Dynamic Subsurface Explosive Vapor Concentrations: Observations and Implications

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Conventional vapor intrusion characterization efforts can be challenging due to background indoor air constituents, preferential subsurface migration pathways, sampling access, and collection method limitations. While it has been recognized that indoor air concentrations are dynamic, until recently it was assumed by many practitioners that subsurface concentrations did not vary widely over time. Newly developed continuous monitoring platforms have been deployed to monitor subsurface concentrations of methane, carbon dioxide, oxygen, hydrogen sulfide, total volatile organic constituents, and atmospheric pressure. These systems have been integrated with telemetry, geographical information systems, and geostatistical algorithms for automatically generating two- and three-dimensional contour images and time-stamped renderings and playback loops of sensor attributes, and multivariate analyses through a cloud-based project management platform. The objectives at several selected sites included continuous monitoring of vapor concentrations and related physical parameters to understand explosion risks over space and time and to then design a long-term risk reduction strategy. High-frequency data collection, processing, and automated visualization have resulted in greater understanding of natural processes, such as dynamic contaminant vapor intrusion risk conditions potentially influenced by localized barometric pumping. For instance, contemporaneous changes in methane, oxygen, and atmospheric pressure values suggest there is interplay and that vapor intrusion risk may not be constant. As a result, conventional single-event and composite assessment technologies may not be capable of determining worst-case risk scenarios in all cases, possibly leading to misrepresentation of receptor and explosion risks. While dynamic risk levels have been observed in several initial continuous monitoring applications, questions remain regarding whether these situations represent special cases and how best to determine when continuous monitoring should be required. Results from a selected case study are presented and implications derived. © 2011 Wiley Periodicals, Inc.

INTRODUCTION

Vapor intrusion (VI) describes a phenomenon whereby volatile contaminants released to soil or groundwater are transported to buildings in the vicinity of a contaminant plume. Specific contaminants can include volatile organic compounds, select semivolatile organic compounds, and select inorganic compounds, such as elemental mercury and hydrogen sulfide, and methane (Interstate Technology & Regulatory Council, 2007). ASTM International, Inc. (2008, 2010) describes a vapor encroachment condition as "the

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presence or likely presence of contaminant of concern vapors in the subsurface of the target property caused by the release of vapors from contaminated soil or groundwater either on or near the target property."

VI has garnered considerable attention over the past few years for many reasons. A primary reason has to do with the fact that for the majority of contaminant releases, the vapor pathway often was not considered or typically was not given as much attention as the groundwater transport pathway. While many fine exceptions exist, until very recently, the emphasis on groundwater monitoring has dominated the environmental assessment and remediation industry. Newer techniques for assessing vadose zone vapor constituents have given rise to more regulatory concern about potential VI conditions. Another key reason that interest in VI has become more prevalent is because legal actions have resulted in large financial awards to plaintiffs. As a consequence, concerns about potential legal implications have resulted in a greater emphasis on VI assessment as part of due diligence during property transactions. Release of regulatory guidance, training workshops, and news highlights about large-scale legal awards have brought increased attention to the VI pathway.

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Until relatively recently, soil vapor surveys using a direct push system coupled with field analytical capabilities typically were used to evaluate potential for subsurface contaminant presence. Often identification of key constituents can indicate whether contaminants have been released and can offer insight regarding the spatial distribution of the release and how best to design a monitoring well network (ASTM, 2006). Some researchers have even used biogenic versus fixed gas ratios to locate where free petroleum product is located along the capillary fringe and water table depths (Marrin, 1991). Because the soil gas survey measurements were used as indicators of potential groundwater threats, typically they were classified as field screening techniques. For instance, data from these surveys, while very helpful, especially as an initial characterization step for volatile contaminant release sites, typically would not be adequate to perform conventional risk assessments.

