Passive to Active Tie-In for Soil Gas Surveys: Improved Technique for Source-Area, Spatial Variability, Remediation-Monitoring, and Vapor-Intrusion Assessment

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The mass-to-concentration tie-in (MtoC Tie-In) correlates passive soil gas (PSG) data in mass to active soil gas data in concentration determined by the US EPA Method TO-17 or TO-15. Passive soil gas surveys consist of rapid deployment of hydrophobic sorbents (dozens to several hundred locations typically installed in one day) to a depth of six inches to three feet in a grid pattern with exposure in the field from three days to two weeks to target a wide variety of organic compounds. A power function is used on a compound-to-compound basis to correlate spatially varying mass (nanograms) from selected locations within a passive soil gas survey to concentration ($\mu g/m^3$) at those same locations. The correlation from selected PSG locations is applied to the remainder of the PSG grid. The MtoC Tie-In correlations provide added value to a PSG survey, with the PSG data then used to estimate risk throughout the limits of the investigation for quantitative assessment.

The results from a site in northern California show the MtoC Tie-In correlations for both benzene and total petroleum hydrocarbons (TPH). The correlations are applied on a compound-to-compound basis to the remaining locations in the PSG grid to provide an estimate of concentration that can be used for comparison to risk/screening levels or fate-and-transport diagnostic tools (partitioning equations, solubility laws, etc.). An example of how the correlations are applied is presented in tabular form. The results from a chlorinated solvent survey show the MtoC Tie-In correlation from a site in Maryland for tetrachloroethene (PCE). In this instance, there was a near-perfect relationship between the PSG mass and the active soil gas concentration (R^2 value of 1). The concentration estimated throughout a PSG grid enables a vast new realm of interpretive power at sites. Several other sites are discussed, including an example application for groundwater. © 2009 Wiley Periodicals, Inc.

INTRODUCTION

The mass-to-concentration tie-in (MtoC Tie-In) correlation relates passive soil gas (PSG) data in mass to active soil gas data in concentration determined by US EPA Method TO-17 or TO-15. To obtain quality data, passive soil gas samples must be analyzed following US

EPA Method 8260B, or equivalent, that includes internal standards and surrogates with all analyses to obtain quality data. A power function is used on a compound-to-compound basis to correlate *mass* nanograms (ng) from selected locations within a passive soil gas survey to *concentration* ($\mu g/m^3$) at those same locations. The correlation from selected PSG locations is applied to the remainder of the PSG grid. The MtoC Tie-In correlation provides added value to a PSG survey, and the PSG data can then be used to estimate risk throughout the limits of the investigation with a concentration array. The MtoC Tie-In brings PSG testing to a Level III/IV tool for quantitative assessment as opposed to a screening tool/semiquantitative method as defined by the US EPA (1988).

BACKGROUND

The MtoC Tie-In correlation provides added value to a PSG survey, and the PSG data can then be used to estimate risk throughout the limits of the investigation with a concentration array.

The interpretation of time-integrated PSG surveys can be augmented whereby select locations at a site are chosen where active soil gas measurements can be used to develop a relationship between passive soil gas mass and active soil gas concentration. This is termed *mass-to-concentration tie-in*, or MtoC Tie-In. At the completion of a PSG survey, select locations where PSG samples were obtained are developed into shallow active soil gas vapor ports (e.g., three to five locations for surveys less than 50 PSG locations and 5 to 10 percent for surveys over 100 PSG locations). The tie-in locations should be chosen such that there is adequate distribution across the mass ranges encountered on a chemical of concern (COC) by COC basis from the PSG results, and the active soil gas sampling times should be determined in accordance with the detection limit—that is, the mass found at the PSG location and the sampling volume to be used for the active sampling. Upon completion of the active soil gas sampling at the select locations of the PSG survey, a correlation can be established between PSG mass and active soil gas concentrations that can be applied to the remaining PSG locations across the site. For example, for a PSG survey that consisted of 100 locations with tie-in correlations measured at five of these locations, the established correlation between mass and concentration can be applied at the remaining 95 locations to provide a concentration estimate on a COC by COC basis. These concentration estimates can be used to (1) determine regions across the PSG grid where additional investigation is needed, (2) establish regions across the PSG grid where there are either exceedances in regulatory screening levels or risk-based cleanup levels, and (3) assess areas in the PSG grid where vapor-intrusion issues are of concern. The benefits of using the tie-in correlations across the PSG grid instead of collecting only active soil gas measurements are that a large number of sample locations can be simultaneously and rapidly measured to provide concentration estimates over a large area with both minimum disruption/disturbance at a site and in a cost-effective, efficient manner.

