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**A New Device and Method for Measuring Volatile
Compounds in Monitoring Wells**

**(A Research Study of the Monitored Natural Attenuation/Enhanced
Attenuation for Chlorinated Solvents Technology Alternative Project)**

November 6, 2006

Washington Savannah River Company Savannah River Site Aiken, SC 29808	 SRNL SAVANNAH RIVER NATIONAL LABORATORY
Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96- SR18500	

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Executive Summary

Accurate, timely measurement of chlorinated solvents and other volatile contaminants in groundwater is crucial to support responsible environmental management. Traditionally, two distinctly different paradigms have been explored to meet this need – fixed laboratory analysis and “real-time” sensors. While these alternatives remain important, field based and field screening tools represent a potentially useful intermediate approach that balances some of the advantages and disadvantages of the traditional “end-member” paradigms. The value of accurate, in-field measurements during characterization was recognized in recent sampling/decision methods, such as the TRIAD approach (ITRC, 2003). Strategies that support gathering accurate data on the timescales representative of the rate of change of the system (e.g., months to years, not seconds to minutes) is key for long-term monitoring for chlorinated solvent plumes in which attenuation based remedies are being considered. A team of researchers developed a down-well sampling device that, when used in combination with field gas analysis tools, provides data in the field. The test results indicate this tool, as configured, will provide accurate measurements (as compared with laboratory methods) at concentrations in the hundreds of ppb or higher range, but require confirmatory traditional sampling with laboratory analysis at concentrations approaching 20 ppb and less. The logistics and costs of the sampling device were somewhat complex. The results of the study, while equivocal, generally suggest that future development of this type of in-field technique may be warranted.

Introduction

Over the past three decades, much progress has been made in the remediation of soil and groundwater contaminated by chlorinated solvents. Yet these pervasive contaminants continue to present a significant challenge to the U.S. Department of Energy (DOE), other federal agencies, and other public and private organizations. The physical and chemical properties of chlorinated solvents make it difficult to rapidly reach the low concentrations typically set as regulatory limits. These technical challenges often result in high costs and long remediation time frames. In 2003, the DOE through the Office of Environmental Management funded a science-based technical project that uses the U.S. Environmental Protection Agency’s technical protocol (EPA, 1998) and directives (EPA, 1999) on Monitored Natural Attenuation (MNA) as the foundation on which to introduce supporting concepts and new scientific developments that will support remediation of chlorinated solvents based on natural attenuation processes. This project supports the direction in which many site owners want to move to complete the remediation of their site(s), that being to complete the active treatment portion of the remedial effort and transition into MNA.

The overarching objective of the effort was to examine environmental remedies that are based on natural processes – remedies such as Monitored Natural Attenuation (MNA) or Enhanced Attenuation (EA). The research program did identify several specific opportunities for advances

based on: 1) mass balance as the central framework for attenuation based remedies, 2) scientific advancements and achievements during the past ten years, 3) regulatory and policy development and real-world experience using MNA, and 4) exploration of various ideas for integrating attenuation remedies into a systematic set of “combined remedies” for contaminated sites. These opportunities are summarized herein and are addressed in more detail in referenced project documents and journal articles, as well as in the technical and regulatory documents being developed within the ITRC.

Three topic areas were identified to facilitate development during this project. Each of these topic areas, 1) mass balance, 2) enhanced attenuation (EA), and 3) innovative characterization and monitoring, was explored in terms of policy, basic and applied research, and the results integrated into a technical approach. Each of these topics is documented in stand alone reports, WSRC-STI-2006-00082, WSRC-STI-2006-00083, and WSRC-STI-2006-00084, respectively. In brief, the mass balance efforts are examining methods and tools to allow a site to be evaluated in terms of a system where the inputs, or loading, are compared to the attenuation and destruction mechanisms and outputs from the system to assess if a plume is growing, stable or shrinking. A key in the mass balance is accounting for the key attenuation processes in the system and determining their rates. EA is an emerging concept that is recognized as a transition step between traditional treatments and MNA. EA facilitates and enables natural attenuation processes to occur in a sustainable manner to allow transition from the primary treatment to MNA. EA technologies are designed to either boost the level of the natural attenuation processes or decrease the loading of contaminants to the system for a period of time sufficient to allow the remedial goals to be met over the long-term. For characterization and monitoring, a phased approach based on documenting the site specific mass balance was developed. Tools and techniques to support the approach included direct measures of the biological processes and various tools to support cost-effective long-term monitoring of systems where the natural attenuation processes are the main treatment remedies. The effort revealed opportunities for integrating attenuation mechanisms into a systematic set of “combined remedies” for contaminated sites.