Direct push-based soil vapor surveys typically are performed by advancing a probe to a target depth, drawing a vapor sample with a vacuum, collecting vapor in a sampling receptacle, then soon thereafter analyzing the sample for volatile constituents (ASTM, 2011a, 2011b). In general, the probe is advanced to different locations and various depths with key objectives (e.g., extent and distribution of release and plume, level of contamination and spatial footprint of concentration ranges, three-dimensional distribution of specific constituents, etc.) driving the characterization campaign. The process is iterative: samples are collected and analyzed, then the probe is repositioned to collect additional samples. Therefore, while it is possible to generate a three-dimensional conceptualization of the distribution of the sample results, the key assumption is that the system and, therefore, the concentration distribution will be stable during the sampling campaign. ASTM (2011a) further states:

> The data produced using this method should be representative of the soil gas concentrations in the geological materials in the immediate vicinity of the sample probe or well at the time of sample collection (that is, they represent a point-in-time and point-in-space measurement). The degree to which these data are representative of any larger areas or different times depends on numerous site-specific factors. . . . In some cases, the soil gas concentrations may be affected by rainfall or changes in barometric pressure. The magnitude of any such effects is not well known, but is believed to be minimal at sampling depths $\geq$1.5 m.

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ASTM has established a working group to develop a standard practice for monitoring soil vapor in the vadose zone. These approaches typically entail deployment of a material that will entrain the volatile constituents onto a collection device, allowing the devices to equilibrate for several hours or days, then retrieval of the devices for laboratory analyses. Passive approaches have several cost benefits when compared to direct push soil vapor survey approaches. In addition, a vacuum is not induced during sample collection (which could impact results). Since the sorbing materials are designed to equilibrate with the environment, a key assumption is that the concentration distribution will also be stable during the sampling campaign.

Atmospheric pressure is the force per unit area exerted against a surface by the weight of air above that surface in Earth's atmosphere. This pressure typically is measured by a barometer and often is referred to as barometric pressure. Air typically flows from high pressure to low pressure. The phenomenon whereby air exchanges between the subsurface and ground-level elevations is referred to as barometric pumping. When atmospheric pressure is higher than the subsurface pressure, air is induced to flow through wells open to the air into the subsurface. Conversely, when atmospheric pressure is lower than subsurface pressure, air can flow out of wells into the atmosphere, taking with it volatile gas–phase constituents. Therefore, when barometric pressures decrease at the ground surface, soil vapors can migrate through soil pores or conduits open to the surface. It has long been known that barometric pumping occurs in the subsurface (Auer, Rosenberg, Birdsell, & Whitney, 1996; Rossabi, 1999). In fact, devices for exploiting these observations by enabling passive vapor extraction have been developed and commercialized.

When buildings are in direct contact with the soil, barometric pumping also can induce vapor intrusion. Advection-driven pressure differentials between the building interior and the immediate subsurface can transport soil gas indoors (Johnson & Ettinger, 1991). Gas-phase chemicals can enter buildings through cracks, seams, utility penetrations in subsurface walls and floors, or through floors in contact with the ground surface.

New sensor devices and data processing platforms allow for continuous monitoring of multiple variables simultaneously. As a result, hazardous situations can be rapidly identified; in some cases, remediation responses are automatically triggered. The effort discussed in this article focuses on a neighborhood near an active oil and gas production field in Kuwait where multiple homes recently exploded. Automated sensor-based continuous monitoring was employed as part of an investigation to identify causes. While additional work will be required to completely understand the mechanics involved, preliminary observations warrant immediate consideration of key factors related to whether risk levels remain static and whether current industry practices are capable of identifying worst-case scenarios and raise new questions about how best to identify when continuous monitoring would be required to minimize negative receptor and property impacts.

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METHODS AND MATERIALS

GasClam Sensor Network

The GasClam (Ion Science, Fowlmere, United Kingdom) is a subsurface vapor monitoring device capable of continuous measurement of methane, total volatile organic constituents, carbon dioxide, oxygen, hydrogen sulfide, and atmospheric pressure. Originally developed for landfill vapor monitoring, the GasClam is also well suited for vapor intrusion applications. Methane and carbon dioxide are measured using an infrared technique, while oxygen and hydrogen sulfide are measured via electrochemical detection. Total volatile organic constituents are measured via photoionization detection. Atmospheric pressure is monitored with a piezoelectric sensor. The entire system is housed in a stainless steel case, weighs 6 kilograms, is battery operated (2 alkaline D cells for up to 3 months of continuous measurement), and can be integrated with telemetry for remote data retrieval.