MtoC Relationship for Chlorinated Compounds at a Single PSG Location

An example of the relationship between PSG mass and active soil gas concentration is shown in Exhibit 1, which shows the correlation between PSG mass and active soil gas concentration for four compounds at one location. In this instance, the most impacted PSG location, from an array of 22 samplers at the site, was chosen for follow-up sampling using US EPA Method TO-15. The site is located in Indiana, and the investigation took place in November 2003 at a former dry-cleaning facility inside the building. The PSG samplers were exposed for six days in the shallow vadose zone and were deployed to a
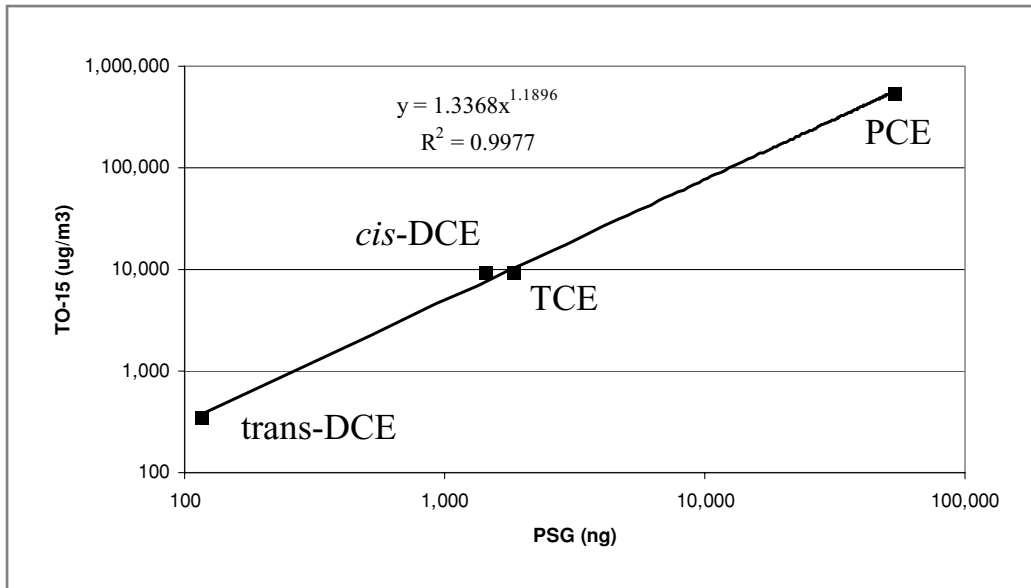
Exhibit 1. Mass-to-concentration relationship for four chlorinated compounds at a site in Indiana

depth of 14 to 16 inches below grade. An active soil gas sample was collected through the concrete slab with a vapor probe set to a depth of 18 inches. The active sample was collected over a period of 24 hours in a six-liter canister.

The relationship between the passive and active data across the four compounds is very strong, with a nearly perfect correlation factor. The time-integrated PSG mass collected over a six-day period is related to a shorter-term active soil gas sample concentration through the correlation above. The utility of PSG as an investigatory tool is greatly enhanced by relating active soil gas concentration to the array of deployed samplers.

MtoC Relationship for Chlorinated Compounds at Multiple PSG Locations

An example of the relationship between PSG mass and active soil gas concentrations at three different locations at a site in the eastern United States demonstrates the spatial strength of the correlations. Thirty-seven PSG samplers were exposed for a period of seven days in the subsurface at this site. Three PSG locations were chosen for follow-up sampling using active sampling via US EPA Method TO-17, with 30-minute soil gas samples taken at a flowrate of 20 mL/min (US EPA, 1999, 2002). The site is located in northern Maryland, and the investigation took place in September 2007 at a former dry-cleaning facility, with samples collected beneath the concrete slab. Exhibit 2 shows tetrachloroethene (PCE) results for both passive and active samples at the three tie-in locations.

The relationship between the time-integrated PSG and active soil gas data is nearly perfect. The spatial characteristics between active and passive soil gas sampling are impressive at this site. The three tie-in points are approximately 20 feet apart in a triangular configuration. The correlation was applied at other parts of the site where the PSG survey revealed other significant quantities of PCE. The active soil gas probes were

$$y = 3.5778x^{0.8223}$$
$$R^2 = 0.9916$$
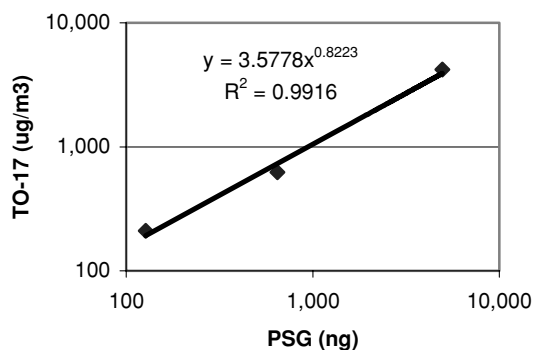
Exhibit 2. Mass-to-concentration relationship for PCE at three locations at a site in Maryland

installed to a depth of 18 inches and contained a sand pack. Additional discussion on the typical soil gas probe installation is provided below.

At each tie-in location, the field technician drilled three holes through the slab. Each hole was drilled using a hammer drill with a 1.5-inch diameter drill bit to a depth of 18 inches. A 0.25-inch diameter length of Teflon® tubing was lowered down the hole until it was approximately 1 inch from the bottom of the hole. The tubing had a screen implant inserted in the lower end of the tubing to prevent the uptake of particulate matter. The end of the tubing extending above the slab had a stainless steel valve that was swaged to it prior to sampling.

