standards.

The soil desorption process is known to involve two distinct phases: a rapid desorption from the soil surface occurring within 24 h and a much slower diffusion-limited desorption from the interior of the soil matrix occurring over a period of days to years (5,19). This biphasic desorption pattern is most pronounced in aged soils where a significant fraction of contamination is located in the interior of the soil matrix. For example, despite its high volatility and degradability, 1,2-dibromoethane (EDB), a soil fumigant, was found (8) in agricultural topsoil 19 years after its last known application. The persistence of EDB was attributed to desorption half-times of 2-3 decades at 25^{0}C (2). For trichloroethylene (TCE), a continuous desorption study (10) of long-contaminated soils revealed persistence of 18% of the initial TCE concentration after desorption with 24000 pore volumes of water. In a subsequent study (3) on simultaneous desorption of Trichloroethylene, tetrachloroethylene, toluene, and xylene, a substantial portion (48-94%) of the sorbed contaminant mass resisted desorption after 7 days of contact time. TCE soil concentrations at the Picatinny Arsenal were found to be 1-3 orders of magnitude greater than predicted using soil-gas concentrations and equilibrium conditions (18). The present study found the purge-and-trap, as compared to hot solvent extraction, only recovered 42% and 4.8%, respectively, of TCE in long-contaminated clays and silty loam soils.

Even in freshly spiked soils, desorption rates of pollutants can be 1-3 orders of magnitude smaller than equilibrium predicted rates (4). Clean soils spiked with halogenated aliphatic hydrocarbons for 24 or 72 hours resisted desorption after 16 extractions of 24 to 72 hours each (6). These observations bring into question the occurrence of desorption equilibrium necessary for validity of the purge-and-trap measurements in the freshly spiked and aged soils.

Previous analysis of EDB in long-contaminated soils has shown that purge-and-trap is less effective than extraction at 75^{0}C with organic solvents such as methanol, acetonitrile or acetone (2,6,8), recovering less than 11% of the total EDB found by hot solvent extraction(8). Our purpose in the present study was to extend these results to a larger class of VOCs in aged field samples. Hot methanol extraction proved to be more effective than the EPA-approved purge-and-trap technique. For three long-contaminated soils containing such VOCs as Trichloroethylene, benzene, toluene, chloroform, methylene chloride, and Cis-1,1-dichloroethylene, recovery from purge-and-trap ranged between 1.5 up to 41% that of hot methanol extraction.

Slow desorption is recognized as a serious obstacle to soil remediation technologies(11,14,20-23). For such technologies as pump and treat, vapor extraction, and bioremediation to be

effective, soil contaminants must be accessible. To simulate the effect of vapor extraction on the efficiency of the purge-and-trap methodology, we subjected the Louisiana soil to a week of air stripping. Purge-and-trap recovered only 58% of the methylene chloride, 4.1% of the Cis 1,1-Dichloroethylene and 5.6% of the TCE that hot methanol extraction was able to recover. These results indicate the purge-and-trap is not a reliable method for evaluating vapor extraction as a remediation technology.

It is clear from the results of this and previous studies that the best overall choice for measurement of soil VOCs is hot methanol extraction, since this method yields a more accurate analysis, regardless of the age of contaminated soil. The VOC data from three different soil types clearly demonstrate the limitations of the EPA-approved purge-and-trap method, which can bias analytical results by several orders of magnitude depending on soil type and chemical properties. We suggest that EPA review the use of purge-and-trap as a method for measuring VOCs in soils.

REFERENCES

1-Environmental Protection Agency. 40 CFR Ch. 1 Pt. 261, App. III (7-1-94 Edition), 67.

2-Steinberg, S.M.; Pignatello, J.J.; Sawhney, B.L. *Environ. Sci. Technol.* **1987**, *21*, 1201-1208.

3-Pavlostathis, S.G.; Mathavan, G.N. *Environ. Sci. Technol.* **1992**, *26*, 532-538.

4-Kan, A.T.; Fu, G. *Environ. Sci. Technol.* **1994**, *28*, 859-867.

5-Fares, A.; Kindet, B.T.; Lapuma, P.; Perram, G.P. *Environ. Sci. Technol.* **1995**, *29*, 1564-1568.

