Development and Testing of a Field Screening Method Based on Bubbling Extraction and Photoionization Detection for Measurement of Benzene and Total VOCs

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Abstract

A field screening method was developed for rapid measurement of benzene and gasoline range total petroleum hydrocarbons (TPHg) concentrations in groundwater. The method is based on collecting photoionization detector (PID) measurements from vapor samples. The vapor samples are collected by bubbling air through groundwater samples (air sparging) with a constant volume, temperature and sparging rate. The level of accuracy, sensitivity, precision, and statistical significance of the estimated concentrations, derived from the screening method, are comparable to conventional laboratory analytical results at concentrations equal to or greater than 150 µg/L for benzene and greater than 50 µg/L for TPhg. The method’s concentration estimations can assist in making real-time decisions regarding location of dissolved plumes and light nonaqueous phase liquid (LNAPL) source zones at many fuel release sites. The screening method was tested in the laboratory and in the field with 208 and 107 samples, respectively. The study concludes that the screening method can be used as a tool to aid in completing a site conceptual model as well as analyzing groundwater from monitoring wells.

Introduction

A well-developed site conceptual model (SCM) provides enough information for evaluation of exposure pathways and spatial distribution of potential contaminants of concern. The SCM requires site assessment activities that are often associated with extensive analytical laboratory testing of soil and groundwater. Laboratory testing can be time-consuming and costly, especially if dissolved plume delineation efforts include repeated mobilizations to characterize the full extent of the plume. Furthermore, chemicals released in the subsurface environment tend to have heterogeneous spatial distributions associated with the volume of the release, the chemical properties, site stratigraphy and groundwater movement. The United States Environmental Protection Agency (USEPA) recognizes this challenge and has promoted the use of expedited site assessments (USEPA 1997), the triad approach (ITRC 2007), demonstrations of method applicability (DMA; USEPA 2008), high-resolution site characterization (USEPA 2013) among other initiatives; as ways of streamlining site assessment activities. The triad approach involves three elements: systematic project planning, dynamic work plan strategies, and real-time measurement technologies (ITRC 2007). Development of innovative field screening tools for site assessment falls into the real-time measurement technology element and also influences the dynamic work element. USEPA also recognizes that new technologies and methods need to be evaluated promptly to quickly ascertain whether the new technique is suitable for the site in terms of data quality objectives, cost and effectiveness (USEPA 2008).

The increase in the use of innovative field screening tools for real-time assessment of chemical contamination for rapid vertical and horizontal source zone or dissolved plume delineation has led to less reliance on laboratory testing as evidenced by the use of direct-push tools to characterize the subsurface (membrane interface probe [MIP], laser-induced fluorescence, and others). Field screening tools bypass the wait for traditional laboratory analytical results in favor of nearly real-time results that facilitate quick decisions, for example, on monitoring well placement or areas requiring further characterization. Semi-quantitative methods, as defined by USEPA, provide order of magnitude estimations of contamination (e.g., 10s, 100s and 1000s of micrograms per liter [µg/L]); semi-quantitative methods can be used for defining the location of known types of contamination (USEPA 1997). MIP is an example of a semi-quantitative
A direct-push tool that has successfully been used in the field to measure relative concentrations of volatile organic compounds (VOCs) in the subsurface (USEPA 1997).

Accuracy, sensitivity, and precision of these semi-quantitative methods are typically lower compared to certified analytical laboratory measurements but, in many cases, are sufficient to make real-time decisions in the field. MIP can be relatively expensive and difficult to obtain in many parts of the world where availability of this specialized equipment is limited. Development of screening tools that are cost-effective, easy to use, and deployable anywhere in the world is needed for site characterization in remote areas; where environmental impacts exist but the available technologies are limited. USEPA’s DMA (USEPA 2008) provides a framework to (1) compare a field-based method with a more established laboratory method, and (2) test whether a particular tool will work on a specific site.

The main focus of this study is a comparison of a new field-based groundwater analytical method with a more established laboratory method and to demonstrate the potential applicability of the new method to identify light nonaqueous phase liquid (LNAPL) source and dissolved plume areas. This aligns with the first component of the DMA. The second part of the DMA (evaluate applicability of a new method for a particular site) is a necessary step that will need to be followed if the method described herein is being considered for a particular site.