An important portion of this project was a suite of 14 research studies that supported the development of the three topic areas. A research study could support one or more of these three topic areas, with one area identified as the primary target. The following report documents the results of the testing of a down-well sampling device for volatile organic compounds that minimizes waste generation and provides “real-time” analytical results. This effort was led by Kirk Cantrell of Pacific Northwest National Laboratory. This study supports the topic area(s) of characterization and monitoring. The objective of the study was to test a new field sampling device (Microsparger) that provides in-field results of volatile organic compound concentrations.

The MNA/EA Project’s Technical Working Group identified a 4-phased process for characterization and monitoring (WSRC-STI-2006-00084). The first phase of this process, identified as “screening characterization” is aimed at identifying major attenuation mechanisms. Concentration data measured over time or distance, as described in the *EPA Technical Protocol for Evaluating Natural Attenuation of*

Chlorinated Solvents in Groundwater (EPA, 1998) is one potential set of data collected during this phase. Traditional types of infrastructure, such as monitoring wells, will be used during screening characterization. The third phase of the 4-phased process, identified as “process monitoring” is aimed confirming the attenuation capacities and rates measured during characterization as well as setting-up the transition to system performance monitoring. As with screening characterization, traditional types of data collection are envisioned during this phase. Development efforts supporting collection of traditional data types that will produce tools that result in minimizing investigation derived waste and in providing rapid generation of accurate results are encouraged. The microsparger is a tool designed to support data collection associated with both the screening characterization and process monitoring stages for MNA and EA of chlorinated solvents.

While use of the microsparger did not generate investigation derived waste under the test conditions and provided results in the field, the results of the study did not provide conclusive evidence that this technology is well suited for the typical site being considered for MNA nor that the data obtained is of equivalent quality at the low end of the concentration range (<100 ppb). At TCE concentrations in the 0 to 100 ppb range, typical for sites in an MNA setting, the test results were biased high. The researchers recommended that at concentrations of 20 ppb or less, that confirmatory water samples with traditional GC analysis be collected. The microsparger design is relatively complicated and requires the use of a water pump. The advantage of the microsparger is that the volatile contaminants in the water are transferred to the gas phase within the confines of the wellbore, eliminating the transfer of contaminated groundwater to the surface. However, the researchers were not able to produce accurate results at the concentration ranges of interest for MNA and EA applications.

The review of this research by the Technical Working Group (TWG) produced mixed results. The TWG was supportive of exploiting phase transfers and gas phase sampling. The generation of no investigation derived waste was seen as a plus. There were several design and operational issues that concerned the TWG, including a similar level of down-well infrastructure as is required by a traditional water-well. A major concern was the inability to measure low concentrations as would be expected in the region of a plume where MNA is occurring without the need for confirmatory water samples. While the concept behind the microsparger has merit, the reviews of the TWG did not indicate the use of this tool would meet the goals for characterization and monitoring tools as described in the MNA/EA Project document *Characterization and Monitoring of Natural Attenuation of Chlorinated Solvents in Ground Water: A Systems Approach* (WSRC-STI-2006-00084).

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A New Device and Method for Measuring Volatile Compounds in

Monitoring Wells

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Abstract

The ability to quickly measure dissolved volatile compounds in the field is important to facilitate timely characterization decisions and to optimize remediation systems. A device was designed and tested that is easy to use, provides accurate and reproducible data, and minimizes waste generation. The most important improvement over current methods is the device provides results immediately after measurement.

The device is designed to convert dissolved volatile compounds to the vapor phase for measurement using commercially available gas analyzers. The measured concentration of volatile compounds in the vapor phase is used to calculate the equilibrium concentration in the dissolved phase using Henry's Law.

The device was tested in the laboratory and field using the common groundwater contaminant trichloroethylene (TCE). Laboratory test conducted over a concentration range of 11 to 7000 ppb TCE in water. These results indicate that equilibrium is reached in less than one minute. At the high end of this concentration range results were within 10% of that measured by a standard laboratory GC method. At the low end the system was bias high, but was still within a factor of 2 of the GC result. A wide variety of other volatile compounds can also be measured. In-well measurements with the device in

combination with a photoacoustic gas monitor could be made within about 5 minutes and within 7% of measurements made using standard laboratory gas chromatography (GC) methods for samples above 20 ppb. Results below about 20 ppb were systematically higher than the standard laboratory GC method.

