Ground Water Monitoring&Remediation

A New Screening Method for Methane in Soil Gas Using Existing Groundwater Monitoring Wells

by Kenneth P. Jewell and John T. Wilson

Abstract

Methane in soil gas may have undesirable consequences. The soil gas may be able to form a flammable mixture with air and present an explosion hazard. Aerobic biodegradation of the methane in soil gas may consume oxygen that would otherwise be available for biodegradation of gasoline hydrocarbons. The consumption of oxygen by methane may increase the chance of completing a vapor intrusion pathway for benzene. A protocol was developed to sample soil gas from conventional groundwater monitoring wells that had some portion of their screen in the vadose zone. This protocol was applied at 12 gasoline stations in Oklahoma. The soil gas as collected from the monitoring wells was not flammable, due to low concentrations of oxygen. However, soil gas at five of the 12 sites could form flammable mixtures in air. To allow a simple comparison of the possible effect of methane on vapor intrusion of benzene, characteristics of the sites were matched to computer simulations published by others. At three of 11 sites, the methane in the soil gas might cause unacceptable concentrations of benzene in a hypothetical receptor. Ethanol is readily fermented to methane. The increased use of ethanol in gasoline raises concerns about methane at gasoline spill sites. At five sites with high concentrations of methane, the concentration of ^{14}C in methane was used to determine the source of the methane. At four sites, the majority of the methane was produced from anaerobic biodegradation of petroleum, and not from ethanol or another biofuel. At three sites, the maximum possible contribution of methane from ethanol or another biofuel was 5.1% of total methane. At a fourth site, the maximum contribution of ethanol or another biofuel to methane was 31% of the total methane. At the fifth site, the methane came from a leak of natural gas.

Introduction

For years, it has been recognized that methane is often associated with spills of petroleum fuels (Marrin 1989; Jones and Agostino 1998). If this methane finds its way into soil gas there may be two undesirable consequences. First, the soil gas may be flammable or form a flammable mixture with air (Coward and Jones 1931). If this soil gas enters a confined space, it may impose an explosion hazard. The second consequence is associated with vapor intrusion from gasoline hydrocarbons. Methane is readily degraded by aerobic microorganisms. The stoichiometry of biodegradation [$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$] predicts that two parts by volume of oxygen are required to degrade one part of methane. If the soil gas is 21% oxygen by volume, then biodegradation of a little more than 10% methane can consume all the oxygen in soil gas.

One of the goals of this study was to develop and evaluate a protocol to sample soil gas from groundwater monitoring wells that had some portion of their screen in the vadose zone. As part of that effort, we evaluated the performance of two commercially available field meters that can measure concentrations of methane, oxygen, and carbon dioxide in gas. A second goal was to better understand the hazards associated with spills of motor gasoline and the associated production of methane at the sites in Oklahoma. The protocol was applied to determine the concentrations of oxygen, methane, benzene, and total gasoline hydrocarbons in soil gas. This information was used to evaluate the possibility that methane in soil gas might contribute to the intrusion of benzene vapors into buildings.

A procedure from Abreu et al. (2009) was applied to evaluate intrusion of benzene vapors into buildings. We compared the conditions at the sites in Oklahoma to the results of computer simulations as summarized by Abreu et al. (2009). From the comparison, we identified an attenuation coefficient that best describes the reduction of hydrocarbon vapors

---

doi: 10.1111/j1745-6592.2011.001345.x

between the vapor source and the indoor air of a hypothetical receptor. The concentration of benzene in indoor air at a hypothetical receptor was estimated by multiplying the vapor attenuation coefficient by the concentration of benzene measured in the soil gas. The estimated benzene concentrations were then compared to the United States Environmental Protection Agency (U.S. EPA) Generic Screening Level for indoor air (U.S. EPA 2002).

Ethanol is readily fermented to methane (Powers et al. 2001). The increased use of ethanol in motor fuel has raised concerns about methane at gasoline spill sites (Freitas et al. 2010; Powers et al. 2001). Freitas et al. (2010) studied six gasoline spill sites in Sao Paulo, Brazil. They collected groundwater samples to determine concentrations of dissolved methane and the $\delta^{13}C$ of methane. Then, they compared the $\delta^{13}C$ of the dissolved methane to the range of $\delta^{13}C$ in ethanol used in motor fuel. Results showed that the methane could be attributed to ethanol at two stations and to petroleum at two other stations. At the two remaining stations, methane in one well at a station could be attributed to ethanol while methane in another well at the same station could be attributed to petroleum, perhaps indicating more than one release at these two sites.

Freitas et al. (2010) also suggested that naturally occurring ^{14}C in methane could be used to associate methane with ethanol or petroleum. As ^{14}C decays, the proportion of ^{14}C will decline over time compared to the stable isotopes ^{13}C and ^{12}C. While the proportion of ^{14}C in biofuels is near the modern proportion of ^{14}C in atmospheric carbon dioxide, ^{14}C is not detectable in petroleum.

The proportion of ^{14}C in methane or carbon dioxide has been used successfully at spill sites to track the source of methane or carbon dioxide. Lundegard et al. (2008) showed that methane in groundwater from a gasoline spill site had a high proportion of ^{14}C. This methane could not be attributed to petroleum. The most plausible alternative for the source of the methane was decomposition of wood fibers in lake sediments at the site. Lundegard et al. (2000) showed that methane associated with a spill of diesel fuel had no detectable ^{14}C. If the methane came from native organic matter in the soil profile, some detectable proportion of ^{14}C would be expected. They concluded that the methane must have been produced from anaerobic biodegradation of diesel fuel. Conrad et al. (1997) showed that carbon dioxide in soil gas at a gasoline spill site had a very low proportion of ^{14}C. They were able to demonstrate that the carbon dioxide came from aerobic degradation of methane which was originally produced by methanogenesis of petroleum hydrocarbons.

To identify the source of methane in soil gas, we determined the proportion of ^{14}C in methane in soil gas. We corrected the proportion of ^{14}C in methane in soil gas for methane that might have been produced from the reduction of dissolved organic carbon (DIC) in groundwater.

Methods

Field Sites

The Petroleum Storage Tanks Division of the Oklahoma Corporation Commission (OCC) identified sites in central and southeastern Oklahoma that had experienced a recent confirmed release of motor gasoline. These sites also had monitoring wells in the fill that housed the underground storage tank (UST) or in the aquifer immediately adjacent to the UST. Information was not available to the OCC or the tank owners regarding the content of ethanol in the gasoline that was released.

The sites are identified by the name of the town or city where the release occurred. In the case of Oklahoma City, the sites are further identified by the street. To maintain confidentiality, the sites are not uniquely identified. Three of the sites (OKC-S.E. 29th, OCK-N. May, and OKC-N.E. 23rd) were in metropolitan Oklahoma City. The other sites (Wapanucka, Antlers, Beggs, Pickett, Pauls Valley, McAlester, Henryetta, and Maysville) were in cities and towns in the southeastern quadrant of Oklahoma. Each station was sampled at least once in 2009, and twice in 2010.

Monitoring Wells

Most of the monitoring wells were constructed with 2-inch (5.1 cm) interior diameter (ID) polyvinylchloride (PVC) pipe installed in 6-inch (15 cm) ID augured boreholes. Two of the wells were 4-inch (10.2 cm) PVC pipe installed in a 10-inch (25 cm) borehole. The screened interval was protected by a filter pack, or by tank-fill material. If wells were installed in aquifer material, there was at least 1 foot of bentonite seal above the filter pack, and one foot of cement grout above the bentonite seal. Wells in tank fill did not have a bentonite seal. Most of the wells had 10 feet (3.0 m) of screen with the center of the screen near the average depth to water. The wells were fitted with an EX-Cap® that provided a port to extract air (Atlantic Screen and Manufacturing, Inc., Milton, Delaware). When 4-inch wells were sampled, a reducer was used to join the 2-inch Ex-Cap to the 4-inch riser of the wells.