Field screening tools such as photoionization detector (PID) and flame ionization detector (FID) instruments, detect VOCs in air. At fuel release sites, PIDs are used to measure volatile aromatic hydrocarbons in the low carbon range, such as benzene. These aromatic hydrocarbons have a high ionization potential derived from their carbon number (between 6 and 12), functional groups, and bonding type (Langhorst 1981). A PID response is typically recorded as a concentration in parts per million by volume (ppmv). The reading is commonly referred to as “VOC concentration as hexane or isobutylene,” depending on the instrument calibration gas. In site assessment activities, a soil headspace VOC concentration ranging from more than 10 ppmv (weathered diesel) to more than 1000 ppmv (recent gasoline releases) is considered an LNAPL source zone (Alaska DEC 2011; CA SWRCB 2012).

Newer PID instruments (e.g., UltraRae PID, RAE Systems Inc.) can provide targeted quantification for certain VOCs when coupled with a pre-treatment step, usually a carbon filter; that allows a certain degree of specification of only a specific VOC of interest (e.g., benzene) to reach the detector. FID instruments use a hydrogen flame to combust organic compounds hence FIDs cannot only detect aromatics but any compound that has a carbon-hydrogen bond, such as aliphatic compounds found in fuels.

PIDs and FIDs are adequate for detecting highly contaminated soil (i.e., source zones) from fuel releases. However, such instruments are not designed to measure dissolved concentrations in groundwater unless additional steps are undertaken to collect an air sample. For example, Adamson et al. (2009) developed protocols for using field PID instruments to assess VOC concentrations in groundwater by measuring headspace concentrations in monitoring wells (Adamson et al. 2009, 2012). The approach described by Adamson et al. (2012) is based on the hypothesis that portable vapor-phase monitoring instruments can be used to accurately determine VOC concentrations in water presumed to be under equilibrium conditions. This approach focused on collecting split vapor samples in monitoring wells at different headspace locations and measuring the vapor concentrations using a portable gas chromatography and a ppbRAE 3000 PID. Additionally, Adamson et al. (2012) tested passive vapor diffusion and passive diffusion bag samplers in monitoring wells.

As opposed to Adamson’s approach for sampling headspace of monitoring wells, this paper describes the development and evaluation of a field screening analytical method that involves active air bubbling and stripping of volatiles from the water sample; which main purpose is the rapid onsite analysis of groundwater samples derived from site assessment activities. Another use of the method could be the analysis of VOCs collected from groundwater monitoring wells during routine groundwater sampling events.

Air sampling methods that are based on equilibrium partitioning using vapor-filled polyethylene bags and airtight syringes have been used to demonstrate that an air sample can yield a representative sample of groundwater conditions for organic compounds and dissolved gases (Vroblesky et al. 1996; Vroblesky and Campbell 2001; Divine and McCray 2004; Spalding and Watson 2006, 2008; McLeish et al. 2007). These sampling approaches require equilibration time after sampler deployment to allow groundwater to reach: (1) chemical equilibrium and (2) equilibrium from environmental disturbances caused by sampler introduction. Equilibration time is dependent on sampler design and temperature. In contrast, our method is analytical, and relies on the mechanism of purge and trap for sample preparation after sample collection. Sample collection does not require downhole equilibration time. In our study we developed and tested the method for benzene and total petroleum hydrocarbons (TPHs); whereas vapor-filled polyethylene bags and airtight syringes have been tested and developed for a variety of chemical compounds. Another difference is that our field screening analytical method does not require the sample to be analyzed in an analytical laboratory.

Portable field devices have been developed to analyze VOCs for site assessment and groundwater monitoring (Frog-4000 GC-PID [Gas Chromatography-PID] by Defiant Technologies Albuquerque, New Mexico, Tridion-9 GC-MS [GC-Mass Spectrometry] by Torion Technologies Inc. American Fork, Utah and others). The main differences between our method and those devices are: (1) the portable field devices use a gas chromatography column to separate the target analytes and our method uses a carbon filter to provide limited speciation of benzene as evidenced by our experimental results, and (2) the portable field devices integrate all the components of the device in one instrument, whereas our method relies on the use of several “off the shelf” components that were selected because they are already widely and effectively used in the field in many parts of the world. Selection of
commonly used components allows for ease of use from an availability, field personnel training and cost effectiveness point of view. A similar purge and trap method using a high-efficiency UV cell as a detector has been tested successfully for analysis of benzene in wastewater applications (Camou et al. 2008).