After the tubing was lowered into the hole, dry, clean silica was slowly poured into the hole until reaching the lower level of the concrete slab. A layer of granular bentonite, approximately one inch thick, was then poured on top of the silica and moistened by adding distilled water. This process was repeated until the hydrated bentonite filled the annular space of the hole to grade. The hydrated bentonite was then compacted around the tubing and finished once again to grade. Using a 60-mL syringe, the sampling hole and train were slowly purged of three soil gas pore volumes, and the valve was left in the closed position.

MASS-TO-CONCENTRATION TIE-IN: PETROLEUM HYDROCARBON SITE

The following results from a site in northern California show the MtoC Tie-In correlations for both benzene and total petroleum hydrocarbons (TPH) from C5 to C10. Thirty-six time-integrated PSG samplers were exposed to soil gas at shallow depths for seven days, and three of those locations, inside a mini-mart, were chosen to conduct the follow-up active soil gas testing as tie-in points, with 20- to 30-minute samples at a flowrate of 20 mL/min. The three tie-in points are approximately 20 feet apart in a triangular configuration. Exhibit 3 shows the MtoC correlations for benzene and TPH C5-C10.

The correlations are applied on a compound-to-compound basis to the remaining locations in the PSG grid to provide an estimate of concentration that can be used for comparison to risk/screening levels or fate-and-transport diagnostic tools (partitioning equations, solubility laws, etc.). An example of how the correlations are applied is illustrated in Exhibit 4, whereby benzene and TPH concentrations are tabulated from the results of the PSG survey and the correlations are applied throughout the remainder of the
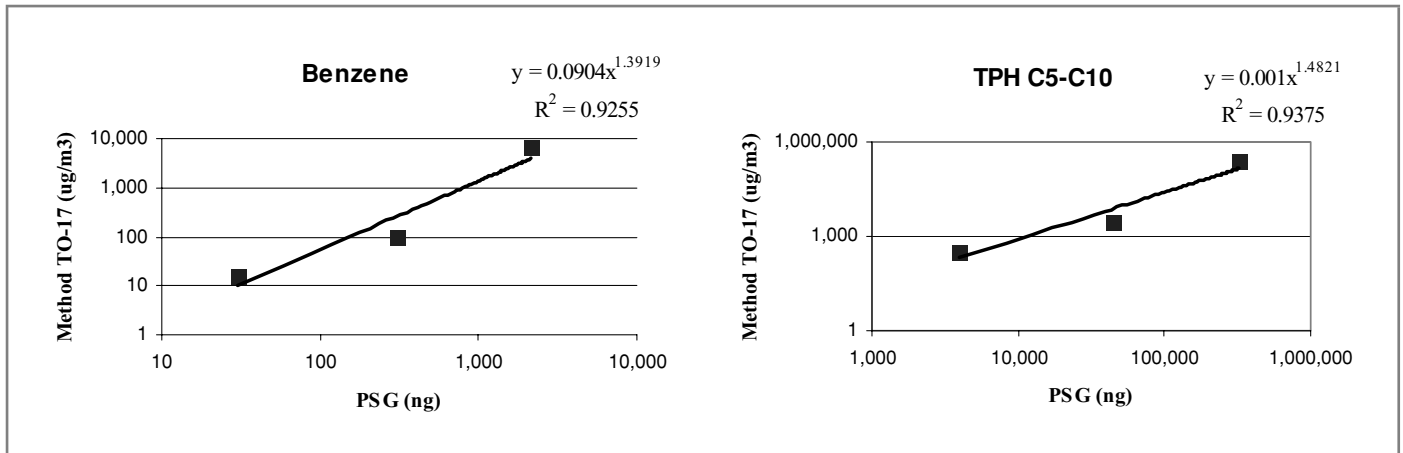
Exhibit 3. Benzene and TPH MtoC relationships from a service station site in northern California

Exhibit 4. Application of tie-in correlation to portion of PSG grid

	Units	SV-14	SV-15	SV-16	SV-17
Benzene	ng	259	28	2,160	2,425
	ug/m3	207	9	**3,957**	**4,649**
TPH C5-C10	ng	58,033	37,313	325,988	460,879
	ug/m3	11,488	5,970	**148,291**	**247,743**

PSG grid. The bolded values indicate values that are above published regulatory screening levels.

A second site in northern California with similar conditions yielded the following correlations and power functions. For the sake of brevity, the graphs are not shown. An example of how to apply the developed correlations is provided below.

<u>Benzene</u>
Active $= 0.8682 \times$ PSG (ng)$^{1.0889}$
$R^2 = 0.8801$
[PSG range 17–14,698 ng and TO-17 range 15.9–62,535 μg/m^3]
Example: A PSG value of 3,000 ng results in 5,307 μg/m^3 [$0.8682 \times$ PSG $(3,000)^{1.0889}$]

<u>TPH C5-C10</u>
Active $= 0.0007 \times$ PSG (ng)$^{1.5946}$
$R^2 = 0.9409$
[PSG range 2,500–612,980 ng and TO-17 range 151–804,083 μg/m^3]
Example: A PSG value of 30,000 ng results in 9,645 μg/m^3 [$0.0007 \times$ PSG $(30,000)^{1.5946}$]