For this project, a total of 20 GasClams were deployed in a neighborhood bordering an oil and gas extraction field, with a special emphasis on two specific depths: 1 meter (m) and 8 m below grade. The units were lowered into monitoring wells screened and sealed at specific depths of interest to avoid cross-contamination and vapor exchanges with the surface. Sensor measurements were made every hour, with each parameter represented as a separate data channel.

The GasClam units were calibrated by measuring standard methane levels set to 0 percent volume to volume (v/v) and 60 percent v/v using certified-grade SIP Analytical standards (Kent, United Kingdom). It is assumed that methane readings above 50 percent represent hazardous conditions. Atmospheric pressure sensors were calibrated using ambient pressure readings from a certified manometer in a calibration laboratory and a 100 millibars pressure applied using a calibrated pressure ring. Oxygen sensors also provide linear output, and calibration includes developing a 2-point standard curve using certified-grade SIP Analytical standards for 0 percent v/v and 20.9 percent v/v.

Waiora Platform

Waiora is a monitoring, reporting, and consensus-based analysis platform that integrates sensors, telemetry, geographical information systems, and automated processing and visualization capabilities to produce real-time geostatistically rendered contour diagrams and multivariate analytical output (Kram, Beighley, & Loaiciga, 2010; Kram, Sirivithayapakorn, & Beighley, 2005; Groundswell Technologies, Inc., Santa Barbara, California). Recent integration with cloud-based Internet technologies allows for robust, scalable, on-demand reporting and project management (Exhibit 1). For the demonstration described, Waiora was integrated with field sensors monitoring soil vapor parameters in a vapor intrusion monitoring context. This demonstration focused on characterizing contaminant and other parameter distributions in three dimensions. More specifically, this pilot project focused on methane, total volatile organic constituents, carbon dioxide, oxygen, hydrogen sulfide, and atmospheric pressure distributions based on GasClam sensor measurements. Data were collected from the sensor network from May 19, 2011, through June 6, 2011. The six channels of data were tracked simultaneously approximately every hour.

Waiora is comprised of a modular configuration that is designed to function like traditional desktop software packages. This automated monitoring, data management, and analysis platform features modules, tabs, tools, time series, contouring, contouring with time series, two-dimensional and three-dimensional playback loops, transect “slicing,”

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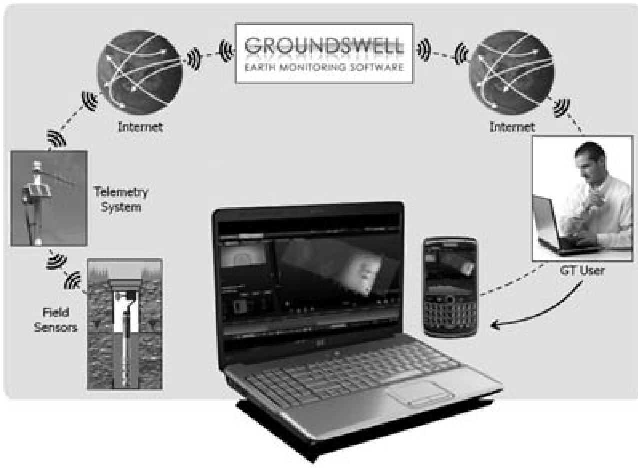

Exhibit 1. Waiora data flow from sensor to web components and end-user

statistical controls, model calibration, and document repository with sharing capabilities. Throughout the Waiora platform, images and tabular results can be exported for use in reports and presentations. High-resolution graphic format options include shapefile, .png, .jpg, and .csv for tabular data. Thresholds can be integrated to trigger notification based on regulatory exceedances and operational constraints required for controllers.