Materials and Methods

The screening analytical method described in this study includes a purge and trap step analogous to USEPA SW846 Method 5030 for vapor collection. USEPA Method 5030 uses an inert gas that it is bubbled through an aqueous sample to allow an efficient transfer of volatile components from the aqueous phase to the vapor phase. The method described herein involves bubbling ambient air through a groundwater sample and collecting the gas that has passed through the water sample in a sampling bag for analysis with a PID. The ambient air is monitored to avoid a bias associated with the potential introduction of ambient VOCs into the vapor sample. Although an inert gas could be used for sparging rather than air, air was chosen to simplify the field application of the method.

Evaluation of the screening method was conducted by:

1. Generating a response curve from the PID readings (obtained from vapor samples collected by using the screening method in the laboratory) and the reference concentrations (i.e., conventional analytical test results of the associated split water samples).
2. Using the response curve, generated from the laboratory experiments, to calculate an estimated water concentration from PID readings obtained from vapor samples collected in the field from groundwater using the field screening method.
3. The estimated concentrations were evaluated against their associated split samples tested using a conventional analytical laboratory (i.e., reference concentrations) in terms of accuracy, sensitivity, precision and statistical significance.

Analytical Equipment

The following detectors were considered for this study:

1. UltraRae PID (RAE Systems Inc., San Jose, California) equipped with a 9.8 eV photoionization lamp and a benzene RAE-sep™ tube for benzene selectivity.
2. MiniRae 3000 PID (RAE Systems Inc.) equipped with a 10.6 eV photoionization lamp.
3. TVA-1000B Flame ionization Detector (Thermo Scientific, Waltham, Massachusetts).
4. MicroFID FID (Photovac Inc., Waltham, Massachusetts), and

Selection of the devices was based on their ease of use, familiarity for field personnel, and relative low cost of rental or purchase. During the initial experimental phase, it became apparent the TVA-1000B FID, MicroFID FID and the colorimetric gas detection tubes showed a weaker correlation with the reference results (i.e., aqueous concentrations reported by analytical laboratory). The colorimetric gas detection tubes also showed lower sensitivity (i.e., high detection limits). Therefore the UltraRae and MiniRae 3000 PIDs were the only devices retained for further evaluation. The experimental results from the UltraRae and MiniRae 3000 PIDs are reported in this paper.

Sample Preparation Equipment and Supplies

The following water and vapor sampling equipment and supplies were selected for this study: 10 mL plastic slip tip syringes with no needle (California Veterinary Supply, Pahrump, Nevada), laboratory 40 mL volatile organic analysis (VOA) vials, rotameter (Equipco, item ROTOMTRIT0300 rotometer size #11; Concord, California), PortaVac portable vacuum pump with vacuum chamber (Equipco), 1/8-inch silicone semi-clear white tubing (McMaster-Carr Santa Fe Springs, California, part no. 51135K16), block heater equipped with an analog controller (VWR Lab Shop Radnor, Pennsylvania, part no. 12621-104), position block (VWR Lab Shop, part no. 12621-138), 1 L Tedlar™ bags, Nylon 1/4-inch 2-way FNPT ball valves (United States Plastic Corporation Lima, Ohio, part no. 22284), adapter with 1/4-inch NPT thread and 1/8-inch barb (Eldon James Denver, Colorado, part no. A4-2BN), humidity filtering II tube for the MiniRAE 3000 and UltraRAE PIDs (RAE Systems Inc.; part no 025-2002-010), humidity filter adapter (RAE Systems Inc.; part no 025-2002-010), and digital hygrometer (Dwyer 485, Dwyer Instruments Inc., Michigan City, Indiana)

Additionally, a special cap with a sampling manifold was manufactured for the 40 mL VOA vials (DV Manufacturing Inc., Livermore, California). The modified cap consists of a stainless steel disk and rubber gasket in place of the VOA’s septum. Welded to the disk are two 1/16-inch inner diameter stainless steel tubes. One of the stainless tubes extends to the bottom of the vial (“air inlet”), and the other ends at the top of the vial (“air outlet”).