MASS-TO-CONCENTRATION TIE-IN: MIXED PETROLEUM HYDROCARBON AND CHLORINATED SOLVENT SITE

A passive soil gas survey was conducted at a site in northern California with an active remediation system that consists of dual-phased extraction for soil vapor and groundwater. The purpose of conducting a time-integrated PSG survey was to characterize the soil gas regime under the slab of an operating business and to screen areas for risk evaluation/further investigation. Upon completion of the PSG survey, active soil gas sampling at five locations was performed to develop an MtoC correlation (four samples at 10 minutes and one sample for 30 minutes at a flowrate of 20 mL/min). The MtoC correlation was used to quantify vapor-intrusion risk and to identify locations of future remediation and investigation efforts. Exhibit 5 shows the five locations of the tie-in points, along with a site map containing the locations of soil borings, groundwater wells, and the location of the treatment plant. The PSG samplers remained in the subsurface for 11 days. Exhibits 6a and 6b shows the spatial distribution from the PSG survey for benzene, toluene, ethylbenzene, and xylenes (BTEX) and PCE, respectively.

> The purpose of conducting a time-integrated PSG survey was to characterize the soil gas regime under the slab of an operating business and to screen areas for risk evaluation/further investigation.

The time-integrated PSG survey for BTEX revealed there are sources of petroleum that are beyond the influence of the current treatment system. In other words, the previous discrete sampling did not reveal the complete picture of the source areas. As an example, there is a total BTEX mass of 198,552 nanograms at PV-8. Exhibit 7 shows the MtoC correlations for both BTEX and PCE from the five tie-in points at the site.

As an example of how to use the MtoC correlations, the active soil gas concentration at PV-1 for BTEX is 8,727 $\mu g/m^3$. All the other non-tie-in PSG locations could also have concentrations developed through the correlations. The discovery of a PCE soil gas plume at the site sourced at PV-9 is a significant finding. The PCE MtoC correlation can be applied at PV-9, and the active soil gas estimate there is 7,487 $\mu g/m^3$. Once again, the other non-tie-in PSG locations' concentrations can be estimated through application of the correlation.

The MtoC correlations, developed for seven compounds at this same site, revealed there is clearly a trend between the range of active soil gas concentrations encountered from the tie-in points and the strength of the correlations. Exhibit 8 is a plot of the range of active soil gas concentrations encountered for each compound versus the strength of the MtoC correlation.

The logarithmic line of best fit reveals two-orders-of-magnitude variability of concentration of any compound results in an R^2 of 0.759, which is very strong and significant. Similarly, at one order of magnitude, active soil gas concentration variability results in a correlation coefficient of 0.590, which is suitable for estimations within an order-of-magnitude variability.

LIMITATIONS OF USING MODELS AND EQUATIONS FROM ESTIMATING ACTIVE SOIL GAS CONCENTRATIONS FROM PASSIVE SOIL GAS DATA

Passive soil gas surveys have historically been labeled a "site screening tool" for finding sources of volatile organic compounds. The MtoC Tie-In concept enables a vast new realm of interpretive power by applying PSG survey results with the developed
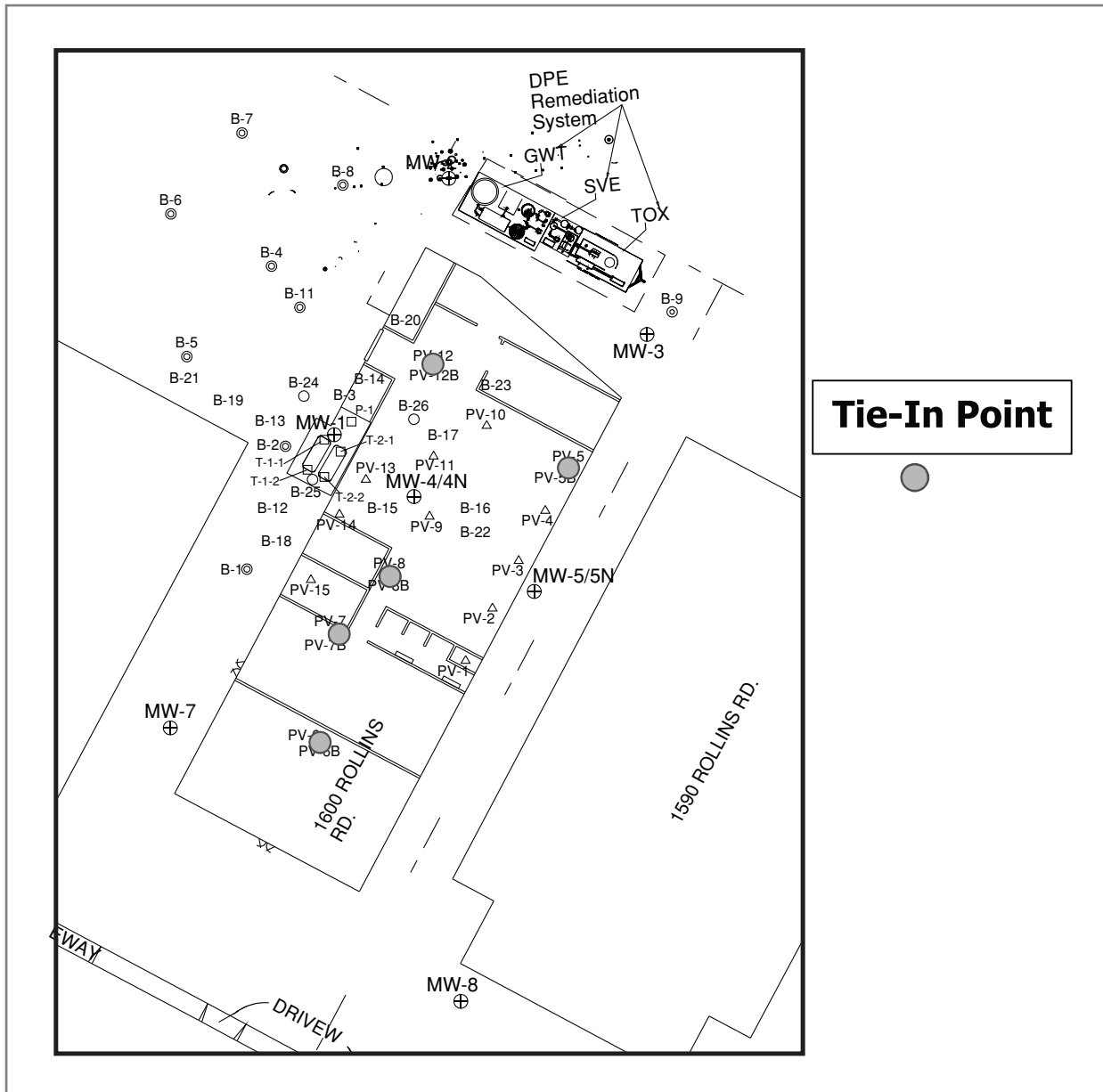
Exhibit 5. Tie-in points for MtoC correlations at an active site in northern California