Waiora processes historical data obtained from site databases as well as real-time data obtained through sensors and telemetry. When integrated with live sensor networks, much of the manual effort currently expended on data collection, report graphics generation, and information dissemination becomes automated, continuous, and integrated into project management protocol. Since Waiora is entirely web based, no software downloads are required, and all data are accessible through a password-protected on-demand configuration from anywhere with an Internet connection.

Waiora is a sensor-neutral platform and is designed to poll either directly from the sensors or from an intermediary data portal at desired frequencies. Sensor data files generated from the sensor networks typically are sent to an ftp site residing on the Internet where they are automatically accessed via a sensor portal and uploaded to the Waiora automated processing and project management platform through the Groundswell or client website. Data are automatically retrieved at a preset frequency from the ftp site and placed within the sensor portal for rapid viewing of the raw data (e.g., within seconds of data transfer), flagging via threshold and search and control commands, and archiving for future review. These files are also automatically normalized for instant automated upload into the Waiora Platform database, where they become available to the end user for performing analytical and visualization tasks. For instance, as new sensor data are uploaded automatically to the Waiora database, the end user gains new time steps, which can be selected for performing time-series analyses and playback loops and for generating reports. The entire data acquisition and management system is maintained within a cloud computing framework, affording streamlined flexibility and stability under variable data loads in an on-demand context. The cloud-based platform can be used to manage multiple sites simultaneously and to perform consensus-based analyses among collaborating users working in remote locations.

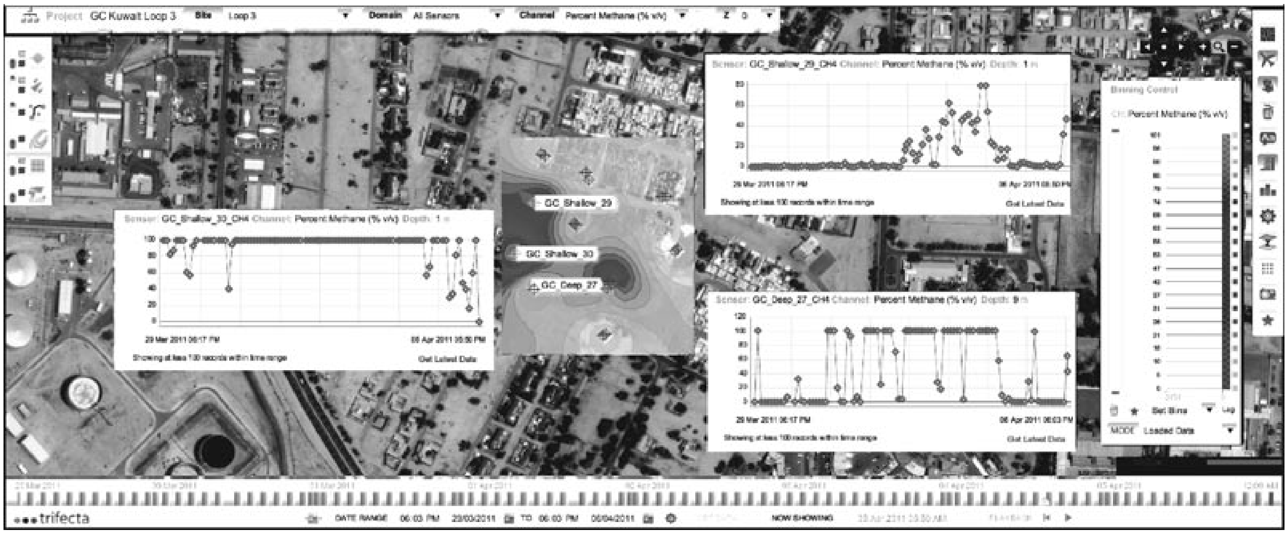

Exhibit 2. Time-stamped methane distribution with time series charts

RESULTS AND DISCUSSION

While six channels of data were tracked simultaneously approximately every hour for several weeks, only a subset of all the data collected are discussed here. Key points related to parameter dynamics, temporal relationships, and trends for selected channels are addressed.