Sample Preparation Procedure

The following steps were taken to prepare the water samples during the laboratory and field experiments prior to the analysis of the vapor sample with the PID:

A water sample was collected by completely filling a 40-mL VOA vial allowing the vial to form a meniscus on the water surface. The VOA vial was capped using the special cap with the modified sampling manifold. Ball valves and Teflon tubing were attached to the manifold’s air inlet and outlet tubing (i.e., long and short tubing, respectively) immediately after sample collection and were turned to the closed position (Figure 1, Step 1). A volume of 10 mL of water was extracted from the VOA vial using a plastic syringe connected to the silicone tubing attached to the manifold’s air inlet and turning the ball valve to the open position (Figure 1, Step 2). Ferrules were used to ensure an air-tight seal between the manifold and the ball valves. The VOA vial, with the tubing and valves attached setup, was then placed in a pre-warmed heater block set at 45 °C (Figure 1, Step 3). The VOA vial was heated for approximately 35 min (except for 3 field samples with heating times closer to 100 min due to slow field processing times for the samples), after which the vial was removed.
from the heater. Next, the air inlet tubing was connected to the rotameter and the air outlet was connected to the inlet port of a vacuum chamber. A Tedlar bag was placed in the vacuum chamber with its valve half open (Figure 1, Step 4). The outlet from the vacuum chamber was connected to the PortaVac vacuum pump via tubing (Figure 1, Step 4).

The water samples were sparged by turning the VOA vial’s inlet and outlet valves to the open position, and turning the vacuum pump on. The air sparged through the water sample was collected in the Tedlar bag within the vacuum chamber. The pump and rotameter flow rates were adjusted by slightly opening the manifold’s air inlet valve until the pump gauge reading was between 7 and 9 inches of mercury (Hg) and air flow measured in the rotameter was between 170 and 200 milliliters per minute (mL/min). During the vacuum pump operation, bubbles began to form in the VOA vial water (Figure 1, Step 4), and the Tedlar bag began to fill up with vapor containing the stripped VOCs. The optimal time to efficiently fill the Tedlar bag was after 3 to 5 min of sparging. When the bag was approximately 90% full, the valve was closed, the pump was turned off, and the rotameter was returned to the closed position. The Tedlar bag was removed from the vacuum chamber and its valve closed immediately.

After sparging, the contents of the Tedlar bag were analyzed with each PID. The Tedlar bag was immediately attached to the MiniRAE 3000 PID device that was equipped with a humidity filter (Figure 1, Step 5). Measurement with the UltraRAE device followed once measurement with the MiniRAE 3000 was complete. The bag valve was closed between readings with the different devices to preserve as much vapor as possible within the bag (PID detectors consume some of the vapors during the measuring step). Humidity readings were collected from both PIDs to monitor humidity accumulation in the sample bag during readings with the digital hygrometer.

Each water sample was replicated (i.e., split) during sample collection to allow analysis by a certified analytical laboratory for benzene and TPHg (EPA Methods 8260 and 8015b, respectively); the analytical laboratory results were used as the reference values for the evaluation of the method (see Results section). The method detection limits (MDLs) for benzene and TPHg were 0.0005 mg/L and 0.050 mg/L for the laboratory methods (standard commercial laboratory MDLs), respectively.

**Sampling and Analysis Program**

Testing and refinement of the field screening method, with associated laboratory analyses, was conducted over the course of approximately 2 years. A total of 315 water samples were analyzed with the field screening method. Laboratory analyses were conducted during the first year at ALS Laboratory Group (Ontario, Canada), and during the second year at Kiff Analytical (Davis, California) for a total of 208 water samples. The laboratory experiments included preparing between 6 and 8 split spiked samples for each target concentration of benzene and TPHg. The target range was from <0.50 to 7,000 µg/L for benzene and <50 to 49,000 µg/L for TPHg. This is a relevant range to determine dissolved plumes and aqueous concentrations representative of LNAPL source zones in the field within the published ranges dictated by equilibrium dissolution models for petroleum hydrocarbons (Rixey 1996; Garg and Rixey 1999). In the presence of residual LNAPL, benzene concentrations in water will be close to the benzene mole fraction in the LNAPL multiplied by the component’s effective water solubility, following Raoults’s Law. Actual measured range (using EPA Methods 8260b for benzene or 8015b for TPHg, respectively) was <0.50 µg/L to 701 µg/L for benzene and <50 µg/L to 6,118 µg/L for TPHg. The laboratory experiments provided an assessment of the screening method under

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**Figure 1. Sample preparation procedure.**
highly controlled conditions with respect to sparging rate, bubbling time, heating time, and temperature; and allowed the optimization of VOC transfer rates for vapor sample collection. Benzene and TPHg standards were prepared for the laboratory experiments, thus avoiding the use of methanol due to PID sensitivity to this compound (Camou et al. 2008). Benzene and gasoline were diluted in water without any co-solvent, to avoid co-solvency interference with the PID measurements, and using sonication to reach the desired dissolved concentration for the highest target concentration spikes. Spike concentrations were validated by testing a replicate for each target concentration using EPA Methods 8260b for benzene and 8015b for TPHg.