Soil Gas Sampling

A diaphragm vacuum pump (ILMVAC® type MPC 104 Ep, ILMVAC GTmbH, Ilmenau, Thuringia, Germany) was used to extract soil gas from the screened interval exposed above the water table. The soil gas sample passed through a 1-L glass flask that acted as a trap for water, and then to the diaphragm pump. The pump could move as much as 12 L/min of air. The vacuum generated on the headspace of the well was monitored by a Magnehelic differential pressure gauge that was referenced to the atmosphere (reporting range 0–50 inches of water, Dwyer® Instruments Inc., Michigan City, Indiana). The flow rate of the sample gas was measured with a rotometer located on the effluent side of the pump. The flow was adjusted with a needle valve between the pump and rotometer. The gas on the effluent side of the needle valve was at atmospheric pressure.

The effluent of the rotometer went to a tee split to create a path for gas sample collection and to provide an outlet for excess gas. Most of the sample gas was discharged to the atmosphere. A minor portion of the sample gas was drawn to two field instruments by pumps built into field instruments. The field instruments together drew approximately 0.5 L/min of air. The detectors that measure methane in the field instruments are also sensitive to petroleum hydrocarbons. The instruments were protected by an activated carbon trap that was designed to remove hydrocarbons but not methane from the gas sample.

At most monitoring wells, the flow rate of gas was controlled at 10 L/min. Soil gas was pumped from each well for at least 20 min. The vacuum was monitored to estimate the extent that standing water in the well was drawn up inside the well during sampling. If the water was drawn to a height that totally inundated the well screen, the flow rate of gas was adjusted to reduce the vacuum as needed. As a general rule, the vacuum ranged from 10 to 24 inches of water. For wells that were installed in silty clay, in order to keep the vacuum less than 50 inches of water as indicated by the magnehelic pressure gauge, it was necessary to adjust the flow to 1.5 L/min. For wells that were installed in sandy material, soil gas could be sampled at a rate of 10 L/min whenever at least 2 feet (0.6 m) of screen was exposed to the vadose zone. Where wells were screened in silty clay, 4 or 5 feet (1.2–1.5 m) of screen exposed to the vadose zone were necessary to yield a flow of 1.5 L/min, as indicated by the rotometer.

Samples of the gas that was discharged from the system were collected by water displacement into 165 mL serum bottles, sealed with a Teflon®-faced septum (Wheaton Science Products, Millville, New Jersey), and returned to the laboratory for analysis of concentrations of methane, as well as benzene and other gasoline hydrocarbons by gas chromatography.

Analysis of Gas Samples in the Field

The stream of soil gas that passed through the activated carbon filter was split into two portions. One portion went to a Landtec GEM 2000 gas analyzer and extraction monitor (Landtec North America, Colton, CA). The instrument was equipped with detectors for (1) methane in air, (2) carbon dioxide in air, and (3) molecular oxygen in air. Both carbon dioxide and methane were detected by a dual wavelength infrared cell with a reference channel. Oxygen was detected by an internal electrochemical cell. The Landtec monitor was calibrated in the field against standard gases. The monitor set a zero response against a standard gas that did not contain the analyte and then set a response equivalent to the nominal concentration of the analyte in a second standard gas that did contain the analyte. The oxygen standard had 4 ± 0.08% oxygen with the balance nitrogen. The methane and carbon dioxide standard had 50 ± 1% methane and 35 ± 0.75% carbon dioxide. The monitor was calibrated in the field immediately prior to the beginning of sampling each day. If the meter was turned off at some time during the day, then the calibration was checked by analyzing the standard gases before additional samples were collected and analyzed.

The other portion of soil gas was analyzed in the field using a MSA Orion Plus Multigas Detector (Mine Safety Appliances, Pittsburgh, Pennsylvania). This instrument is specifically designed to monitor hazardous gases in underground mines. It is equipped with monitors for (1) methane in air and (2) molecular oxygen in air. Oxygen is determined by an electrochemical sensor, and methane is determined by an infrared sensor. The Orion Multigas Detector was calibrated before going to the field against a standard gas obtained from the manufacturer. The Orion Plus Multigas Detector set a response equivalent to the nominal concentration of the analytes in the standard gas. The standard gas had 15% oxygen and 1.5% methane.

Trap for Gasoline Hydrocarbons

Both the Landtec Monitor and the Orion Plus Multigas Detector use an infrared detector for methane. These detectors also respond to gasoline hydrocarbons. As described in the user's manuals for the instruments, the detectors are more sensitive to the gasoline hydrocarbons on a percent by volume basis than they are to methane. To avoid reporting gasoline hydrocarbons as methane, the field instruments were protected by a trap containing granular activated carbon. The trap that is supplied by the vendor of the Landtec Monitor is designed for landfill gas and does not have adequate capacity to protect the Monitor from petroleum vapors at gasoline spill site. The Orion Plus Multigas Detector is designed to monitor hazardous gas in habitable spaces and the vendor does not supply a trap.

A high capacity trap was constructed by packing a plastic cylinder with activated carbon. The trap was inserted in the sampling train upstream of the field instruments. The internal diameter of the cylinder was 1.0-inch and the cylinder was 10 inches long. The cylinder was originally designed to contain materials used to purify carrier gas that was supplied to a gas chromatograph (Alltech Associates, Deerfield, Illinois). The granular activated carbon was acquired from Calgon, Inc. (Pittsburgh, Pennsylvania). It is described as 8 × 30 bituminous coal. It was activated by baking in an oven at 93 °C for 8 h.

After the sampling of soil gas was completed at each monitoring well, the proper operation of the activated carbon trap was evaluated by challenging the trap with air containing gasoline hydrocarbons at concentrations that would be expected in air in equilibrium with gasoline. A 165-mL gas sampling bulb with a septum port was plumbed immediately upstream of the activated carbon trap. The bulb was used to create a spike of vapors of gasoline hydrocarbons. To generate the spike, 10 μL of a cocktail of gasoline hydrocarbons was introduced into the bulb through the septum. The cocktail was prepared by combining 3700 μL butane, 3000 μL pentane, 2600 μL hexane, 370 μL benzene, 970 μL toluene, 49 μL ethylebenzene, 140 μL *m* + *p*-xylene, 53 μL *o*-xylene, 26 μL 1,3,5-trimethylbenzene, 74 μL 1,2,4-trimethylbenzene, and 17 μL 1,2,3-trimethylbenzene. The hydrocarbons quickly evaporated in the bulb.

The pneumatic integrity (tightness) of the entire sampling system, including the granular activated carbon trap, was tested by enclosing the sampling system in a plastic bag filled with carbon dioxide gas. The intake to the sampling system was supplied with air from outside the plastic bag. The atmosphere contains approximately 0.04% carbon dioxide. The field instruments displayed concentrations of carbon dioxide to 0.1%. The fittings and connections were tightened and adjusted until the field instruments failed to detect carbon dioxide.

Groundwater Sampling

After soil gas sampling was completed, groundwater samples were collected from the wells. Each well was purged using a peristaltic pump by pumping three well volumes to waste. Duplicate samples were collected in 40-mL volatile organic analysis (VOA) vials and preserved with 1% trisodium phosphate. Samples were immediately placed in an ice chest and transported to laboratory for analysis by gas chromatography.

Laboratory Analysis: Soil Gas

Gas samples were analyzed for methane and benzene using an Agilent Micro 3000 gas chromatograph (GC). The instrument is configured with four miniaturized GC systems in a modular format. All four modules contain a micro-Wheatstone bridge thermal conductivity detector built into a silicon chip. Methane was analyzed on the MS-5A module with argon as the carrier gas. The column was 10 m long and was packed with molecular sieve. Ethylene, ethane, acetylene, propane, and propylene were analyzed on the PoraPLOT U module with helium as the carrier gas. The porous layer open tube (PLOT) column was 8 m long. It was composed of bonded divinylbenzene/ethylene glycol dimethacrylate coated onto a fused silica capillary. *N*-butane, *trans*-2-butene, 1-butene, *iso*-butylene, *cis*-2-butene, *iso*-pentane, *n*-pentane, 2-methyl-2-butene, *trans*-2-pentene, 1-pentene, and *cis*-2-pentene were analyzed on the Alumina module. The column packing was alumina, and the column was 10 m long. The carrier gas was helium. *Iso*-butane and benzene as well as other hydrocarbons with six or more carbon atoms were analyzed on the OV-1 module with helium as the carrier gas. The column was 10 m long and was packed with methyl silicone. Compounds C6+ other than benzene were not separately resolved and quantified.