Exhibit 2 depicts the spatial distribution of methane concentrations in percent volume at a depth of 1 m below grade for a selected time step as well as time series charts for selected data collection points. The time series charts depicting methane percent on the y-axis and time on the x-axis demonstrate that methane concentrations are not static for the selected monitoring locations (Exhibits 2 and 3). Exhibit 4 displays the methane level time-series chart for all the sensors over the selected time range. A temporal pattern can be seen for several of the sensor locations; dramatic drops in methane levels, often rapidly ranging from 100 percent down to 0 percent, appear to occur at specific times during the day. In this case, the majority of these methane level reduction events occur between 9:00 P.M. and 3:00 A.M. local time.

Exhibit 5 displays a three-dimensional image of the distributions of methane for a selected time step, with an aerial photograph of the site overlaying the contoured isosurfaces. This type of image can be used to identify where areas of risk are highest or above a threshold of particular concern. In the context of a playback loop, users can determine when and where risk levels exceed a specific threshold, leading to an understanding of when and where worst-case scenarios are prevalent.

Exhibit 6 shows time-series charts for methane, atmospheric pressure, and oxygen readings. For several sensor locations, there is an inverse correlation between methane and oxygen; every time methane drops and oxygen rises, there is a slight increase in atmospheric pressure in the subsurface. Immediately after methane rises and oxygen falls, the pressure also drops a slight amount. Exhibit 7 displays a timeline of methane and

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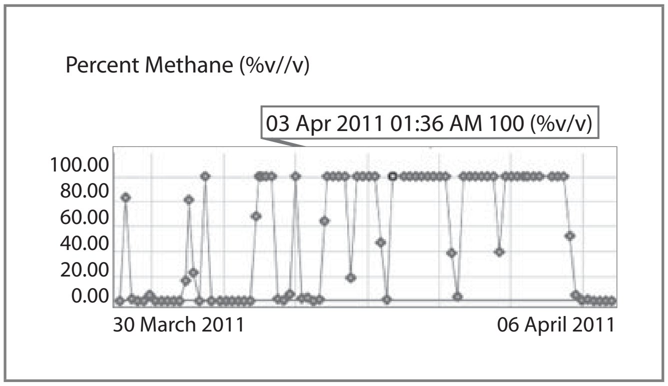

Exhibit 3. Close-up of methane time series chart for a selected data collection point