Field experiments with the screening method were conducted at four fuel sites (2 fuel terminals and 2 service stations) in California. Field experiments included testing between 3 and 6 sample replicates collected from monitoring wells that contained a mix of petroleum hydrocarbon compounds (benzene, toluene, ethyl benzene and xylenes [BTEX], TPHg and TPHd). Sampling monitoring wells, rather than collection of grab groundwater samples during assessment activities was selected as the preferred method for field testing due to the existing historical monitoring data for the sites that allowed for temporal data validation. A total of 107 groundwater samples were analyzed. Sampling of monitoring wells for the field experiments included purging three well casing volumes prior to collection of groundwater samples with disposable bailers. This particular sampling method was used in order to remain consistent with current methods of sampling conducted at the sites. Groundwater was transferred from the bailer into 40 mL VOA vials with no headspace and capped with the modified sampling manifold as previously described. One of each of the groundwater replicate samples was sent to Lancaster Laboratories (Lancaster, Pennsylvania) for standard laboratory analyses (EPA Methods 8260b for benzene or 8015b for TPHg). The laboratory analytical result was considered the reference value for method evaluation. Laboratory results for the field samples ranged from <50 µg/L to 7,000 µg/L for benzene and <50 µg/L to 49,000 µg/L for TPHg.

Quality Assurance and Quality Control

Quality assurance and quality control procedures were followed during the laboratory and field experiments. The PIDs were initially calibrated following the manufacturer’s recommended calibration procedure. During the laboratory experiments, a method blank was prepared for each 10 samples; and one spike sample was prepared for each target concentration. A blank trip sample was prepared for every 10 samples collected during the field experiments. Analyses at the commercial laboratories followed laboratory compliance quality control procedures (e.g., blanks, matrix spikes, matrix spike duplicates, laboratory control samples, and laboratory control duplicate samples).

Ambient air was monitored for background VOCs with the PIDs. Ambient air was also monitored for relative humidity and temperature with the digital hygrometer during the laboratory and the field experiments. Leak testing of the vapor sampling train was performed by running calibration gas (isobutylene) through the sampling equipment and taking PID measurements, with both PID detectors, before the start of the experiments.

Results

Use of Humidity Filters for PIDs

During the early laboratory experiments it was identified that humidity in the vapor stream impacted PID measurements of organic compounds. Therefore, 50 vapor samples were measured with the MiniRAE 3000 PID device with and without a humidity filter attached. Nondetect results were omitted. The results show that PID readings are consistently higher without a humidity filter (Figure 2). The mean PID readings with and without the humidity filter are: 11.42 ppmv and 15.80 ppmv, respectively. On average, data generated without the humidity filter was 38% higher than the data generated with the humidity filter. These results indicate that humidity can impart a positive bias to the vapor concentrations measured with a PID. The PID manufacturer recognizes the potential for bias associated with humidity by reporting that humidity in the air stream can reduce the signal; and water condensation near the sensor can result in false positives (RAE Systems 2010). Humidity bias underscores the importance of using the appropriate humidity filter (which is different from the widely used dust filter) when operating PID instruments. All the screening method results described in this study were conducted using humidity filters.

Screening Method

The evaluation followed the guidelines of USEPA’s DMA (2008) and California Department of Toxic Substances Control (DTSC 1998), and included the following evaluation criteria:

1. Linear regression applied to PID readings and reference values—Linear regression was used to evaluate correlation, slope and y-intercept (USEPA 2008). PID readings vs. reference value response curves were generated and used to calculate the method’s estimated dissolved concentration values.

2. Accuracy and sensitivity—Accuracy is defined as the agreement between the estimated values (predicted from

![Figure 2. MiniRAE 3000 PID measurements with and without a humidity filter.](image)
the response curves) and the reference value. Accuracy is a measure of consistent bias between the estimated and reference values (DTSC 1998). Our data quality objective for accuracy was achieving percent recoveries: between 70% and 130%; consistent with DTSC’s highest data quality levels. Sensitivity is defined as the lowest concentration at which accuracy and precision goals can be achieved (Newell et al. 2013).