The procedure followed Feeney and Larson (2002) with modifications. The method detection limit and quantitation limit for methane were 0.6 and 10 ppm v/v, respectively. The method detection limit and quantitation limit for benzene were 2 and 10 ppm v/v, respectively.

Analysis of Water Samples

Groundwater samples were analyzed for ethanol and benzene by EPA Method 8260. The method detection limit and reporting limit for ethanol were 18 and 100 µg/L. The method detection limit and reporting limit for benzene were 0.1 and 0.5 µg/L.

Analysis of Proportion of ^{14}C (pMC) in Methane and DIC

Selected soil gas samples were sent to Isotech Laboratories, Inc. (Champaign, Illinois) for analysis of ^{14}C in methane in soil gas or ^{14}C in DIC in groundwater. As part of the process to work up the samples for analysis of ^{14}C in methane, Isotech Laboratories collected and reported data on the concentrations of helium, methane, ethane, ethylene, propane, propylene, *iso*-butane, *n*-butane, *iso*-pentane, *n*-pentane, and hexane plus (C6^{+}) in the gas samples. Isotech Laboratories reported that the "analysis based on standards was accurate to within 2%."

The proportion of ^{14}C to stable isotopes of carbon in an environmental sample is conventionally reported as a percent of the proportion of ^{14}C to stable isotopes in an international standard taken to represent modern carbon. The unit is percent modern carbon or pMC. The reporting limit for analysis of ^{14}C in methane or DIC was 2.0 pMC. The precision at the reporting limit was ±0.1 pMC.

Results

Ethanol and Benzene in Groundwater

Ethanol was detected in groundwater at only two sites. At each site, ethanol was detected at only one sampling event, and in only one well. The detected concentrations of ethanol were 134 µg/L at the Beggs site and 323 µg/L at the Henryetta site. Concentrations in all other samples were below the detection limit of 18 µg/L.

Benzene concentrations ranged from 3900 to 0.15 µg/L. The median concentration was 755 µg/L. This distribution is typical of benzene concentrations at other UST release sites in Oklahoma.

Methane, Benzene, and Oxygen in Soil Gas

Figure 1 compares the maximum concentrations of methane in soil gas from any well at any time at each of the 12 sites to the concentration of oxygen. The lower explosive limit (LEL) of methane in air is usually quoted as 4.5–5% v/v. This range of values assumes that the concentration of oxygen is the concentration in the atmosphere. Methane at 6 of the 12 sites exceeded this range; however, oxygen in these samples was much less than oxygen in the atmosphere. Figure 1 is redrawn from a figure originally published by Coward and Jones (1931) to predict explosions of methane gas in coal mines. They assigned concentrations of methane and oxygen in air to three conditions: (1) a range of concentrations that were flammable, that is, were capable of propagating a flame once ignited, (2) a range of concentrations that were not flammable, even if mixed with air, and (3) a range of concentrations that were not flammable, but could be flammable if mixed in the appropriate proportions with air.

Figure 1 is an approximation because it ignores the contribution of gasoline vapors or molecular hydrogen to the flammability of the gas mixture. However, most of the measurements do not fall close to a boundary between the three behaviors, and the figure is generally useful to predict the flammability of the soil gas. None of the soil gas samples collected in this study was flammable. Seven of the samples could never be flammable based on their content of oxygen

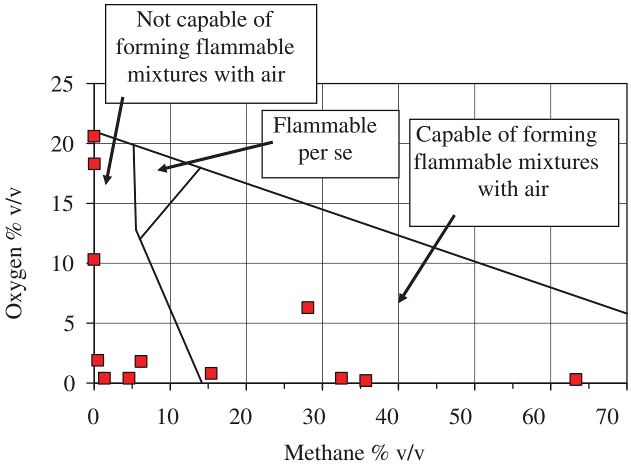

Figure 1. Concentrations of methane and oxygen in soil gas produced from monitoring wells.

and methane. However, five of the soil gas samples could be flammable if mixed in the correct proportions in air.

Where high concentrations of oxygen were present in soil gas, there was generally little methane (Figure 1). Conversely, where high concentrations of methane were present, there was little oxygen. This indicates that the subsurface microorganisms consumed both methane and oxygen until they depleted either methane or oxygen. With the exception of one well at one site (Henryetta), whenever concentrations of methane were above 1%, the concentrations of oxygen were below 2%.

These results are consistent with the distribution of methane and oxygen in the vadose zone at a well-studied spill of crude oil near Bemidji, Minnesota (Amos et al. 2005). At the Bemidji site, when concentrations of molecular oxygen in soil gas were greater than 2%, the concentration of methane was less than 1%. The distribution of methane and oxygen at the Bemidji site was well explained by a transport and fate model that included aerobic biodegradation of the methane and diffusion and advective flow of the gases (Molins et al. 2010). The model predicted that whenever concentrations of oxygen were greater than 2% on a mole fraction basis, the concentration of methane should be less than 1%.

With regard to the anomalous well in Figure 1 that produced high concentrations of methane and high concentrations of oxygen, it is most likely that the well produced soil gas from different depth intervals with different proportions of methane and oxygen. This is a familiar problem in environmental monitoring. Frequently, a monitoring well will produce water that contains both dissolved oxygen and iron(II). Dissolved oxygen should rapidly oxidize iron(II) in groundwater to iron(III). Their presence in the same sample of well water is usually interpreted as evidence that the well produces a mixed sample of groundwater that comes from at least two distinct regions in the aquifer, one containing oxygen but no iron(II) and another one containing iron(II) but no oxygen.

Methane and oxygen in soil gas should follow the same pattern. Concentrations of methane above 1% by volume and oxygen above 2% probably indicate that the well is producing a mixed sample of soil gas. This criterion may prove useful at other sites to screen for the possibility that the well is producing a mixed sample of soil gas. Data on well construction cannot explain why the anomalous well produced high concentrations of methane and high concentrations of oxygen at the same time. The top of the screen was at 3.6 feet (1.1 m) below land surface. The bottom of the screen was at 9.8 feet (3.0 m) and the water table was 9.2 feet (2.8 m).

Figure 2 compares concentrations of benzene in soil gas to concentrations of methane and oxygen. The U.S. EPA screening level for benzene in deep soil gas is 0.98 ppm v/v (U.S. EPA 2002). The method detection limit for benzene (2 ppm v/v) is two-fold higher than the screening level. Soil gas from 13 of the 18 monitoring wells had concentrations of benzene that were at least 10-fold higher than the U.S. EPA screening level for deep soil gas (Figure 2).

Soil gas containing 0.1% or more of methane also contained at least 10 ppm of benzene (Figure 2, panel A). There was a weak trend toward higher concentrations of benzene in the presence of higher concentrations of methane. The Pearson product-moment correlation coefficient (r) between the natural logarithm of concentrations of methane and the natural logarithm of concentrations of benzene was 0.54, significant at 95% confidence.

