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Project Summary

Soil Gas Sensing for Detection and Mapping of Volatile Organics

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The sensing of soil gas for detection and mapping of volatile organics is a relatively new technique that deserves greater attention. Soil organic vapor monitoring has been shown to be a cost effective means of delineating the size and movement of organic contaminants in the subsurface. It has also been shown to provide immediate information of the lateral extent of soil and ground-water contamination and to minimize and more accurately predict the number and location of conventional monitoring wells that must be drilled.

Literature on the technique for mapping soil and ground-water contamination has been increasing, but comprehensive reviews of the method have been limited. This document is meant to be a primer on the current state-of-the-art of soil gas sensing as it relates to the detection of subsurface organic contaminants. It is hoped that such a document will better assist all those individuals who are faced with assessing the extent of contamination of our soil and ground water.

The document begins by outlining many of the parameters (water solubility, microbial influence, ground-water flow, etc.) that must be considered by the scientist before utilizing soil gas sensors in a field monitoring program. Next, the complex soil, air, water, and hydrocarbon system is addressed with an overview of the important processes involved in the transport and fate of organic contaminants in the soil. Additional sections address the correct sampling and analytical methodologies for monitoring volatile organics in the subsurface, covering such sampling methods as headspace, ground probe, flux chamber and passive sampling techniques. Analytical methods include organic vapor analyzers (OVAs) and gas chromatographs with a variety of detectors. A statistical treatment of soil organic vapor measurements is also included to ensure that soil organic vapor monitoring programs address the requirement for data precision. The statistical section also gives greater insight into understanding the spatial patterns of soil organic vapor measurements. Finally, case studies are included to give the unfamiliar reader examples of the design, procedures, and results of soil organic vapor monitoring programs that have been successful in delineating the size and lateral extent of subsurface organic contaminants.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Interest in the measurement of concentrations of volatile organic compounds in the pore-space gases of soil was stimulated by enactment of Superfund (the Comprehensive Environmental Response, Compensation, and Liability Act, or CERCLA) and by the November 1984 reauthorization of RCRA (the Resource Conservation and Recovery Act of 1976) which directed the U.S. Environmental Protection Agency (EPA) to promulgate standards for underground storage tanks to include provisions for leak detection. Soil gas monitoring has been shown to be a useful technique for mapping organic contamination of the subsurface prior to the use of more expensive monitoring methods such as the drilling of wells. Inorganic contamination may be mapped using geophysical methods such as electrical resistivity When organic contamination is commingled with inorganic contaminants, organic contamination may be mapped with geophysical methods; however, when relatively low levels of organic contaminants are not commingled with inorganic contaminants, soil gas monitoring is a useful technique to consider for mapping volatile organics. Table 1 shows that a majority of the contaminants found at Superfund sites are organic comtaminants with volatile organics being common.

A desired goal in many soil gas investigations of organic contamination is to establish a relationship between the organic vapors sampled in the vadose zone to the concentration of contaminants in the ground water. If a relationship can be established, soil gas measurements can be useful in determining the location for monitor wells and assessing the extent of ground-water contamination. If a relationship cannot be established, soil gas monitoring may still be a technique to consider in quickly assessing the extent of contamination of the soil, particularly in the shallow zone being sampled by the probes or passive samplers.

The increasing interest in the detection of leaks from underground storage tanks has further increased the growing interest in soil gas monitoring. Soil gas measurements may be used to locate the source of the leaked material as well as to map the extent of the contamination. Soil gas measurements may be made over time within the excavation zone containing the tank and piping to determine if a tank system is tight. While permanent monitoring of tanks with vapor monitoring in the vadose zone is a relatively new and promising use of soil gas measurements, the monitoring of underground storage tanks for leaks is not the focus of this document.

The Document

Five important areas related to soil gas monitoring are discussed in the document: (1) site specific parameter considerations, (2) transport and retention of organics in soil and ground water, (3) sampling methods, (4) analytical methods, and (5) statistical treatment of soil organic vapor measurements. Two case studies are presented to illustrate how a soil gas survey may be performed and how the data may be displayed and interpreted.

A number of site specific parameters need to be considered in a soil-gas survey. These are listed in Table 2 and covered in further detail in the document.

Further research is required to understand the transport and fate of liquid phase, gas phase, and dissolved hydro-

Table 1. *Most Frequently Identified Substances at 546 Superfund Sites*

Rank	*Substance*	*Percent of Sites*
1	*Trichloroethylene*	33 (b)
2	*Lead and Compounds*	30
3	*Toluene*	28 (b)
4	*Benzene*	26 (b)
5	*Polychlorinated biphenyls (PCBs)*	22
6	*Chloroform*	20 (b)
7	*Tetrachloroethylene*	16 (b)
8	*Phenol*	15
9	*Arsenic and compounds*	15
10	*Cadmium and compounds*	15
11	*Chromium and compounds*	15
12	*1,1,1-Trichloroethane*	14 (b)
13	*Zinc and compounds*	14
14	*Ethylbenzene*	13 (b)
15	*Xylene*	13 (b)
16	*Methylene chloride*	12 (b)
17	*Trans-1,2-dichloroethylene*	11 (b)
18	*Mercury*	10
19	*Copper and compounds*	9
20	*Cyanides (soluble salts)*	8
21	*Vinyl chloride*	8 (b)
22	*1,2-Dichloroethane*	8 (b)
23	*Chlorobenzene*	8 (b)
24	*1,1-dichloroethane*	8 (b)
25	*Carbon tetrachloride*	8 (b)

(a) Source Adapted from McCoy and Associates, The Hazardous Waste Consultant, *March/April 1985, Vol 3, Issue 2*

(b) Compounds amenable to soil-gas surveying—based upon Henry's law constant.