3. Precision—Defined as the agreement between results from the method’s sample replicates. Precision is a measure of random error (DTSC 1998). Our data quality objective for precision was achieving Relative Standard Deviation (RSD) values below 40% which is DTSC’s acceptable limit for analytical laboratory tests. Other states use different acceptable RSD values such as 20% in Arizona for USEPA method 8015 (ADHS 1998), 25% in New Jersey for extractable petroleum hydrocarbons (NJDEP 2010), and 30% to 35% for ITRC’s Incremental Sampling Methodology (ITRC 2012).

4. Statistical significance—To determine whether the difference between the method’s estimated values and the reference values are significantly different with 95% confidence (i.e., 0.05 significance level) using nonparametric and parametric statistical methods (USEPA 2008).

1—Linear Regression

The first step of the evaluation was to apply linear regression and prepare PID response curves using the results of the laboratory experiments: (1) PID readings (ppmv) and (2) associated reference value (analytical laboratory result in μg/L from replicate sample). The linear equations, describing the response curves, were used to estimate dissolved concentrations from the PID readings from the vapor samples using the screening method taken during the field experiments. Nondetect values were removed from the evaluation. The linear regression method expects the input data to have a similar level of variability across the full range of concentrations and follow approximately a normal distribution. Transformations of the data (log or square-root, for example) can be used to meet these assumptions of the data. For this analysis, linear regression was applied to the square-root of benzene concentrations to predict the square-root of PID readings. Plots of the residuals from the fitted curve confirmed that the method assumptions were met.

Figure 3 shows the linear regression graph with the associated fitted equation (i.e., response curve). The response curves have determination coefficients ($R^2$) of 99.2% and 98.4% for the UltraRAE (used for benzene estimation) and MiniRAE 3000 (used for TPhg estimation) PID readings, respectively. Both fitted equations have slopes significantly different from zero with P-values less than 0.0001. The intercept of the fitted response curve represents the average PID reading when the reference value is zero. The intercept values of the response curves are −0.009 and −0.046 for the UltraRAE and MiniRae 3000 PIDs, respectively. However, the intercept values are statistically insignificant (P-values higher than 0.05) and were removed from the response curves.

Figure 4 shows the reference and estimated benzene and TPhg concentrations; the estimated values were calculated using the response curves of Figure 3 without the intercept since they were not statistically significant.

2—Accuracy and Sensitivity

A test of accuracy was conducted using data from the field experiments. Percent recovery between the estimated benzene or TPhg dissolved concentration and the reference value was calculated by dividing the average of the estimated concentrations from replicate samples by the reference concentration value. Nondetect values were removed from the
Figure 4. Reference and estimated benzene and TPHg values based on Figure 3’s response curves and the field measurements.

| Table 1 |
| Percent Recoveries to Quantify Accuracy of the PID Methods |
| Instrument (constituents of interest and number of field samples with detections) | Percent Recovery Between Average Estimated Dissolved Concentration and Reference Value |
| | Concentration Range (µg/L) | Average (%) | Maximum (%) | Minimum (%) | Standard Deviation (%) |
| UltraRAE (benzene, 28) | <0.50–7,000 | 1357 | 12,674 | 36 | 36 |
| | Limited dataset: <150–7,000 | 101 | 137 | 62 | 0.32 |
| MiniRAE 3000 (TPHg, 61) | <50–49,000 | 106 | 590 | 25 | 1.3 |
| | Limited dataset: <150–49,000 | 106 | 590 | 25 | 1.5 |

evaluation. Percent recovery results are shown on Table 1. On average, percent recoveries improved (i.e., approached 100%) for benzene concentrations above 150 µg/L.

In terms of sensitivity, both PID devices measure concentrations as low as 0.1 ppmv (manufacturer’s detection limits specifications and field observations). In the case of the UltraRAE PID, 0.1 ppmv allows for detection of benzene as low as 0.7 µg/L under equilibrium conditions and a temperature of 45 °C (i.e., the method’s extraction temperature).

Table 1 shows percent recovery was poor in the lower concentration range for the estimation of benzene. An analysis of chemical data for each sample with poor percent recoveries indicates that samples with TPHg-benzene ratios higher than 100 have high percent recoveries for the estimation of benzene. This result indicates the benzene estimation method may be more accurate for sites with groundwater chemistry that shows TPHg-benzene ratios lower than 100. Percent recovery for the estimation of TPHg was 106% for the entire concentration range; indicating a level of accuracy comparable to an analytical laboratory result.