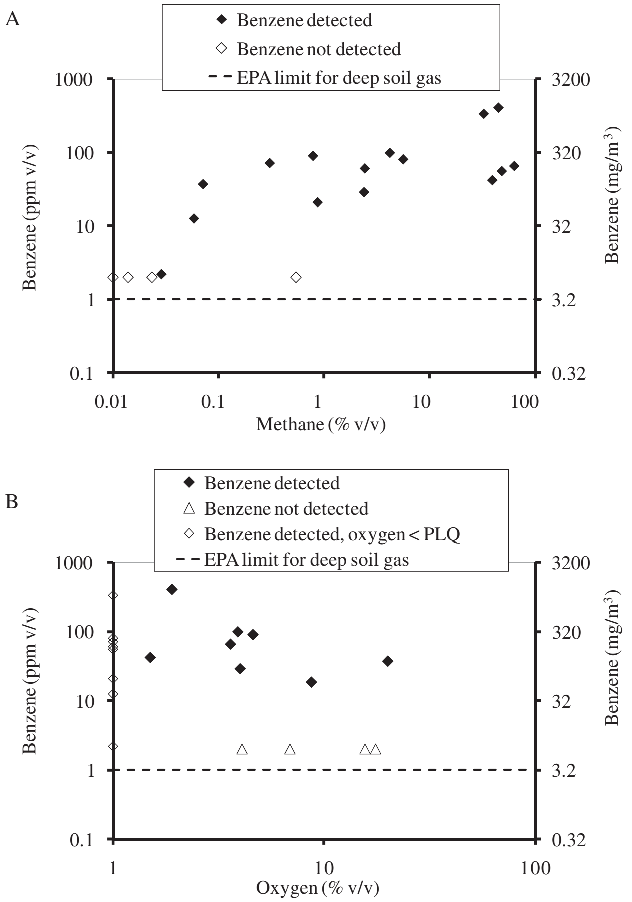

Figure 2. Relationship between concentrations of benzene and the concentrations of methane or oxygen in soil gas at nine confirmed-release sites in Oklahoma. The practical quantitation limit of oxygen in soil gas (PQL in panel B) is near 1% v/v.

Unlike the situation with methane and oxygen, there was no clear relationship between the concentrations of benzene and oxygen (Figure 2, panel B). The correlation coefficient between the natural logarithm of concentrations of benzene above the detection limit and the natural logarithm of concentrations of oxygen above the practical quantitation limit was only –0.18. This value is not statistically significant at 90% confidence.

The soil gas sample with the highest concentrations of benzene had 1.9% oxygen. This concentration of oxygen is low, but is not low enough to preclude aerobic biodegradation of benzene. Alagappan and Cowan (2004) found that the half saturation constant for oxygen consumption by a pure culture of bacteria growing on toluene was as low as 0.74 mg/L, which would be equivalent to 1.6% v/v in air at 17 °C.

The concentration of benzene in the soil gas cannot be understood or predicted from the local concentration of methane or molecular oxygen (Figure 2). To understand the effect of concentrations of methane and oxygen on concentrations of benzene, it will be necessary to integrate the effect of transport processes and degradation processes at site scale.

Conceptual Model for the Effect of Methane on Vapor Intrusion of Benzene

Roggemans et al. (2001) identified discrete patterns of behavior of oxygen and petroleum hydrocarbons in soil gas at fuel spill sites. Their conceptual model considered upward diffusion of the petroleum hydrocarbons from groundwater or a gasoline smear zone and downward diffusion of oxygen from the land surface or an indoor receptor. At sites that followed behavior "A," the interval in the vadose zone between the sources of hydrocarbons and the receptor is divided into two zones: (1) an aerobic zone, where there is a possibility for substantial aerobic biodegradation of benzene, and (2) an anaerobic zone, where concentrations of benzene only attenuate through diffusion along a concentration gradient.

At sites following Behavior "B," oxygen extends throughout the vadose zone, from the source to the receptor. The demand for oxygen is not strong enough to create a zone where oxygen is not available for biodegradation of the petroleum hydrocarbons. At sites following Behavior "C," the concentrations of oxygen in the entire vadose zone are too low to allow aerobic biodegradation.

Longer depth intervals in the aerobic zone provide more opportunity for biodegradation of benzene and reduce the chances for intrusion of benzene vapors. The oxygen demand associated with the aerobic biodegradation of methane at a site should influence and perhaps may determine the pattern of behavior with respect to aerobic biodegradation of benzene in soil gas. Lundegard and Johnson (2006) evaluated the natural attenuation processes associated with spills of petroleum distillate in dune sands in California. At several locations, the oxygen demand of methane diffusing upward in the vadose zone was matched by the supply of oxygen diffusing downward from the soil surface.

DeVaull (2007) developed a series of equations to describe the interaction between the oxygen demand of methane, gasoline hydrocarbons, and soil organic matter and the depth of the transition from aerobic conditions to conditions that do not support aerobic biodegradation of hydrocarbons. As concentrations of methane in deep soil gas increase, the depth interval in the aerobic zone should be reduced. If the aerobic zone is reduced, higher concentrations of benzene should move to the receptor.

Abreu et al. (2009) performed a number of simulations using a three-dimensional numerical model to predict the steady state distribution of oxygen and total hydrocarbons near and beneath a building under a number of representative conditions. They assumed that there was no biodegradation of hydrocarbons when the concentration of oxygen was below 1% v/v. They used the distribution of oxygen and total hydrocarbons and reasonable assumptions about the entry of soil gas into a building and the air exchange within a building, to estimate vapor attenuation factors (α) for hydrocarbons between the source of vapors and indoor air. They then multiplied the vapor attenuation factors (α) by the concentration of benzene in soil gas at the source to estimate the concentration of benzene in indoor air.

In the model projections of Abreu et al. (2009), high concentrations of hydrocarbons in the source, particularly if they occurred within a few meters below the building, resulted in the depletion of oxygen below the building. The low concentrations of oxygen allowed less biodegradation of benzene in soil gas, which resulted in higher predicted concentrations of benzene in indoor air.

If benzene and methane behave as described by DeVaull (2007) and Abreu et al. (2009), methane in the deep soil gas can be expected to increase the chance of completing a vapor intrusion pathway for benzene. The approach of Abreu et al. (2009) was used to make semi-quantitative comparisons of the effect of the particular concentrations of methane at each site on the possibility for vapor intrusion of benzene. These comparisons should not be confused with a formal risk assessment for vapor intrusion at these sites.

Gas samples were acquired in December 2010 and January 2011 from 11 of the 12 gasoline stations in the survey. The water table was too high to allow sampling at one of the sites. Concentrations of methane, ethylene, ethane, acetylene, propane, propylene, *n*-butane, *iso*-butane, *trans*-2-butene, 1-butene, *iso*-butylene, *cis*-2-butene, *iso*-pentane, *n*-pentane, 2-methyl-2-butene, *trans*-2-pentene, 1-pentene, *cis*-2-pentene, benzene, and C6+ were determined in the gas samples.

Figure 10 of Abreu et al. (2009) was used to estimate the vapor attenuation factor (α). To estimate the vapor attenuation factor (α) from the figure, it is necessary to know the depth interval between the source of vapors and the receptor, and the concentration of total hydrocarbons at the source.

Abreu et al. (2009) ran their model simulations for a representative hydrocarbon with the properties of benzene. To express our analytical results in units that can be applied to Figure 10 of Abreu et al. (2009), it was necessary to express the concentrations of methane or gasoline hydrocarbons (reported as ppm v/v) as an equivalent concentration of benzene with units of mg/L soil gas. Because the simulations of Abreu et al. (2009) compared the supply of oxygen to the theoretical demand of oxygen for biodegradation of benzene, the concentrations of methane and gasoline hydrocarbons in soil gas were used to calculate a concentration of benzene that would have the same oxygen demand as the actual concentrations of methane or gasoline hydrocarbons in the soil gas.

Following DeVaull (2007), the stoichiometry of aerobic biodegradation was used to calculate the concentration of molecular oxygen that would be needed to degrade the compounds. Consider as an example the biodegradation of benzene [$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$]. If the concentration of benzene in soil gas were 100 ppm, the estimated concentration of molecular oxygen required to degrade the benzene would be 750 ppm.

The concentrations of all C6+ compounds were determined as a group. Their composite oxygen demand was calculated by assuming that the composite behaved like octane. The oxygen demand of all the gasoline hydrocarbons from ethane to C6+ was summed.