Table 2. *Site Specific Parameter Considerations*

A Chemical and Physical Properties of the Organic Compound

1. *Vapor pressure*
2. *Water solubility*
3. *Henry's law constant*
4. *Concentration*
5. *Organic Distribution coefficient (Koc)*
6. *Density*
7. *Viscosity*
8. *Viscosity*
9. *Boiling point*
10. *Molecular weight*

B. Properties of the Unsaturated Zone

1. *Air filled porosity*
2. *Volumetric water content*
3. *Soil organic matter*
4. *Soil texture*
5. *Vapor pressure of water in the soil pores*
6. *Shape and size of pores*
7. *Depth of unsaturated zone*
8. *Retention*
9. *Temperature and temperature gradients*
10. *Microbial influence*

C. Hydrogeologic Properties

1. *Ground-water flow (direction, velocity, gradient)*
2. *Water table oscillations*
3. *Lithology of the aquifer*

D. Characteristics of the Spill

E. Miscellaneous

1. *Rainfall*
2. *Background water quality*
3. *Barometric pressure and wind*
4. *Promixity to rivers, lakes and pumping wells*

carbons in the ground. What is known about three-phase transport of hydrocarbons is described in a separate chapter in order to provide the reader insight on transport and fate processes that need to be considered in making soil-gas measurements.

A variety of methods have been used in collecting a soil gas sample for analysis, and they are briefly described in a chapter on sampling methods. Soil gas measurements have been made with pipes, evacuated canisters, Tedlar bags, adsorbents, flux chambers, pumps, and syringes. There is no standard method. In general, soil gas methods can be classified into two categories: active and passive methods. Active methods involve the pumping of relatively large sample volumes from the soil whereas passive methods involve relatively little, if any, withdrawal of soil gas from the subsurface. Further research is needed to determine which method is best for obtaining "representative" measurements of soil gas.

A number of analytical methods and instruments exist for measuring organics in the collected soil gas samples. Differing sensitivities exist depending upon the method or instrument selected and the compounds present in the sample. Organic vapor analyzers, field portable and laboratory gas chromatographs, and mass spectrometers are several of the analytical techniques that are described in a chapter on analytical methodologies. The calibration of these methods is also briefly discussed.

The location of soil gas measurements in site investigations may dramatically affect the interpretation of soil gas data. The depth at which measurements are made is an important factor particularly with organic compounds that are prone to biological degradation or chemical transformation. One of the case studies presented in the document illustrates this point with high concentrations of benzene being present in the ground water but not detectable in the vadose zone. The spatial location of soil gas points is another important factor in the mapping of organic contaminants. Too few sample points, or sample measurements made at a higher density in some areas, can affect the interpretation of the collected data through the drawing of inappropriate contour lines around the data points. Another factor, frequently overlooked in soil gas measurements, is the variability in obtaining consistent measurements from a probe and analytical method. While all the factors that can influence soil gas measurements have some effect on the measurement process and the interpretation of the data, some of the factors become more important as greater emphasis is placed on the concentration values being reported from a soil gas survey. Most of the time soil gas measurements are relative measurements that are intended to identify where to drill monitor wells; however, there is a growing trend to use soil gas measurements to define contaminated zones and to establish site clean-up plans. If this trend continues, the evaluation of the factors that influence soil gas measurements will have to be examined further, and the chapter on the statistical treatment of soil organic vapor measurements was intended to offer the reader some insights on how these factors may be evaluated.

Two examples are presented on how soil gas measurements may be used to map ground-water contamination. Gasoline from a leaking underground storage tank was mapped in Death Valley, California, and variables affecting the measurement of soil gas were studied near an industrial site outside of Las Vegas, Nevada. Both studies are used to illustrate some of the limitations of soil gas measurements.

Conclusions

Soil gas measurements are proving to be useful in mapping organic contamination at sites prior to the drilling of monitor wells, or the colection of soil samples. Since soil gas measurements were first made in the early 1900's, measurements of soil gas have increased dramatically within just the past few years to the point where the technique is often considered as a first step in an investigation of organic contamination of the subsurface.

The team of authors who wrote this primer on the method reviewed the literature and used their background to cover five main topics: (1) site specific parameter considerations, (2) transport and retention of organics in soil and ground water, (3) sampling methods, (4) analytical methods, and (5) statistical treatment of soil organic vapor measurements. Two case studies are presented to illustrate how a soil gas survey may be performed and how the data may be displayed and interpreted. While the document was not intended to be a guidance document for making soil gas measurements, some guidance is offered to the reader on important steps and considerations in the conduct of a soil gas study.

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***Jeff van Ee** is the EPA Project Officer (see below).*

The complete report, entitled "Soil Gas Sensing for Detection and Mapping of Volatile Organics," (Order No. PB 87-228 516/AS; Cost: $24.95, subject to change) will be available only from:

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