Additionally, the performance of the method was evaluated by determining the accuracy of the fitted regression model to predict the reference concentrations of the laboratory experiments. Validation subsets consisting of 20% of the total measured samples (i.e., subsets of 21 samples for benzene and 10 samples for TPHg) were randomly selected 100 times (i.e., 100 iterations). The reference concentration for each randomly selected data point was predicted from the response curve (i.e., regression model fit) to the remaining data. The percent recovery of the random samples (for each of the 100 iterations) provides an objective assessment of the accuracy of the method. The results are included in Table 2.

California DTSC defines acceptable levels of accuracy for analytical methods at the highest data quality levels to have percent recoveries between 70% and 130%. On the basis of the iterative analysis of the laboratory experiment data, both screening methods accurately predicted the reference concentrations.

3—Precision

Precision of each method was calculated as the relative standard deviation RSD for the replicate estimated concentrations from the laboratory and the field experiments. RSD is defined as the standard deviation of the replicate estimated concentrations divided by the average replicate
estimated concentration. Replicate estimated concentrations were generated by running the entire screening method on each replicate. The average number of replicates was 5 and 2 for the laboratory and field experiments, respectively. Nondetect values were removed from the evaluation. The results are presented in Table 3. The UltraRAE PID average RSD values were 7% (laboratory data) and 24% (field data) when considering the entire range of benzene concentrations (<0.50 to 7,770 μg/L). The UltraRAE PID RSD values decreased (i.e., improved) when the concentration range was limited to 150 μg/L or higher. The RSD for the higher benzene concentrations was 5% (laboratory data) and 18% (field data). The RSD for MiniRAE PID averaged 12% for laboratory data and 21% for field data when considering the whole range of concentrations (<50 to 49,000 μg/L for TPHg). The RSD values for the MiniRAE decreased (i.e., improved) for the laboratory experiments when the concentration range was limited to 150 μg/L or higher to an average RSD of 8%. The RSD values increased slightly for the field experiments when the concentration range was limited to 150 μg/L or higher for TPHg (from 21% to 23%). The precision evaluation results indicate both PIDs have RSD values below 40% which is the acceptable limit for analytical laboratory tests (DTSC 1998).

### Discussion

Based on our knowledge, this is the first comprehensive study to develop and test a PID-based field method to measure groundwater concentrations of benzene and TPHg via bubbling extraction. Although this approach was developed mainly for groundwater samples collected during site assessment; the method can be used for analysis of groundwater samples collected during routine groundwater monitoring. The novelty of the approach lies in the fact that the field analytical method uses sampling and testing field equipment that is easy to use, familiar to field personnel

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### Table 2

Percent Recovery of the Validation Subsets to Determine Accuracy of Fitted Regression Model

<table>
<thead>
<tr>
<th>Instrument (constituents of interest and number of laboratory samples)</th>
<th>Percent Recovery of the Validation Random Subsets (100 iterations)</th>
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<tr>
<td></td>
<td>Concentration Range (μg/L)</td>
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<tr>
<td>UltraRAE (benzene, 21)</td>
<td>&lt;0.50–7,000</td>
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<td></td>
<td>Limited dataset: &lt;150–7,000</td>
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<tr>
<td>MiniRAE 3000 (TPHg, 10)</td>
<td>&lt;50–49,000</td>
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<td></td>
<td>Limited dataset: &lt;150–49,000</td>
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</tbody>
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### Table 3

RSD to Quantify the Precision the Method

<table>
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<tr>
<th>PID Instrument (constituent of interest)</th>
<th>Type of Experiment (number of samples with detections)</th>
<th>Concentration Range (μg/L)</th>
<th>RSD (%) of PID Readings of Split Samples</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Average (%)</td>
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<tr>
<td>UltraRAE (benzene)</td>
<td>Laboratory (107)</td>
<td>&lt;0.50–7,770</td>
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<td></td>
<td></td>
<td>150–7,770</td>
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<td></td>
<td>Field (28)</td>
<td>&lt;0.50–7,000</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>150–7,000</td>
<td>18</td>
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<tr>
<td>MiniRAE 3000 (TPHg)</td>
<td>Laboratory (50)</td>
<td>&lt;50–6,118</td>
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and has a relatively low cost of rental or purchase. Unlike other analytical methods, the method allows for a relatively short analysis time in the field, eliminating the need to ship samples to a laboratory. The method meets the accuracy and precision DQOs as well as the method’s detection limits (150 µg/L benzene and 50 µg/L TPHg). The method has the sensitivity needed to evaluate LNAPL source zones and dissolved plumes to determine if additional investigation is needed. Benzene and TPHg concentrations of water in the vicinity of LNAPL source areas vary by the constituents’ mole fraction and effective solubility. However in general, the detection limits of the method allow for determination of source areas.