To calculate the concentration of benzene (ppm) with an oxygen demand equivalent to the oxygen demand for methane, or to the total oxygen demand of all the gasoline hydrocarbons, the demand of the hydrocarbons (ppm O_2) was divided by 7.5. To express the concentration of benzene

Table 1

Field Data That Were Used to Estimate Vapor Attenuation Factors (α) of Concentrations of Hydrocarbon Vapors between the Source of the Vapor and the Indoor Air of a Building

Station-Well	Date Sampled	Depth to Water (m)	Depth to Water (m)[1]	Benzene[2] Equivalent to Methane Alone (mg/L)	Benzene[2] Equivalent to Gasoline Hydrocarbons Alone (mg/L)	Benzene[2] Equivalent to Gasoline Hydrocarbons Plus Methane (mg/L)
Wapanucka-MW-1	February 22, 2010	6	5	22	242	264
Antlers-MW-2	January 4, 2011	5.3	5	544	52	597
Beggs-MW-2	December 16, 2010	1.5	1	7	71	78
Pickett-MW-G2	January 3, 2011	1.9	2	302	36	339
Pauls Valley-PW-1	December 15, 2010	3.1	3	36	67	104
McAlester-MW-3	December 27, 2010	0.7	1	1	21	22
Henryetta-N.W.T.P.	December 16, 2010	2.7	3	90	23	113
OKC-S.E. 29th-W-3	December 2, 2010	2.3	2	31	13	44
OKC- N. May-W-1	October 21, 2010	1.4	1	0.12	2	2.5
OKC-N.E. 23rd- TMW-1	March 24, 2010	2.2	2	0.78	6	6.9
Maysville-VW-2	December 16, 2010	3.2	3	0.14	2	2.6

[1] Used to estimate attenuation factor according to Figure 10 of Abreu et al. (2009).

[2] The concentration of benzene with a theoretical oxygen demand that is equivalent to the theoretical oxygen demand of methane or the specified mixture of hydrocarbons.

in mg/L soil gas, the concentration in ppm was divided by 10^6, then multiplied by the vapor density of benzene (2.7, air = 1), and then multiplied by the density of air (1200 mg/L).

Table 1 provides the site data used to extract the estimates of the vapor attenuation factors (α). Data are expressed as the concentrations of benzene that would be equivalent to (1) the concentrations of methane, (2) the concentrations of the gasoline hydrocarbons without methane, and (3) and the concentrations of the gasoline hydrocarbons plus methane. A comparison of (1) and (2) reveals the relative importance of methane or gasoline hydrocarbons as a source of oxygen demand at the various sites. At sites at Antlers, Pickett, Henryetta, and OKC-S.E. 29th, methane was the dominant source of oxygen demand. At the remaining seven sites, methane was a minor portion of the oxygen demand associated with hydrocarbons in soil gas.

Expected Effect of Methane on the Possibility for Vapor Intrusion of Benzene

A value for the attenuation factor was extracted using the concentration of benzene equivalent to all the hydrocarbons except methane and a second factor was extracted using the concentration of benzene equivalent to all the hydrocarbons including methane. The concentration of benzene in the soil gas sample was multiplied by the attenuation factor to predict the concentration in indoor air at a hypothetical receptor. The factors and the predicted concentrations of benzene are presented in Table 2.

In Table 2, the sites are ranked by the predicted concentration of benzene in indoor air in the presence of methane. The U.S. EPA generic screening level for benzene in indoor air is 9.8 ppb v/v (U.S. EPA 2002). At five sites, the predicted concentrations of benzene in indoor air exceeded the screening level (Wapanucka, Antlers, Beggs, Pickett, and Pauls Valley). At three of these sites (Antlers, Pickett, and Pauls Valley) predicted concentrations of benzene in the presence of methane exceeded the screening level while predicted concentrations in the absence of methane did not. At the other two sites, the presence of methane made no difference. Because the attenuation factors were modest and the concentration of benzene was high (Wapanucka) or the source was shallow (Beggs), the predicted concentration in indoor air exceeded the guidelines at these two sites whether methane was present or not.

At the remaining seven sites, the predicted concentrations of benzene in indoor air were below the guideline. At three of the sites, the predicted concentration was within an order of magnitude of the guideline (McAlester, Henryetta, and OKC-S.E. 29th). At the McAlester site, methane made no difference, while at the sites at Henryetta and OKC-S.E. 29th; the predicted effect of methane was substantial. At the remaining three sites, the predicted concentrations of benzene in soil gas were far below the guideline, and there was no predicted effect of methane on concentrations of benzene in indoor air.

Production of Methane from Petroleum or Ethanol

Ethanol in gasoline is made from grain or cane sugar. The pMC of ^{14}C in ethanol in gasoline should be near 100%. Petroleum has no detectable ^{14}C, and the pMC of petroleum is effectively 0.0%. Table 3 presents a simplified view of the anaerobic biodegradation of petroleum or ethanol to methane and carbon dioxide. Calculations in Table 3 assume that all petroleum behaves like benzene or like a hypothetical alkane with the empirical formula of CH_2. The calculations

Table 2
The Concentration of Benzene in Soil Gas, the Vapor Attenuation Factors (α) Estimated from Conditions at the Sites, and the Screening Level Prediction of the Concentration of Benzene Vapor That Might Be Expected in a Building When Methane Is and Is Not Considered in the Calculation of the Attenuation Factor

				U.S. EPA Generic Screening Level for Indoor Air = 9.8E−03 ppm (v/v)		
Station-Well	**Benzene ppm (v/v)**	**α Without Methane**	**α With Methane**	**Predicted Indoor Air Concentration Without Methane ppm (v/v)**	**Predicted Indoor Air Concentration With Methane ppm (v/v)**	**Ratio of Predicted Indoor Air Concentrations With/Without Methane**
Wapanucka-MW-1	1030	2.0E−04	2.0E−04	2.1E−01	2.1E−01	1.0E+00
Antlers-MW-2	177	1.0E−10	8.0E−04	1.8E−08	1.4E−01	8.0E+06
Beggs-MW-2	118	6.0E−04	6.0E−04	7.1E−02	7.1E−02	1.0E+00
Pickett-MW-G2	22	7.0E−06	1.0E−03	1.5E−04	2.2E−02	1.4E+02
Pauls Valley-VPW-1	99	4.0E−06	1.0E−04	3.9E−04	9.9E−03	2.5E+01
McAlester-MW-3	37	7.0E−05	8.0E−05	2.6E−03	3.0E−03	1.1E+00
Henryetta-N.W.T.P.	18	2.0E−08	1.0E−04	3.7E−07	1.8E−03	5.0E+03
OKC-S.E. 29th-MW-3	51	2.0E−07	2.0E−05	1.0E−05	1.0E−03	1.0E+02
OKC-N. May-MW-1	2	1.0E−05	1.0E−05	2.0E−05	2.0E−05	1.0E+00
OKC-N.E. 23rd- MW-1	2	6.0E−08	6.0E−08	1.2E−07	1.2E−07	1.0E+00
Maysville-VW-2	2	6.0E−10	6.0E−10	1.2E−09	1.2E−09	1.0E+00

Table 3
Stoichiometry of Fermentation of Aromatic Compounds, Alkanes, and Ethanol

Fuel	**Aromatic Compounds in Petroleum**	**Alkanes in Petroleum**	**Ethanol**
Stoichiometry of reaction	$2CH + 2H_2O \rightarrow$ $CH_3COOH + H_2$	$2CH_2 + 2H_2O \rightarrow$ $CH_3COOH + 2H_2$	$CH_3CH_2OH + H_2O \rightarrow$ $CH_3COOH + 2H_2$
	$CH_3COOH \rightarrow$ $CO_2 + CH_4$	$CH_3COOH \rightarrow$ $CO_2 + CH_4$	$CH_3COOH \rightarrow$ $CO_2 + CH_4$
	$H_2 + 0.25CO_2 \rightarrow$ $0.25CH_4 + 0.5H_2O$	$2H_2 + 0.5CO_2 \rightarrow$ $0.5CH_4 + H_2O$	$2H_2 + 0.5CO_2 \rightarrow$ $0.5CH_4 + H_2O$
Fraction CH_4 from fuel	4/5	2/3	2/3
Fraction CH_4 from DIC	1/5	1/3	1/3
Expected pMC in CH_4	= (4/5)* pMC petroleum + (1/5)* pMC DIC	= (2/3)* pMC petroleum + (1/3)* pMC DIC	= (2/3)* pMC ethanol + (1/3)* pMC DIC

in Table 3 also assume that the fermentation reaction is the only pathway for biodegradation. Reactions with electron acceptors such as oxygen, nitrate, or sulfate are ignored. The fermentation reactions also produce molecular hydrogen which can be used by bacteria to convert DIC into additional methane. As a result, some fraction of the carbon in methane produced at a fuel spill comes from the fuel and some fraction comes from DIC in the groundwater.

At sites with high concentrations of methane, soil gas was analyzed for pMC of methane and groundwater was analyzed for pMC of the DIC. Equations in Table 3 were used to estimate the pMC of methane that would be expected if methane were produced from ethanol or produced from petroleum.