correlations for risk evaluation, vapor-intrusion assessment, source identification, and identification of regions that require additional investigation. One of the important assets of using the correlation is that the active soil gas concentrations are measured in the field as opposed to the application of an equation or model with several independent variables. The authors emphasize this point, for there are several limitations to the use of equations and models that are discussed in some detail below.

The application of models or equations to convert PSG data to active soil gas concentrations will always be questioned because the determination of independent variables is problematic, as are the underlying assumptions embedded with the equations/models. Models provide predictive capability, but their reliability is difficult to
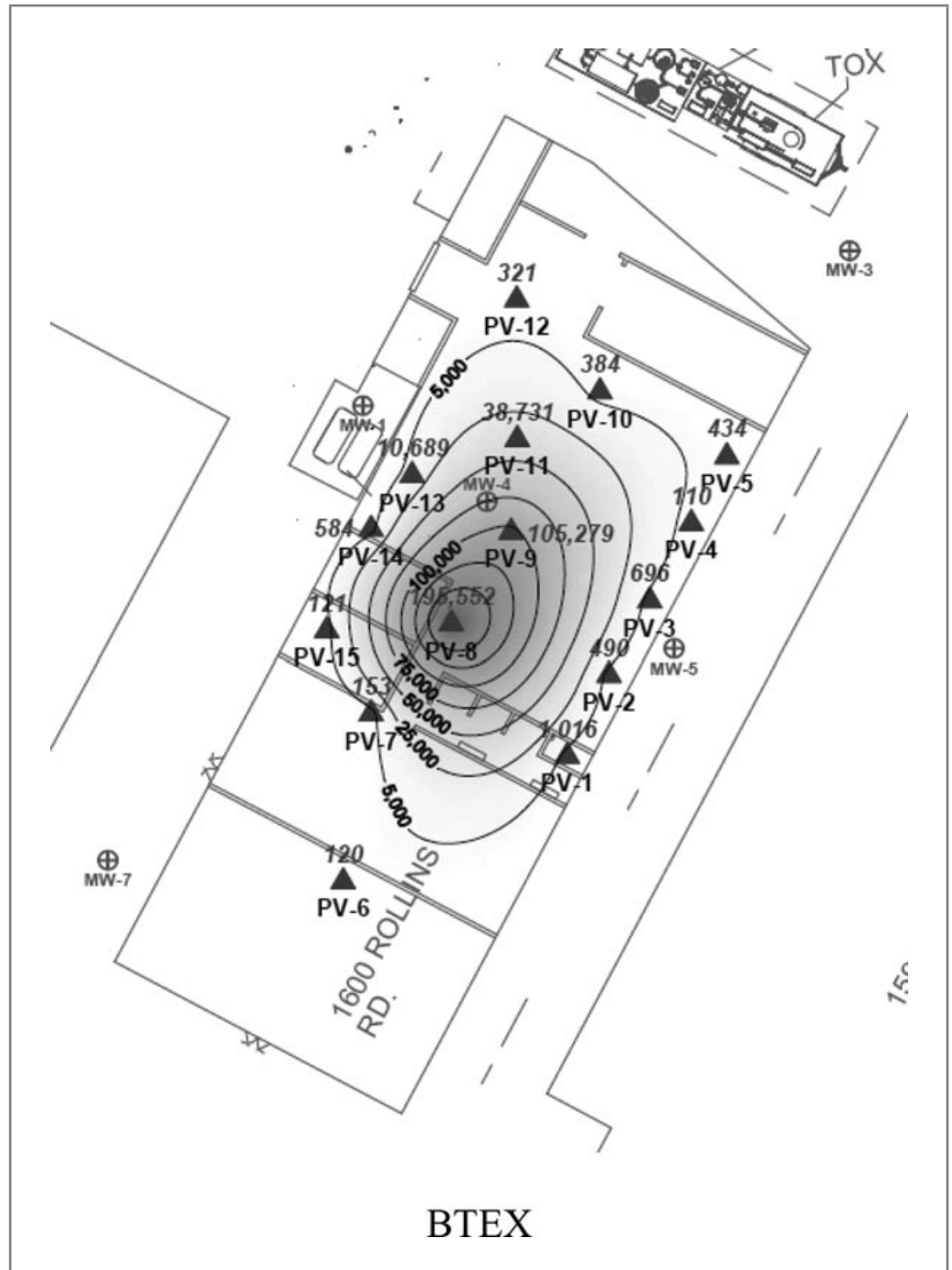
**Exhibit 6a.** PSG survey spatial variability summary for BTEX (units of ng)