Introduction

There is a significant need in environmental studies for rapid and reliable field measurement of volatile organic contaminants in groundwater. This is particularly important for characterization and remediation activities that depend on these results for making timely decisions. To address this need, a device has been designed (Gilmore et al. 2002) that fits in a standard groundwater monitoring well and allows for rapid measurement of dissolved volatile compounds in the field. The principle of the device is to establish equilibrium between a volume of air (≈ 0.6 L) inside a cylindrical chamber with groundwater containing dissolved volatile compounds. Equilibrium is promoted by spraying (partial atomization) groundwater through the air in an equilibration chamber (Figures 1 and 2). The volatile compound concentration is then measured in the gas phase using commercially available gas analyzers. The concentration of the volatile compound in the vapor is used to calculate the equilibrium concentration in the dissolved phase using Henry's Law.

Currently, the standard method for measuring volatile compounds in groundwater is to collect a water sample from a well which is then sent to a laboratory for analysis by gas chromatography. The most significant improvement this new method offers over the conventional method is the ability to conduct rapid, real time measurements. Results

using the device described here can be obtained in approximately 5 minutes compared to the days to weeks with the conventional method. Also, waste generation, sample preservation, shipping, and accompanying paperwork are substantially reduced.

Results of laboratory and field-testing of the device are presented here. In this study, tests were conducted with trichloroethylene (TCE), a common groundwater contaminant. It was demonstrated that the device is both easy to use and produces accurate and reproducible results.

Materials and Methods

The device was designed to fit within 2-in. diameter or larger groundwater monitoring wells. The device is composed of a 1.5 in. diameter cylinder, constructed of 316 stainless steel, which is open at the bottom and closed at the top (Figures 1). When the device is lowered into water, a volume of air is trapped in the headspace of the equilibration chamber. A small (1.75-in. diameter) submersible pump (Fultz SP-300) is attached below the chamber by 3/8-in. stainless steel tubing. The pump operates on 24v direct current (DC) and is used to circulate water from below the device into the air trapped within the equilibration chamber through a spray tube. Fine streams of groundwater spray against the walls of chamber to promote volatilization of the compounds of interest, resulting in rapid equilibration between the dissolved phase and the air in the headspace of the equilibration chamber (Figure 2). Once equilibrium is reached, a vapor sample from the equilibration chamber is drawn to a gas analyzer at the surface and the vapor concentration is measured. To calculate the concentration in groundwater, the temperature and Henry's law constant for the constituent of interest

must also be known. The temperature is measured directly with a thermocouple attached to the device. Henry's law constants are available from published sources (Heron et al. 1998; Mackay and Shiu, 1981). Henry's Law can be written as:

$$C = K_H P$$

where C is the molar concentration of the solute of interest, P is the partial pressure or concentration of the solute in the gas phase, and K_H is Henry's law constant on the molar concentration scale.

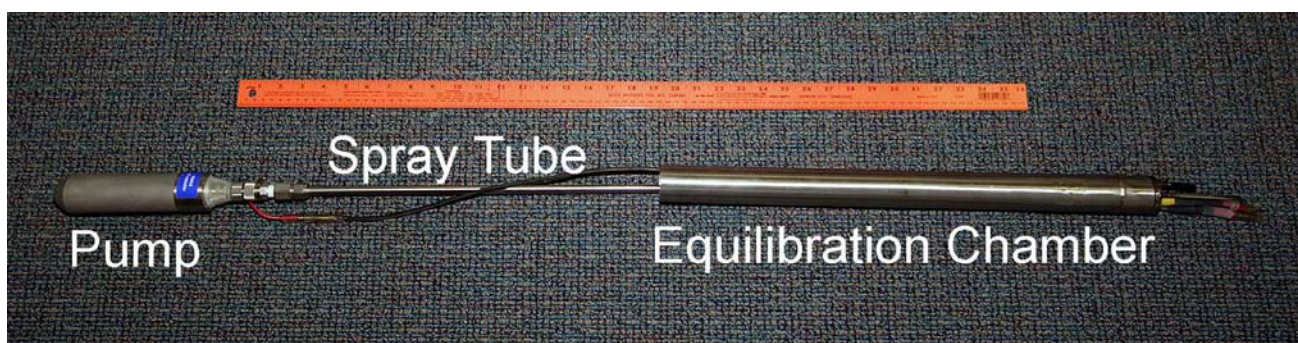


Figure 1. Dissolved Volatile Sampling Device.