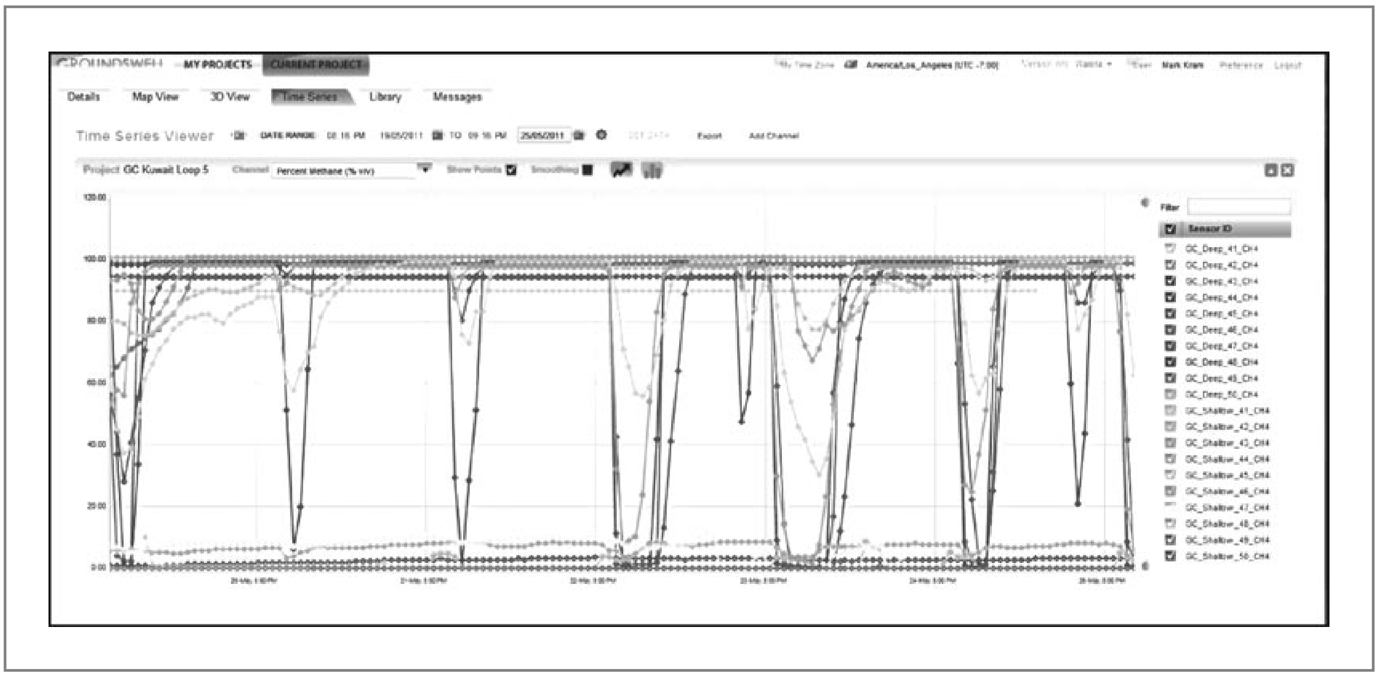

Exhibit 4. Methane time series chart for multiple sensor locations

atmospheric pressure distributions at 1 m depth. High-risk levels of methane appear to be either migrating from the south toward the northeast or from deeper zones as pressures drop. This is a very interesting interplay of multivariate parameters and suggests that vapors may be moving in response to pressure changes. Further analyses are necessary to confirm whether barometric pumping is occurring.

Most conventional subsurface VI characterization methods can be described as active (where samples are extracted by drawing an aliquot into a sampling receptacle and subsequently analyzed) or passive (where devices are deployed with a trapping material or mechanism that is retrieved after a preset duration prior to sample analysis). Each of these methods has its merit and can be useful for understanding subsurface VI risks under static conditions. However, since these represent noncontinuous approaches (e.g., active soil vapor–sampling campaigns typically represent multiple point-in-time and point-in-space measurements later compiled for a snapshot spatial rendering over the campaign time

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Exhibit 5. Time-stamped three-dimensional methane distribution underlying an air photo of a residential neighborhood