defend with limited site-specific data (Interstate Technology and Regulatory Council [ITRC], 2007). The use of models and equations may be useful at the very preliminary stages of an investigation; however, their predictions will be superseded by the collection of site-specific data. The use of extreme and nonrepresentative assumptions is the most common weakness of predictive modeling (ITRC, 2007). When models and equations are used for the determination of active soil gas concentration estimates, an additional layer of
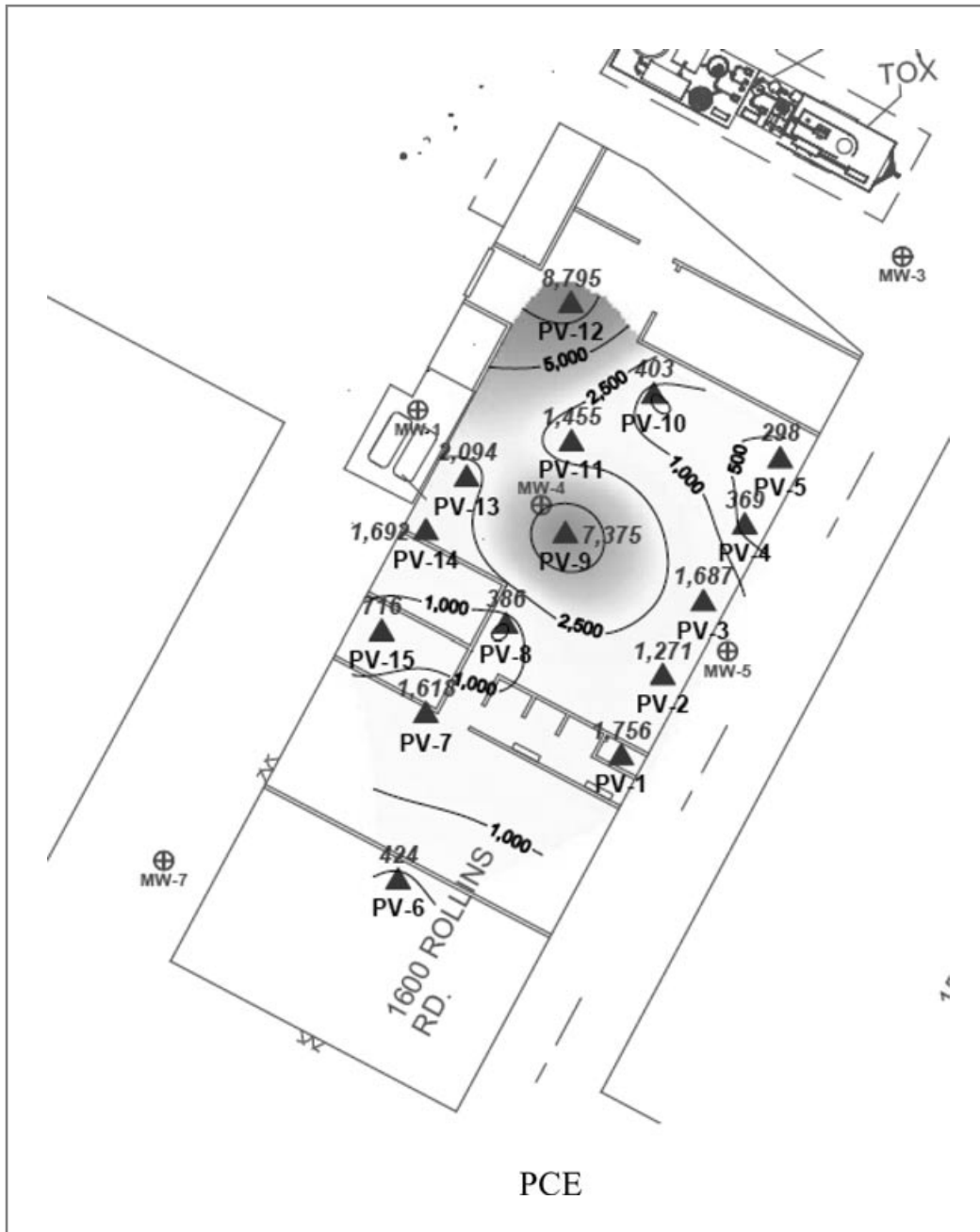
Exhibit 6b. PSG survey spatial variability summary for PCE (units of ng)