The volatile compound used for this study is TCE (trichloroethylene). The gas phase was analyzed using the Innova 1312 Photoacoustic Multi-Gas Monitor. Other commercially available gas analyzers such as a portable gas chromatograph (GC) or the photo-ionizing detector (PID) could also be used for analysis (although PIDs may be only semi-quantitative in the presence of interferences). Tests conducted by the EPA found the Photoacoustic monitor to be accurate, and suitable for field use (EPA 1998). A Genie Model 101 membrane separator was placed in line with the vapor sample inlet hose to prevent any liquid from accidentally entering the gas analyzer.

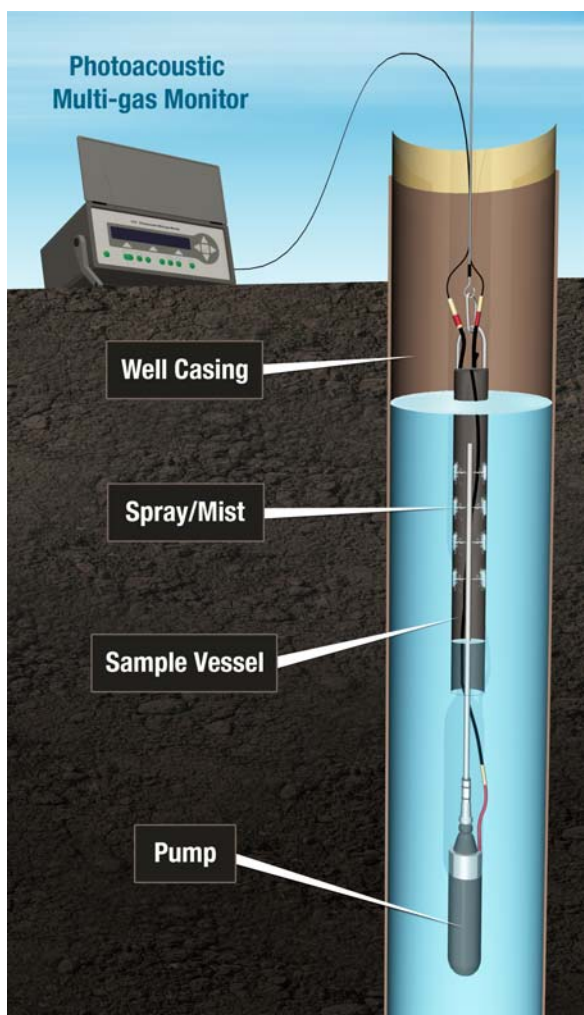


Figure 2. Diagram of Dissolved Volatile Sampling Device in a Well.

The precision and accuracy of the Photoacoustic monitor system has been assessed in a study conducted under the EPA's Environmental Technology Verification Program (EPA, 1998). Instrument precision was determined using four sets of replicate samples containing known concentrations of TCE. The relative standard deviations for TCE measurements ranged from 4 to 22% (EPA, 1998). Instrument accuracy was evaluated using known standards. The range of absolute percent differences for TCE was 5 to 48% (EPA, 1998).

The device was tested in the laboratory using a simulated well setup with a 6-ft long section of 4-in. diameter stainless steel well casing that was capped at one end. Approximately 18 L of de-ionized water containing a known concentration of TCE was added to the simulated well for each experiment. A stock solution of reagent grade TCE (EM Science) diluted in methanol was used to make up the experimental solutions. Temperature measurements were taken with a calibrated thermocouple. Prior to each TCE test run, a water sample was collected for later GC analysis using standard laboratory methods (EPA 1986, Method SW846 8260B). For GC measurements calibration was conducted immediately prior to sample analysis. The calibration curve used for this work produced an R-Squared of 0.9978. A calibration check conducted at the end of the sample run provided a result that was within 97.5% of the expected value.

The device was field tested in a series of groundwater monitoring wells at a site with TCE contaminated groundwater. The site was located on the U. S. Department of Energy's Savannah River Site near Aiken, South Carolina. During the tests, the wells were also sampled with a bailer for later laboratory analysis by GC. Results of both the field and laboratory testing are discussed in the following sections.