The mass balance of pMC in methane is expected to follow Equation 1;

$$\begin{aligned} \text{pMC}_{\text{measured}} = {} & F_{\text{petroleum}} *\text{pMC}_{\text{expected from petroleum}} \\ & + F_{\text{ethanol}} *\text{pMC}_{\text{expected from ethanol}} \end{aligned} \tag{1}$$

where $\text{pMC}_{\text{measured}}$ is the pMC of methane in soil gas, $F_{\text{petroleum}}$ is the fraction of total methane contributed by fermentation of petroleum, $\text{pMC}_{\text{expected from petroleum}}$ is calculated from the formulas in Table 1, F_{ethanol} is the fraction of total methane contributed by fermentation of ethanol, and $\text{pMC}_{\text{expected from ethanol}}$ is calculated from the formulas in Table 1. Assuming that $F_{\text{petroluem}} = (1 - F_{\text{ethanol}})$, Equation 1 was solved for the F_{ethanol}.

Table 4
Prediction of the Fraction of Methane in Soil Gas That Is Produced from Ethanol, Based on a Comparison of Measured Percent Modern Carbon (pMC) in Methane in Soil Gas to the pMC Expected if the Methane Came from Either Aromatic Compounds or Alkanes in Petroleum or from Ethanol

				pMC Expected in CH_4 if CH_4 Is from			Production of CH_4 from Ethanol if the Balance Is CH_4 is from	
Location	CH_4 % v/v	pMC in CH_4	pMC in DIC	Alkanes	Aromatic Compounds	Ethanol	Alkanes	Aromatic Compounds
Pickett	21.9	<0.4						
Pauls Valley	5.32	6.5	24.3	8.1	4.9	74.8	2.4%	None expected
Henryetta	17.0	9.1	27.4	9.1	5.5	75.8	5.1%	None expected
Wapanucka	14.0	10.9	73.2	24.4	14.6	91.1	None expected	None expected
Antlers	35.0	27.0	43.0	14.3	8.6	81.0	25%	19%
Antlers	30.7	30.8	43.0	14.3	8.6	81.0	31%	25%

Equation 1 was solved once assuming the methane from petroleum came from a hypothetical alkane and again assuming the methane came from benzene (Table 4).

At the Pickett site, the pMC in methane was below detection (Table 4). The soil gas had relatively low concentrations of gasoline-range alkanes (11,000 ppm v/v, data provided by Isotech Laboratories) and it contained helium (0.0035%) suggesting that the methane came from a leaking natural gas line and not from fermentation of components of the fuel spill. At three other sites (Pauls Valley, Henryetta, and Wapanucka), the estimated contribution of ethanol to methane in soil gas was undetectable or was so small as to be inconsequential. At the Antlers site, the contribution of ethanol was more significant. On the basis of an original sample of methane in soil gas and a second sample taken 20 days later, the methane produced from ethanol could range between 19% and 31% of the total production of methane, depending on the component of petroleum that contributed the bulk of the methane.

This evaluation assumes that ethanol or another biofuel is the only plausible source of modern carbon to methane. There are other plausible sources including methane from natural organic materials (Lundegard et al. 2008). As a result, this approach cannot unequivocally associate methane with biofuels in a spill. The values of 19–31% of methane from ethanol should be considered an upper boundary on the contribution of a biofuel to methane production.

Overall, fermentation of petroleum was the major source of methane in soil gas. The fuels that were released at the 12 sites in this study should have contained no more than 10% ethanol. The contribution of ethanol (or any other biofuel) to methane production at these gasoline spill sites in Oklahoma was minor.

Performance of Field Instruments

The survey of recent confirmed-release sites in Oklahoma indicated that conventional monitoring wells can be used to sample soil gas. The average depth to water in the monitoring wells was near 10 feet (3 m). The volume of air in the headspace of a 2-inch diameter well was near 6 L. The air was pumped at 10 L\min for 20 min. Under typical conditions the air in the headspace was turned over approximately 30 times before samples were collected for analysis at the fixed base laboratory. At a minimum, five volumes of headspace were extracted before samples were taken for analysis.

The methane data presented in Figures 1 and 2 were determined on samples of soil gas that were analyzed by gas chromatography. The analysis was supported by a Standard Operating Procedure with a full package of quality assurance/quality control measures. However, to be able to know when it is appropriate to collect samples to send back to a fixed base laboratory, the field sampler requires some indication in real time of concentrations of methane and oxygen in the gas being sampled.

To our knowledge, there is no field meter that is expressly designed to sample methane, carbon dioxide, and oxygen in soil gas at gasoline release sites. Therefore, we evaluated the suitability of two instruments that were designed to analyze gas for other purposes. The Landtec GEM 2000 is specifically designed to monitor gas produced from municipal solid waste landfills. The Orion Plus Multigas Detector is designed to monitor hazardous gas in habitable spaces such as coal mines. We evaluated the performance of these instruments in the laboratory by comparing their response against standard gases. Standard gases were obtained from Scott Specialty Gases (Plumsteadville, PA) with nominal concentrations of methane v/v of 1.01%, 1.5%, 9.99%, and 50.0% at an accuracy of ±2% of the nominal value. The standard gases were submitted to the sampling train.

Results are presented in Figure 3. There was good agreement between the nominal concentration in the standards and the concentrations reported on gas samples that were collected by water displacement and analyzed by gas chromatography.

The standard operating procedure for the GC analysis allowed an accuracy of 85–115% between the determined values of calibration check standards and their nominal values. The percent error between the reported values of 12

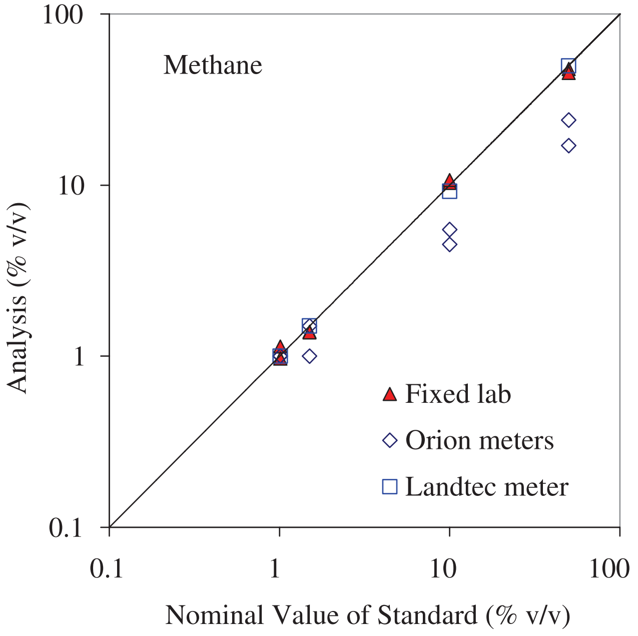

Figure 3. Validation of analyses of methane in gas by field meters and gas chromatography against standard gases.

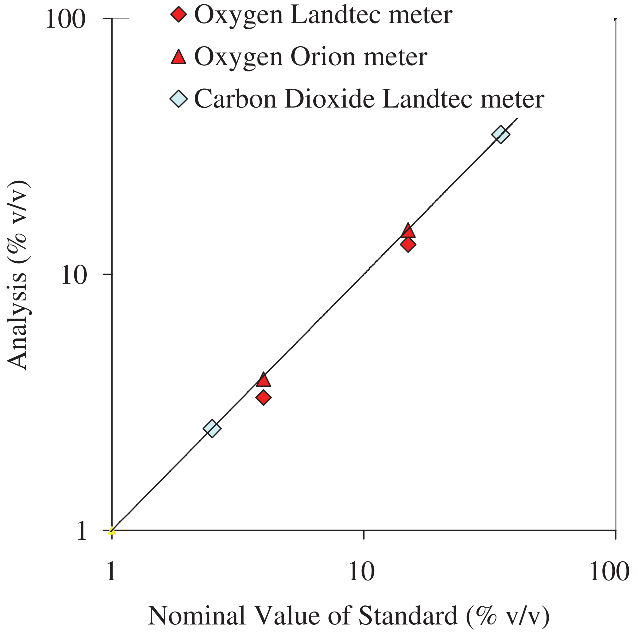

Figure 4. Validation of analyses of oxygen and carbon dioxide in gas by the Landtec Monitor and Orion Plus Multigas Detector against standard gases.

readings of the standard gases and their nominal concentrations was no more than ±12.9%.