regulatory hurdles will be necessary. They are but are not limited to a sensitivity analysis, parameter estimation difficulties, overcoming skepticism, and conceptual model issues. The use of equations or models to determine active soil gas concentrations from PSG survey results presents challenges, and direct field measurements are the preferred option. Therefore, applying a time-integrated PSG survey with an established MtoC Tie-In correlation allows one to provide concentration data estimates for a large PSG grid that are based on site-specific measurement.
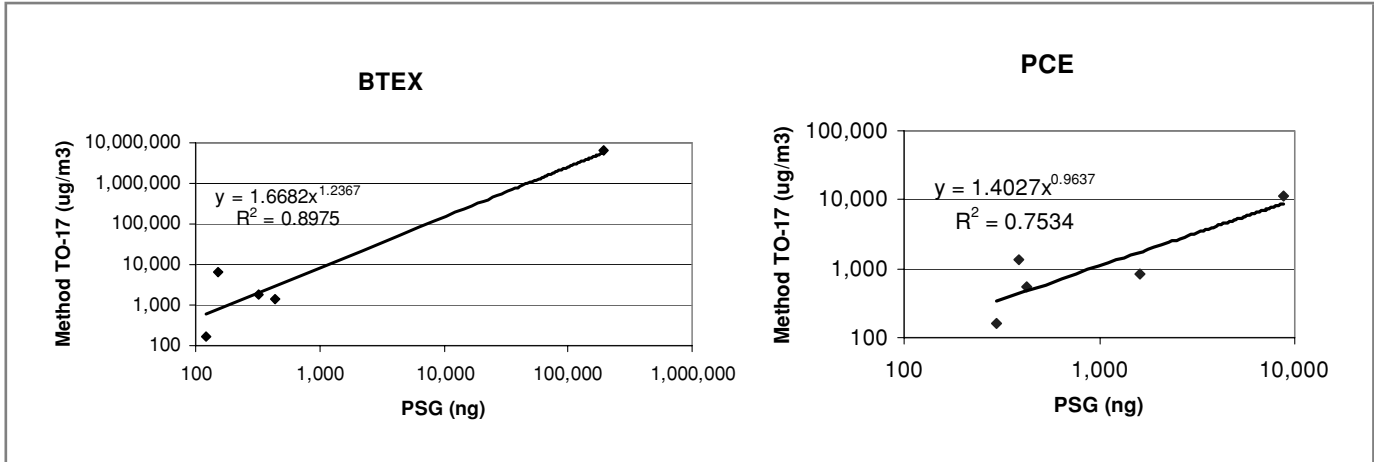
Exhibit 7. MtoC correlations for BTEX and PCE at site in northern California
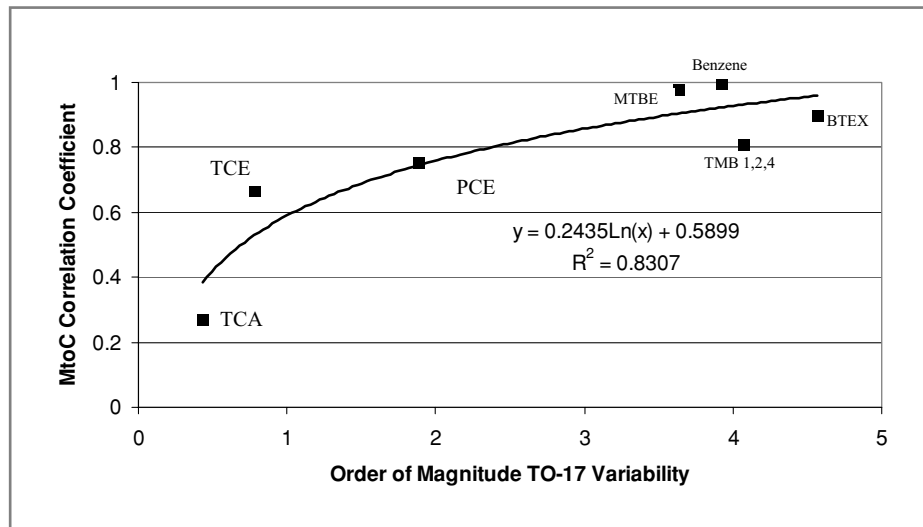
Exhibit 8. Relationship between MtoC correlation and soil gas concentration range for the tie-in points