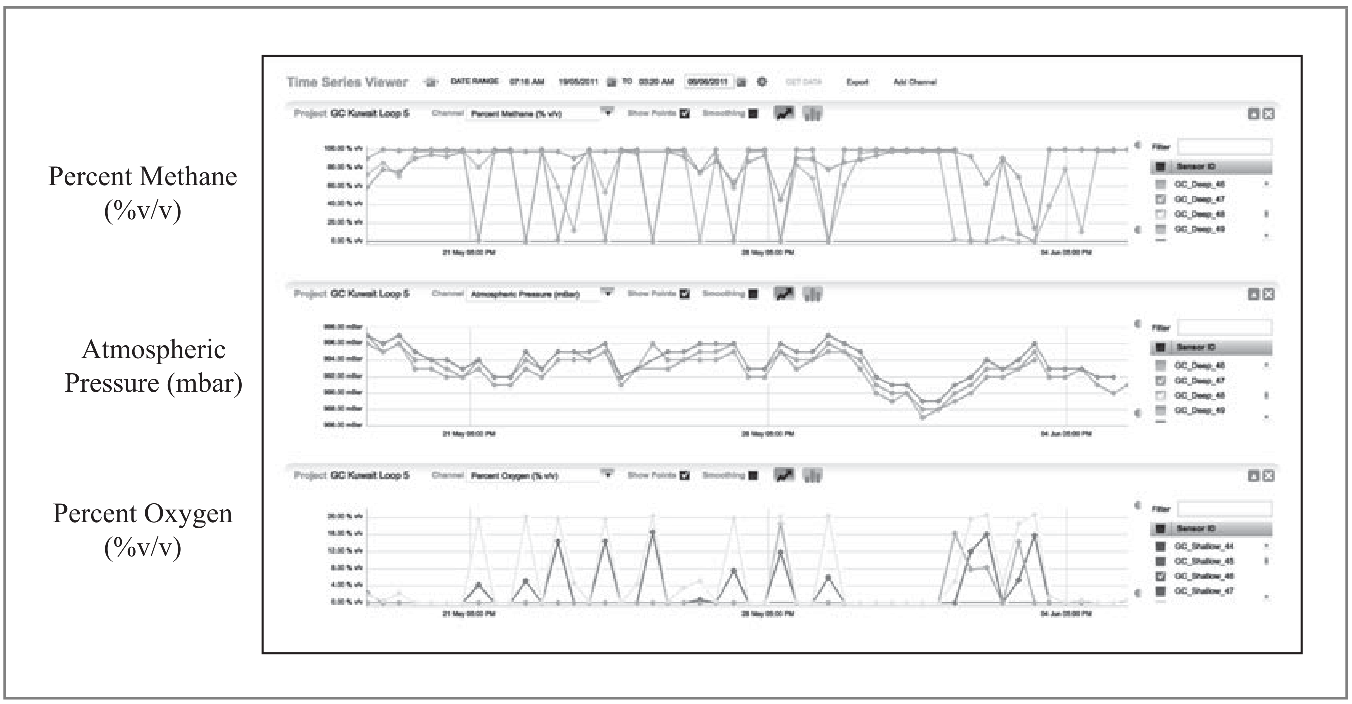

Exhibit 6. Time series charts for methane, atmospheric pressure, and oxygen sensors, respectively

duration), they may not always be appropriate for identifying worst-case scenarios, particularly under dynamic settings such as those observed for this investigation. Composite passive samplers also represent point-in-time and point-in-space approaches. Furthermore, they could be susceptible to adsorbent concentration fluctuations when subsurface concentrations are dynamic and equilibrium between the sorbing medium and subsurface conditions adjusts as conditions change.

Given the limited number of cases in the United States documented to date where subsurface vapor concentrations fluctuate, it is not yet certain how prevalent dynamic