The first part of the study provided quantification on the positive bias that humidity imparts on PID measurements. The data generated without the humidity filter was on average 38% higher than the dataset generated with the use of a humidity filter. High humidity tends to decrease the detector response because the water vapor can absorb and diffuse the light that is trying to ionize the compounds that are passing under the ionization lamp; thus decreasing the number of compounds being ionized. However, when water condenses on the detector surface it can cause communication between the sensing and bias the electrodes in the detector resulting in an increased response. The detector measures electrical current and; if there is a link between the two electrodes the response will increase as seen in the experimental results. This result underlies the importance of using the appropriate humidity filter when operating PID instruments.

The second part of the study was to develop the screening method in the laboratory and test it in the field to measure dissolved benzene concentrations as equal to or greater than 150 µg/L and TPHg concentrations greater than 50 µg/L in groundwater samples. The results of the method evaluation indicate that there is good agreement between the PID readings and the reference values (i.e., analytical laboratory concentrations) with determination coefficients ($R^2$) of 99% or higher. The MDLs were set by the accuracy and precision DQOs as well as an evaluation of sensitivity.

However, accuracy seemed to be the central DQO governing the MDL for benzene due to the low recoveries found below 150 µg/L for benzene. Accuracy, measured as percent recovery, of the method for estimating benzene is markedly improved (percent recovery 101% on average) if the detection limit is increased to 150 µg/L; otherwise the percent recovery is 1357% (on average). High percent recoveries for benzene estimation are associated with TPHg-benzene ratios above 100 in the sample, indicating the water has a high aromatic and aliphatic component relative to benzene. Low accuracy in benzene measurements for samples with a relatively high TPHg component may be explained by the low separation capability of the carbon filter in the PID detector for other aromatic compounds present in the sample which pass through the carbon filter and are detected by the PID.

This finding underscores the importance of the field calibration step (i.e., generating site-specific response curves) of the method to understand the chemical composition of the TPHg mixture.

TPHg percent recovery was 98% indicating a level of accuracy comparable to an analytical laboratory result at concentrations as low as 50 µg/L. California DTSC defines acceptable levels of accuracy for analytical methods at the highest data quality levels to have percent recoveries between 70% and 130%. In terms of sensitivity, both PID devices measure concentrations as low as 0.1 ppmv based on the manufacturer’s detection limits specifications and field observations. In the case of the UltraRAE PID, 0.1 ppmv allows for detection of benzene as low as 0.7 µg/L under equilibrium conditions for a temperature of 45 °C, which avoids the risk of false negatives of the method. However we do not recommend using the method to detect concentrations lower than 150 µg/L for benzene due to low accuracy.

Precision or reproducibility, measured as RSD (DTSC 1998), indicates RSD values based on estimated benzene and TPHg values are less than 40% which is comparable to analytical laboratory results. The statistical evaluation of the differences between the estimated and the reference concentrations indicated no bias in benzene estimation. The method may impart a limited negative bias for estimation of TPHg concentrations as shown by the nonparametric Wilcoxon signed-rank test results. This could be explained by the inherent differences between EPA Method 8015 for TPHg and the field PID measurement. EPA Method 8015 for TPHg uses an FID as the detector device which measures all compounds with a carbon-hydrogen bond whereas the PID detector measures compounds with a relative ionization potential (i.e., aromatics). Hence the PID-based method has a slight negative bias compared to EPA Method 8015 for TPHg if the TPHg mixture contains a lower proportion of aromatic compounds than aliphatic compounds due to the effects of advanced biodegradation in LNAPL plumes. Negative bias for measuring TPHg is not expected for LNAPL plumes in the early stages of development such as those found during initial site assessment after a recent fuel release.

The study concludes that the screening method can be used to help support rapid quality decisions made in the field to assist in evaluating locations of LNAPL source areas and dissolved plume areas. The detection limits of the method (i.e., 150 µg/L for benzene and 50 µg/L for TPHg) are sufficiently low to differentiate LNAPL source zones and dissolved plumes. A field calibration, such as one recommended by DMA (USEPA 2008), is suggested to ensure the results are calibrated to the site-specific chemical composition of the groundwater samples.

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