GROUNDWATER PLUME DEFINITION USING PASSIVE SOIL GAS DATA

The MtoC Tie-In correlation can also be used in a groundwater environment as well. An example application is provided in the following discussion. A total of three groundwater monitoring wells were installed in close proximity to three PSG locations at a site in Utah. The depth to groundwater was approximately 10 to 12 feet below grade. One of the primary purposes of the PSG survey was to guide the placement of permanent groundwater monitoring wells in a previously uninvestigated area of the site. The monitoring wells were installed several months after the PSG survey was performed. An analysis of the PSG masses to the measured groundwater concentrations from the permanent groundwater monitoring wells was performed. The results of this analysis are shown in Exhibit 9, along with an exponential line of best fit, equation, and correlation
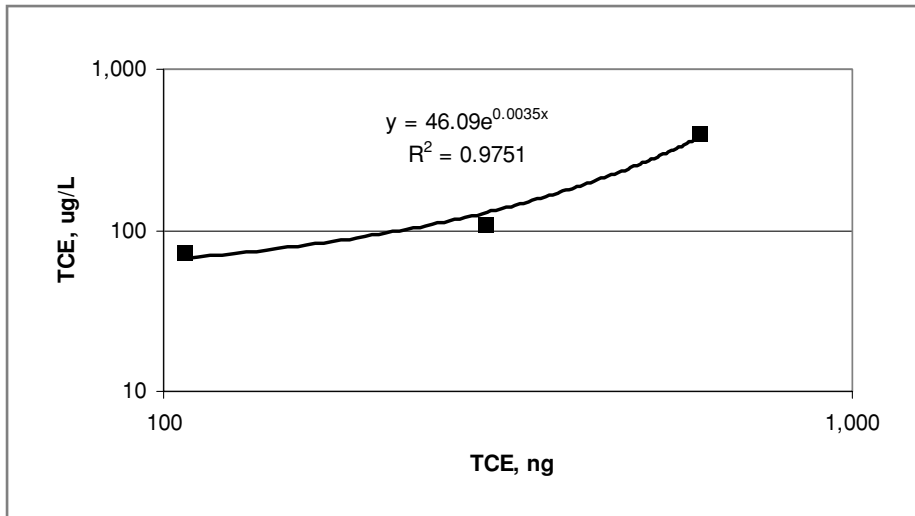
Exhibit 9. Correlation of PSG results from SG-1, 2, and 7 with nearby groundwater monitoring wells

Exhibit 10. Example application of correlation of TCE results for PSG mass and groundwater concentrations for the maximum soil gas encountered at the site

Locale	PSG, ng	Estimated GW, ug/L	Actual GW, ug/L	Delta
SG-7	600	376	400	−23.6
SG-1	294	129	110	19.0
SG-2	107	67	74	−7.0
SG-23	922	1,162	Not Sampled	

Note: The Delta column provides the differences between the actual and estimated groundwater concentrations by applying the site-specific correlation equation.

coefficient. The correlation coefficient suggests 97.51 percent of the variability is accounted for.

The correlation between the PSG masses and the groundwater concentrations for TCE is excellent for the three sample pairs. The equation can be used to estimate the groundwater concentration at other points in the PSG grid. An illustration of using the exponential line-of-best fit is shown in Exhibit 10 for the maximum PSG location (SG-23).

The table illustrates the application of the correlation between PSG results with permanent groundwater monitoring wells that were installed shortly after the PSG survey was performed. The estimated concentration of TCE at a groundwater well that is installed in close proximity to SG-23 is 1,162 μg/L. If there are risk-based cleanup levels established at the site for groundwater that would trigger remedial measures, then the equation can be used to establish regions of high risk that should be verified with a permanent groundwater well. The inherent assumption with applying the correlation, however, is that there are similar soil and groundwater sources with respect to the soil gas

mass measured with the PSG samplers. In other words, if all the soil gas mass in the correlations was from TCE off-gassing from the groundwater plume, then the same assumption would apply at all the locations where the correlation was applied. If there was a recent release in soil, as an example, the soil gas and groundwater relationship should be used with caution.

CONCLUSIONS

The MtoC Tie-In correlations can be implemented at sites at various stages of investigation and/or remediation to estimate concentrations throughout a PSG grid that enables a vast new realm of interpretive power by applying PSG surveys. The following is a summary of the conclusions from this article:

- The MtoC Tie-In correlations provide a useful and time-integrated tool to assess site risks and to determine regions of vapor-intrusion concerns.
- The MtoC Tie-In results have been used successfully to estimate concentrations at PSG locations for the express purpose of comparison to regulatory screening levels and to assess potential areas for active remediation under regulatory oversight.
- The MtoC Tie-In correlations developed at selected points within a PSG grid are strong on a compound-to-compound basis for organic compounds typically encountered at petroleum hydrocarbon—and chlorinated solvent—impacted sites.
- The MtoC Tie-In results can be used for fate-and-transport diagnostic tools (partitioning equations, solubility laws, etc.) in order to determine areas for additional investigation and zones of biodegradation, and to assess natural attenuation factors.
- The MtoC correlations are established using a power function to fit PSG mass and TO-17/TO-15 active soil gas concentration.
- There is a strong relationship between the variability of measured soil gas concentration from the MtoC tie-in points and the R^2 (goodness of fit). The application of an example fitted logarithmic MtoC equation reveals that two-orders-of-magnitude variability of a compound concentration results in an R^2 of 0.759.
- The use of equations or models to determine active soil gas concentrations from PSG survey results presents challenges, and direct field measurements are the preferred option.
- The MtoC Tie-In correlation can also be used in a groundwater environment as well. An example application was provided that had an R^2 of 0.9751.

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