6-Pignatello, J.J. *Environ. Toxic. and Chem.* **1990**, *9*, 1107-1115.

7-Pignatello, J.J.; Frink, C.R.; Marin, P.A.; Dorste, E.X. *J. Contamin. Hydrol.* **1990**, *5*, 195-214.

8-Sawhney, B.L.; Pignatello, J.J.; Steinberg, S.M. *J. Environ. Qual.* **1988**, *17*, 149-152.

9-Witkowski, P. J.; Gaff, P.R.; Ferrara, R.A. *J. Contamin. Hydrol.* **1988**, *2*, 249-269.

10-Pavlostathis, S.G.; Jaglal, K. *Environ. Sci. Technol.* **1991**, *25*, 274-279.

11-Travis, C.C.; MacInnis, J.M. *Environ. Sci. Technol.* **1992**, *26*, 1885-1887.

12-Conder, J.R.; Young, C.L. *Physicochemical Measurement by Gas Chromatography*. John Wiley and Sons: New York, 1979.

13-Laub, R.J.; Pecsok, R.L. *Physicochemical Measurement by Gas Chromatography*. John Wiley and Sons: New York, 1978.

14- Hatzinger, P.B.; Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 537-545.

15-Pignatello, J.J.; Ferrandino, F.J.; Huang, L.Q. *Environ. Sci. Technol.* **1993**, *27*, 1563-1571.

16-Brusseau, M.L.; Jessup, R.E.; Rao, P.S.C. *Environ. Sci. Technol.* **1991**, *25*, 134-142.

17-Wu, S.C.; Gschwend, P.M. *Environ. Sci. Technol.* **1986**, *20*, 717-725.

18-Smith, J. A.; Chiou, C. T.; Krammer, J. A.; Kile, D. E. *Environ. Sci. Technol.* **1990**, *24*, 676-683.

19-Mackay, D.M.; Cherry, J.A. *Environ. Sci. Technol.* 1989, *23*, 630-636.

20-Di Toro, D.M.; Horzempa, L. M. *Environ. Sci. Technol.* 1982, *16*, 594-602.

21-Coates, J.T.; Elzerman, A.W. *J. Contam. Hydrol.* 1986, *1*, 191-210.

22-Pignatello, J.J.; Huang, L.Q. *J. Environ. Qual.* 1991, *20*, 222-228.

23-Scribner, S.L.; Benzing, T.R.; Sun, S.; Boyd, S.A. *J. Environ. Qual.* 1992, *21*, 115-120.

26-McCall, P.J.; Agin, G.L. *Environ. Toxicol. Chem.* **1985**, *4*, 37-44.

27-Hamaker, J.W.; Thompson, J.M. In *Organic chemicals in the Soil Environment*; Goring, C.A. I., Hamaker, G. L., Eds.; Marcel Dekker: New York, 1972; pp 49-143.

30-Hiatt, M.H. Analysis of fish and sediment for volatile priority pollutants. *Anal. Chem.* **1981**, *53*, 1541-1543.

31-Spraggins, R.L.; Oldham, R.G.; Prescott, C.L.; Baughman, K.J. Organic analyses using high-temperature purge-and-trap techniques. In *Advances in the identification and analysis of organic pollutants in water*, Vol. 2; Keith, L.H., Ed.; Ann Arbor Sci. Publ.: Ann Arbor, MI, 1981; pp 747-761.

2-Chiou, C. T.; Kile, D. E.; Malcolm, R. L. *Environ. Sci. Technol.* **1988**, *22*, 298-303.

3-Chiou, C. T.; Shoup, T. D. *Environ. Sci. Technol.* **1985**, *19*, 1196-1200.

4-Smith, J.A.; Witkowski, P. J.; Chiou, C. T. *Rev. Environ. Contamin. Toxicol.* **1988**, *103*, 127-151.

14-Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **1979**, *13*, 241-248.

15-Schwarzenbach, R.P.; Westall, J. *Environ. Sci. Technol.* **1989**, *5*, 1360-1367.

16-Hermosin, M.C.; Martin, P.; Cornejo, J. Adsorption mechanisms of Monobytylin in clay minerals. 1993, *27*, 2606-2611.