Laboratory Results

The device was tested in the laboratory with four different TCE concentrations (11.1, 62.6, 643, and 7020 ppb). Lower concentrations were not investigated because the photoacoustic gas analyzer produced a bias that increased with decreasing concentrations for groundwater samples (see later discussion). The drinking water standard for TCE is 5 ppb. At each concentration, the test solution was circulated through the device for 0.25,

0.5, 1, 2, 3, and 4 minutes to determine the optimal equilibration time. The results of these experiments are shown in Figures 3 to 6. The results clearly indicate the pumping or circulation time required for reaching equilibrium between the aqueous phase and the gas phase is approximately 1 minute regardless of concentration. For pumping times of one minute or more, the results are very consistent. Table 1 shows the average and standard deviation for measurement results with pumping times of 1 minute or more. These results indicate a precision of better than 4% for all concentrations tested. Included in the table for comparison are the results determined with the more standard laboratory GC technique. In this study the GC result is assumed to be the correct value. The ratio of device measurement results over the GC result is also shown in Table 1. The device results are higher than the GC results, with the relative discrepancy increasing with decreasing concentration. At the highest concentration tested, the device has a small high bias (approximately 10%). At the lower concentration the bias is higher at about 100%. The reason for this systematic error is not known at this time; however, it is believed to be due to the photo-acoustic gas analyzer. Similar results with the photo-acoustic gas analyzer were observed by EPA (1998) during analysis of TCE in groundwater using a static headspace method.

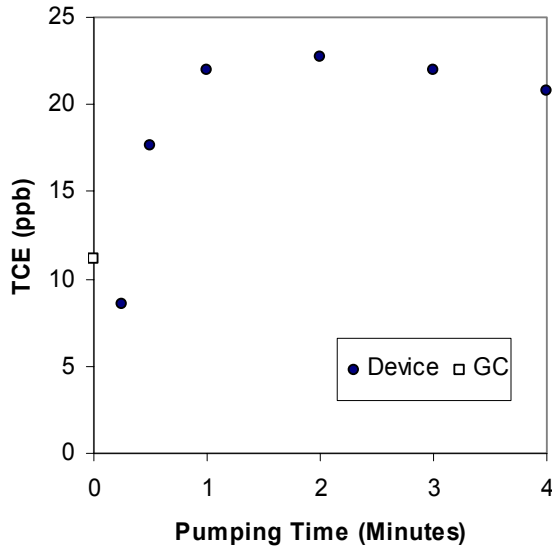


Figure 3. Measurement results at 11.1 ppb TCE (GC analysis).

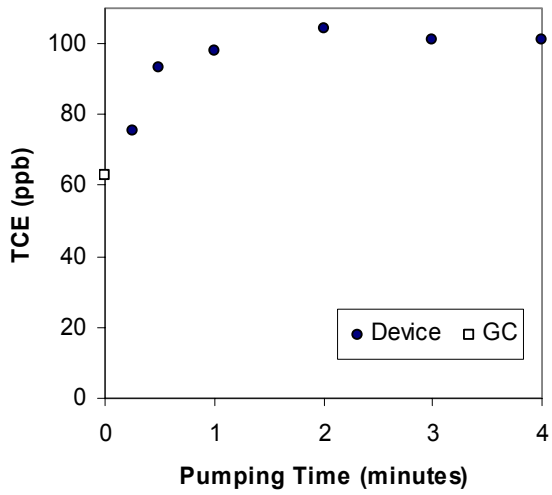


Figure 4. Measurement results at 62.6 ppb TCE (GC analysis).

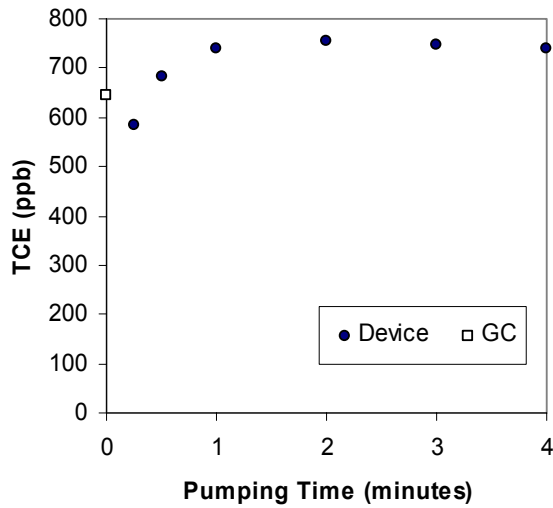


Figure 5. Measurement results at 643 ppb TCE (GC analysis).