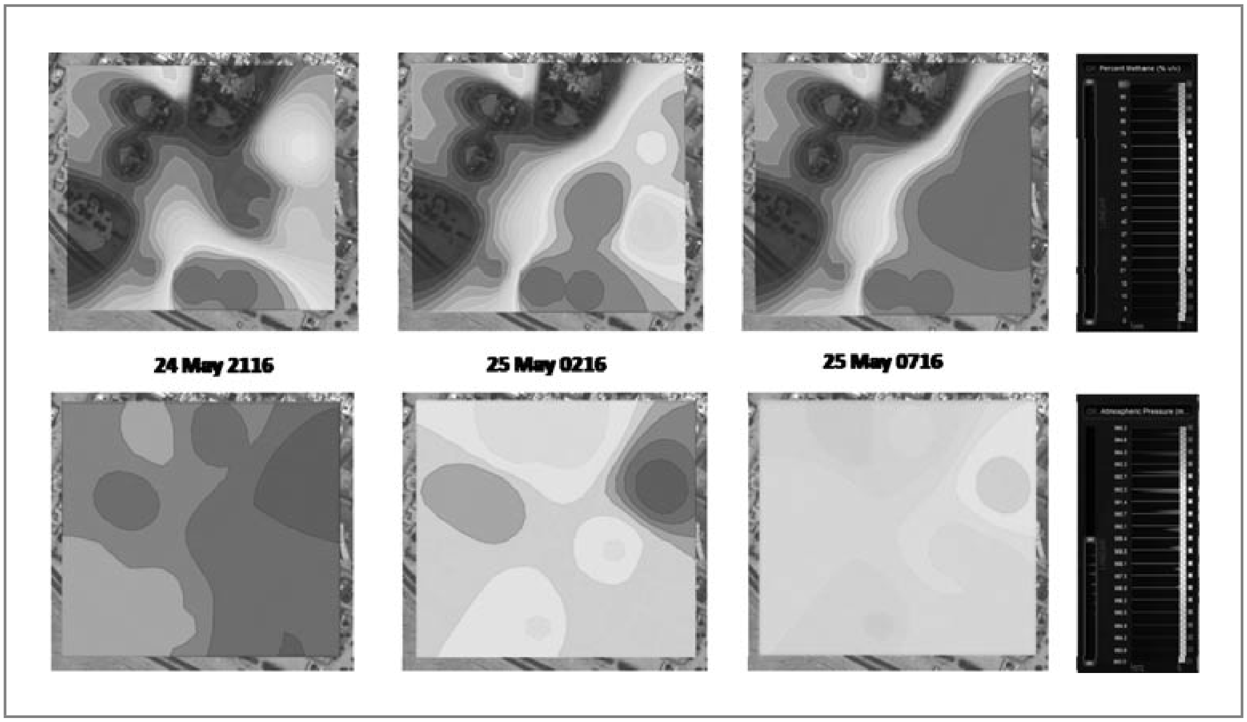

Exhibit 7. Timeline of methane and atmospheric pressure at 1m depth

conditions may be. Several European investigators have observed similar methane fluctuations and relationships with atmospheric pressure at numerous sites since continuous monitoring (e.g., on the order of every hour) has been implemented at petroleum release sites (Contaminated Land: Applications in Real Environments, 2011). This suggests that it would be prudent for practitioners to deploy continuous monitoring systems to evaluate when and where these types of changes might occur when VI is of concern and to integrate this approach into conceptual site models, particularly when relationships between concentration and pressure are documented. As more cases are analyzed, it could be possible to draw conclusions about when and where it would be appropriate to use traditional approaches based on site-specific temporal and geospatial observations of worst-case scenarios resulting from natural (e.g., barometric) and anthropogenic (e.g., building ventilation) activities and processes. Furthermore, European practitioners are currently advocating the use of exposure risk weighting based on duration of concentration threshold exceedances as well as concentrations. If adopted, this method eventually could lead to more flux- and temporal-based VI risk analyses.

CONCLUSIONS

Continuous subsurface vapor monitoring approaches are relatively new and offer several advantages. For instance, they can provide a more complete understanding about underground conditions, fate, and risk than many other characterization options that do not include measurement of parameter levels and distributions over time. Of most significance, continuous subsurface vapor monitoring approaches can enable practitioners to characterize worst-case exposure and explosion risk scenarios when subsurface vapor encroachment conditions are not static.

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Seven conclusions can be drawn from the continuous monitoring field campaign described, including:

1. Subsurface vapor concentrations can be extremely dynamic in at least some situations.
2. Explosion and exposure risk levels can therefore also be dynamic.
3. Additional work will be required to be able to determine when dynamic risk conditions exist.
4. For the site considered here, an inverse correlation exists between methane and oxygen levels for several of the monitoring locations, and interactions and exchanges appear to be related to atmospheric pressure changes.
5. Continuous monitoring of subsurface vapor constituents represents a robust option when the objective is to characterize worst-case risk scenarios.
6. Three-dimensional distributions of subsurface vapor constituent levels can reveal where high-risk subsurface areas exist relative to receptors and explosion hazards.
7. Continuous sensor-based monitoring of the three-dimensional distributions of subsurface vapor constituent levels can enable practitioners to design and deploy customized remedial responses to reduce explosion and exposure risks that exceed user-selected thresholds.

It is anticipated that the proliferation of continuous monitoring efforts will lead to similar conclusions at other sites. As a result, future characterization efforts, legal decisions, and restoration activities could be impacted by approaches that include continuous sensor-based monitoring.

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