There was also good agreement between the standards and the concentrations reported by the Landtec Monitor. The percent error was 8% or less. Two separate Orion plus Multigas Detectors were evaluated. At a methane concentration of 1% v/v, readings from the Orion Detector were in good agreement with the nominal concentrations of the standards. The percent error was 1.0% or less. At higher concentrations, the meter readings of the Orion plus Multigas Detectors were significantly less than the nominal concentrations of the standards. The percent error for analysis of 10% methane on the two meters was 45 and 55% of the nominal value; the percent error for analysis of 50% methane was 52 and 66%.

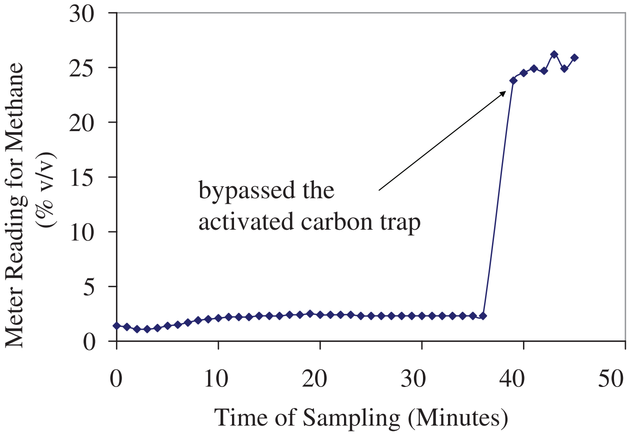

Figure 5. Effect of the activated carbon trap on the concentrations of methane reported by the Landtec Monitor.

The performance of the meters is consistent with their intended application. The Orion Plus Multigas Detector is designed to provide a warning to industrial workers when they experience a dangerous atmosphere. Workers would not stay in environments with 10 or 50% methane. The Landtec Monitor was designed to measure concentrations of methane in soil gas in emissions for landfills. Concentrations of 10 and 50% methane are very plausible in landfill gas.

Figure 4 compares the performance of the field meters for oxygen and carbon dioxide. The standard gases contained 4.0 or 15% oxygen and 2.4 or 35% carbon dioxide. The Relative Percent Difference (RPD) between the nominal value of the standard gas and meter readings for oxygen on the Orion Plus Multigas Detector was 2.5% or less; the RPD for the Landtec Monitor was 18% or less. The RPD for carbon dioxide on the Landtec Monitor was 0.6% or less.

Importance of an Activated Carbon Trap

Figure 5 presents the effect of the trap on the concentrations of methane reported by the Landtec Monitor under typical conditions. Concentrations of methane reached a steady state after 10 min of pumping and maintained the steady state for an additional 25 min. When the activated carbon trap was bypassed, the meter reading changed from 2.5% methane to 25% methane. If the field meters are not protected from gasoline hydrocarbons, they will report the gasoline hydrocarbons as methane. Because the meters are sensitive to vapors of gasoline hydrocarbons, this can lead to substantial error.

The detectors for carbon dioxide and molecular oxygen work on a different principle; they are not subject to interference from petroleum hydrocarbons.

Field Evaluation of the Activated Carbon Trap

Bypassing the trap is one method to determine that the trap is functioning properly in the field. However, this approach does not directly evaluate the capacity of the trap

Table 5

Comparison of the Concentrations of Methane Reported by Gas Chromatography to Concentrations Reported by Field Meters When the Meters Are Protected by an Activated Carbon Trap

Location and Monitoring Well	Methane (% v/v) GC Fixed Base Lab	Landtec Field Meter	Orion Field Meter
Antlers-MW-2-A	44.8	61.4	27.2
Henryetta NW-TP-1	10.0	18.4	9.9
Pauls Valley VPW-3	4.0	5.1	3.5
Pauls Valley VPW-3 10N	3.6	4.5	3.2
Wapanuka-MW-1 A	2.5	4.3	4.6
OKC-S.E. 29th Street	1.3	2.3	1.8
Antlers GMW-5	0.8	1.9	1.6
Henryetta NW-TP-1E	0.5	0.7	0.8
OKC-N.E. 23rd Street TMW-3-A	0.1	0.1	0.1
OKC-N.E. 23rd Street TMW-2-A	0.0	0.0	0.0
OKC-N.E. 23rd Street TMW-1-A	0.1	0.0	0.1
Maysville N.E. Well	0.0	0.0	0.0
Pickett-MW-2-4"	0.0	0.6	0.6

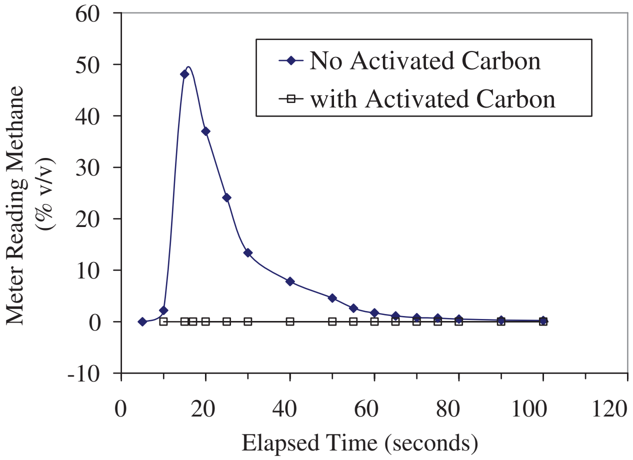

Figure 6. Capacity of the granular activated carbon filter to remove gasoline vapors and prevent spurious readings for methane in the Landtec Monitor.

to protect the meter from interference from gasoline hydrocarbons. To ensure that the trap was operating effectively, the trap was challenged with vapors of gasoline hydrocarbons. A cocktail of gasoline hydrocarbons was added to a 165-mL gas mixing bulb that was inserted upstream of the trap. When the hydrocarbons evaporated in the bulb, they produced concentrations of gasoline hydrocarbons that are similar to the concentrations that would be expected in air that has equilibrated with gasoline. At a flow rate of 10 L/min, the gas in the mixing bulb represents a ten second pulse of gasoline vapors presented to the activated carbon filter and then to the field meters. Figure 6 presents a typical response when the trap is challenged with gasoline hydrocarbons. If the trap is bypassed, the pulse of gasoline vapors is recognized as a high concentration of methane. When the trap is present, the gasoline hydrocarbons have no effect on the meter response.

In the field, the performance of the activated trap was evaluated by challenging the trap with gasoline vapors as described above. This was done immediately after the soil gas data was collected at each monitoring well. If the challenge produced a detectable meter response, the trap was replaced with an unused trap, and the well was sampled again.

Comparison of Methane Reported by GC and Field Meters

Table 5 compares the meter readings from the field instruments on selected wells to the concentrations of methane reported by gas chromatography. The wells were selected to represent a range of concentrations of methane in soil gas. In each case the meters were protected by an activated carbon trap and the trap was evaluated by a challenge with gasoline vapors. The Landtec Monitor consistently over-reported concentrations of methane. Occasionally, the Orion Plus Multigas Detector under-reported concentrations of methane. For samples with methane concentrations of 0.5% v/v or higher, the average relative percent difference (RPD) between the reading from the Landtec Monitor and the analysis by gas chromatography was 62%. The average of the absolute values for the RPD between the readings of Orion meters and the analysis by gas chromatography was 43%.

Conclusions

At 12 gasoline service stations in Oklahoma, conventional groundwater monitoring wells yielded tens of liters of soil gas within 20 min whenever the top of the screen was above the level of standing water in the well. At these sites, the conventional groundwater monitoring wells were a useful alternative to sample soil gas.

At five sites, there is a possibility that methane in soil gas may present an explosion hazard if the soil gas finds its way to a confined space and mixes with air to the bring the concentrations of oxygen and methane within the flammable limits.

At three of the 11 sites in the survey, the presence of methane in soil gas might have allowed concentrations of benzene in indoor air at a hypothetical receptor to exceed the U.S. EPA generic screen level when they otherwise would not exceed the limit.