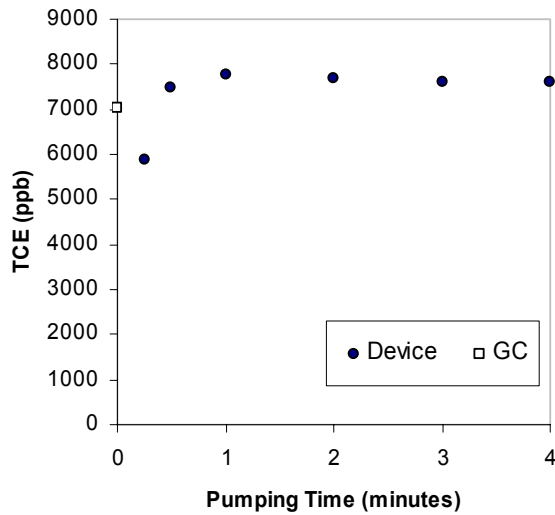


Figure 6. Measurement results at 7020 ppb TCE (GC analysis).

Table 1. Average and standard deviation results for device, GC result and ratios of device result over GC result.

Device (ppb)	GC method (ppb)	Device/GC
21.9±0.8	11.1	1.97
102±2	62.6	1.63
747±8	643	1.16
7640±50	7020	1.09

Field Results

The device was field tested in five groundwater monitoring wells known to be in an aquifer contaminated with TCE. In each monitoring well, the device was tested at least twice. These results are shown in Table 2. With the exception of the lowest concentration wells (27C and 27), the device results and the GC results compare favorably. For example, the average difference between the device result and the GC result for wells 37C, 46C and 39C is 7%.

Table 2. Device versus GC results for a number of TCE contaminated wells at the Savannah River Site.

Well ID	Sample #	Sample Date	Microsparger Result ppb	GC Result ppb
37C	1	4/12/05	66.4	56.7
37C	2	4/12/05	54.6	56.7
37C	3	4/13/05	62.6	46.6
46C	1	4/13/05	63.8	60.7
46C	2	4/13/05	62.4	60.7
39C	1	4/13/05	20.6	21.2
39C	2	4/13/05	20.2	21.2
27C	1	4/13/05	11.0	4.5
27C	2	4/13/05	11.2	4.5
27	1	4/13/05	11.0	1.8
27	2	4/13/05	11.7	1.8

Discussion

Results from both laboratory and field testing indicate that the device produces reasonably accurate and reproducible results over relative broad range of TCE concentrations. At low TCE concentrations (~ 10 ppb and less), the results are biased high. As a result, confirmatory analysis by conventional laboratory GC methods is recommended for low concentrations (those near the compliance standard of 5 ppb).

Benefits of this new device over the conventional method of sample collection in the field followed by laboratory analysis are that it generates no waste, and produces rapid results in real time. Additional cost benefits are expected because samples do not have to be collected for shipment to an offsite laboratory. A disadvantage of this new method is that when paired with the photo-acoustic gas analyzer a high bias is observed for TCE measurements in groundwater. However, this is not considered a problem with the device itself.

Conclusions

A device was developed that is capable of measuring groundwater concentrations of volatile compounds in the field in real-time. The device is designed to equilibrate volatile compounds dissolved in groundwater with a volume of air in the device for measurement with a gas analyzer. Once the equilibrium vapor concentration is measured, the dissolved concentration of the volatile compound is calculated using Henry's Law. This study indicates that the device produces rapid, reasonably accurate, and reproducible results over a broad range of TCE concentrations.

This new approach to field measurement of volatile compounds demonstrates significant advantages over the standard the method of collecting samples in the field and shipping offsite for laboratory analysis. The results presented indicate that this new method for measuring volatile compounds in groundwater is potentially very useful for monitoring the progress of groundwater remediation programs (including those that rely on natural attenuation either wholly or in conjunction with other remediation options)

when large numbers of well measurements are required in real time. As concentrations approach 20 ppb and less, confirmatory GC analyses should be conducted.

Acknowledgement

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