The source of the methane in soil gas was determined at five sites where the concentrations of methane in soil gas were substantial. At one site, the methane came from a leaking natural gas line and not from a spill of motor fuel. At the remaining four of the sites, the majority of the methane was produced from anaerobic biodegradation of petroleum. At one site, the contribution of ethanol or other biofuel to total methane production was in the range of 19–31%. At the three remaining sites, the contribution of ethanol to methane production was nondetectable, or amounted to at most 5.1% of total production.

Field meters were useful for screening concentrations of methane in soil gas. However, because of the large relative percent difference between meter readings and concentrations of methane determined with a gas chromatograph, it is probably not appropriate to substitute meter readings from field instruments for analysis of methane by gas chromatography. The best use of the screening meters is to monitor changes in concentrations of oxygen, methane, and carbon dioxide as soil gas is extracted from the well. This information is useful to determine the most appropriate time to collect samples for analysis at a fixed base laboratory.

Caveat

Gas samples in the laboratory were analyzed for concentrations of benzene using a micro gas chromatograph with a thermal conductivity detector. This was done to increase the ease of sampling and analysis and reduce the cost of the survey. If soil gas analyses are to be used to support regulatory decisions, the samples should be analyzed using an approved protocol, such as EPA TO-15 (U.S. EPA 1999).

Acknowledgments

The Petroleum Storage Tank Division of the OCC provided access to their records, arranged for access to the field sites, and helped with some of the field sampling. Staff of Shaw Environmental and Infrastructure, Inc. in Ada, OK (including Tracy Pardue, Lisa Hudson, and John Cox) conducted the laboratory analyses. Kristie Hargrove with U.S. EPA provided advice on the calibration and operation of the Landtec Monitor. We appreciate the suggestions and comments of three anonymous reviewers. Cherri Adair and Cindy Paul with U.S. EPA also reviewed the manuscript and provided helpful suggestions. We thank Mark Toso of the Minnesota Pollution Control Agency for giving us the idea to build an activated carbon trap that was adequate to remove the interference from gasoline hydrocarbons.

Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here through in-house efforts. It has not been subjected to review by the Agency or by the OCC, and therefore does not necessarily reflect the views of the Agency, or of the Petroleum Storage Tank Division of the OCC, and no official endorsement should be inferred.

All research projects making conclusions or recommendations based on environmental data and funded by the U.S. EPA are required to participate in the Agency Quality Assurance Program. This project was conducted under an approved Quality Assurance Project Plan. Information on the plan and documentation of the quality assurance activities and results are available from J.T.W.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

Abreu, L.D.V., R. Ettinger, and T. McAlary. 2009. Simulated soil vapor intrusion attenuation factors including biodegradation for petroleum hydrocarbons. *Ground Water Monitoring and Remediation* 29, no. 1: 105–117.

Alagappan, G., and R. Cowan. 2004. Effect of temperature and dissolved oxygen on the growth kinetics of *Pseudomonas putida* F1 growing on benzene and toluene. *Chemosphere* 54: 1255–1265.

Amos, R.T., K.U. Mayer, B.A. Bekins, G.N. Delin, and R.L. Williams. 2005. Use of dissolved and vapor-phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface. *Water Resources Research* 41: W02001. doi: 10.1029/2004WR003433.

Conrad, M.E., P.F. Daley, M.L. Fischer, B.B. Buchanan, T. Leighton, and M. Kashgarian. 1997. Combined ^{14}C and δ^{13}C monitoring of in situ biodegradation of petroleum hydrocarbons. *Environmental Science and Technology* 31, no. 5: 1463–1469.

Coward, M.F., and G.W. Jones. 1931. *Limits of Inflammability of Gases and Vapors.* US Bureau of Mines Bulletin, 279.

DeVaull, G.E. 2007. Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. *Environmental Science and Technology* 41, no. 9: 3241–3248.

Feeney, M., and P. Larson. 2002. *Complete Analysis of Refinery Gases in Seconds Using the Agilent 3000 Micro Gas Chromatograph*, Agilent Technologies publication 5988-6700EN. http://www.chem.agilent.com/Library/applications/5988-6700EN.pdf (accessed November 1, 2010).

Freitas, J.G., B. Fletcher, R. Aravena, and J.F. Barker. Methane production and isotopic fingerprinting in ethanol fuel contaminated sites. *Ground Water* 48, no. 6: 844–857.

Jones, V.T. III, and P.N. Agostino. 1998. Case studies of anaerobic methane generation at a variety of hydrocarbon fuel contaminated sites. *Chemicals in Ground Water: Prevention, Detection, and Remediation; Conference and Exposition,* November, 11–13. *Texas, Houston.*

Lundegard, P.D., R. Haddad, and M. Brearley. 2008. Methane associated with a large gasoline spill: forensic determination of origin and source. *Environmental Geosciences* 5: 69–78.

Lundegard, P.D., and P.C. Johnson. 2006. Source zone natural attenuation at petroleum hydrocarbon spill sites—II: application to a former oil field. *Ground Water Monitoring and Remediation* 26, no. 4: 93–106.

Lundegard, P.D., R.E. Sweeney, and G.T. Ririe. 2000. Soil gas methane at petroleum contaminated sites: Forensic determination of origin and source. *Environmental Forensics* 1: 3–10. doi:10.1006/enfo.1998.0002.

Marrin, D.L. 1989. Soil gas analysis of methane and carbon dioxide: Delineating and monitoring petroleum hydrocarbons. *Proceedings, NWWA Conference on Hydrocarbons and Organic Chemicals in Ground Water*, Houston, TX; 357–367.

Molins, S., K.U. Mayer, R.T. Amos, and B.A. Bekins. 2010. Vadose zone attenuation of organic compounds at a crude oil spill site-Interactions between biogeochemical reactions and multicomponent gas transport. *Journal of Contaminant Hydrology* 112: 15–29.

Powers, S.E., C.S. Hunt, S.E. Heermann, H.X. Corseuil, D. Rice, and P.J.J. Alvarez. 2001. The transport and fate of ethanol and BTEX in groundwater contaminated by gasohol. *Critical Reviews in Environmental Science and Technology* 31, no. 1: 79–123.

Roggemans, S., C.L. Bruce, and P.C. Johnson. 2001. *Vadose Zone Natural Attenuation of Hydrocarbon Vapors: An Empirical Assessment of Soil Gas Vertical Profile Data. API Technical*

Bulletin No. 15., Washington, DC: American Petroleum Institute.

U.S. EPA. 2002. *OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*. EPA530-D-02-004, Table 2a.

U.S. EPA. 1999. *Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)* EPA/625/R- 96/010b.

Biographical Sketches

Ken Jewell *is an Environmental Scientist with the U.S. EPA's Ground Water and Ecosystem Restoration Division in Ada, Oklahoma. He received his B.S. in Environmental Science from East Central University in 1995. He can be reached at Jewell.Ken@epa.gov.*

John Wilson, *corresponding author, is a Research Microbiologist for U.S. EPA's Ground Water and Ecosystem Restoration Division in Ada, Oklahoma. He has a Ph.D. in Microbiology from Cornell University. He can be reached at Wilson.Johnt@epa.gov.*

Exclusive New Insurance Programs for

NGWA Scientists & Engineers Division

NGWA knows most small firms find coverage too expensive to purchase. For these firms, establishing and maintaining a good client base is difficult because many companies will not do business with smaller firms unless they carry adequate liability insurance. Partnering with leading insurance providers, NGWA has developed a cost-effective solution for the Scientist & Engineers section of the NGWA. Presenting a new professional liability insurance program tailored for part-time, small and mid-sized consulting firms.

Program Features

- Professional Liability Coverage
- Coverage with 'A' Rated Insurance Company
- $1,000,000 per occurrence limit
- Low minimum premiums
- Higher limits and additional coverages are available
- College & University Professors
- Partnerships
- Corporations
- Sole Proprietorships and LLC
- Students (meeting minimum qualifications)
- Part-Time Consultants

Jane Rogers, CIC
Environmental Underwriting Solutions
One Perimeter Park South, Suite 405N
Birmingham, AL 35243
Phone: 866-547-8963
Fax: 866-547-8964
email: jane.rogers@eususa.com
WEB: www.eususa.com

national ground water association

For more information, please visit our website at: **http://www.ngwa.org/eoinsurance**