Sustainable, Low-Profile Investigation Technique Finds Numerous Contaminant Sources: Bronx Borough, New York City Example

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ABSTRACT: A cost-effective and non-intrusive technique was implemented to characterize a multi-acre area within New York City as part of an Urban Renewal Area program in order to identify areas where contamination is present in soil, groundwater, and/or soil vapor, and to accurately guide further site investigation activities. The New York City Department of Health (NYCDOH) and the U.S. Environmental Protection Agency (USEPA) chose a passive soil gas (PSG) investigation technique to cover approximately 150 acres in a mixed residential and light industrial neighborhood. Using a state-of-the-art sampling system in both sampler design and sample analysis, a broad range of volatile and semi-volatile organic compounds can be identified, including chlorinated solvents and petroleum hydrocarbons.

The samplers were installed via a small diameter (2cm) hole advanced to a depth of approximately 90 cm using a hand-held rotary hammer drill. The samplers were deployed in a grid/transect-pattern along public right-of-ways to cover the area while virtually eliminating underground utility concerns and generating no waste from soil cuttings. Three-hundred and twenty-four (324) samplers were installed and left in the subsurface for seven days, after which time they were shipped back to the laboratory. The samplers were analyzed following EPA Method 8260C utilizing advanced thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) instrumentation, which does not generate any solvent waste. The resulting analytical data was computerized into compound-specific data files that contained 49 compounds. The spatial distributions of numerous compounds of interest were examined by contour maps that enabled a depiction of the mass changes across the area.

The resulting data from the survey revealed several previously unknown potential sources of petroleum hydrocarbon and chlorinated solvents in the mature urban neighborhood, which present at a minimum the potential for future on-site vapor intrusion issues. As an example of the information available from the survey, tetrachloroethylene (PCE) was recorded at 173 locations with eleven separate/distinct areas of elevated measurements. A statistical evaluation of eight compounds revealed the detections generally followed a Frechet probability distribution. The discovery of these source areas while only sampling in public right-of-ways (e.g., through sidewalks and ornamental tree boxes with no need for property access permissions), with a relatively non-obtrusive technology, provided NYCDOH and the USEPA a powerful tool for potential enforcement follow-up and an invaluable site-management tool.

INTRODUCTION

The use of passive soil gas (PSG) sampling for the identification of soil and groundwater source areas and vapor intrusion pathways is an effective tool for site investigation, spatial variability assessment, and remediation design (O`Neill et al, 2010). PSG sampling and analytical methods are used to target a broad range of volatile and

semi-volatile organic compounds (VOCs and SVOCs), even when present at low concentrations. It is necessary to use state-of-the-art sampling and analytical procedures to provide the foundation for this highly sensitive technology to identify trace levels of compounds present in the vapor phase. The purpose of the work described in this paper was to determine potential sources, plume extent and vapor intrusion risks over a large area in urban environment in the Bronx Borough, New York.

Small, easy-to-carry field kits containing detailed instructions and the requested number of field samples are provided so a project manager can have the samplers installed by local personnel at a convenient schedule. To install a PSG Sampler, an approximately 2 cm diameter hole is made to a 30 to 80 cm depth using a hammer drill, slide hammer, or other comparable equipment. The PSG sampler (which contains two sets of hydrophobic adsorbent cartridges) need only be installed in the upper portion of the hole. The samplers are exposed to subsurface gas for approximately three to 14 days, depending on the objectives of the investigation and the compound concentrations that are expected to be present at the site. Following the exposure period, the Samplers are retrieved and shipped to BEACON's laboratory for analysis.

The samplers in this investigation were deployed in a grid/transect-pattern along public right-of-ways to cover the area while virtually eliminating underground utility concerns and generating no waste from soil cuttings. A trip blank, which remains with the other PSG samples during preparation, shipment, and storage, is included with each batch of up to 40 field samples.

The samplers were analyzed following EPA Method 8260C utilizing advanced thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) instrumentation, which does not generate any solvent waste. Samples for this project were analyzed for a broad range of organic compounds from vinyl chloride to naphthalene. Analytical results were based on a five-point initial calibration, and internal standards and surrogates were included with each sample analysis to provide high quality and defensible data. The sampler design includes two sets of adsorbent cartridges, which allows for confirmatory or duplicate analysis from any selected location.

FIELD SAMPLING PROGRAM

A cost-effective and non-intrusive technique was implemented to characterize a multi-acre area within New York City as part of an Urban Renewal Area program in order to identify areas where contamination is present in soil, groundwater, and/or soil vapor, and to accurately guide further site investigation activities. Following a demonstration of method applicability (DMA) study where two competing passive soil gas technologies were evaluated, the New York City Department of Health (NYCDOH) and the U.S. Environmental Protection Agency (USEPA) chose Beacon Environmental`s passive soil gas (PSG) investigation technique to cover approximately 150 acres in a mixed residential and light industrial neighborhood. Using a state-of-the-art sampling system in both sampler design and sample analysis, a broad range of volatile and semi-volatile organic compounds can be identified, including chlorinated solvents and petroleum hydrocarbons.

An environmental consulting company (confidential) contracted Beacon Environmental in December 2007 to provide 324 PSG samplers, which were placed at a depth of 20 cm in holes that were drilled to a depth of 90 cm. The samplers were left in

the subsurface for seven days and were retrieved in late December 2007. Figure 1 shows the passive soil gas locations across the site.

   After the samplers were retrieved, the results were reported to the client five days after the samplers arrived at the laboratory. The resulting analytical data was computerized into compound-specific data files that contained 49 target compounds. The spatial distributions of numerous compounds of interest were examined by contour maps that enabled a depiction of the mass changes across the area.

DISTRIBUTION OF SELECT ORGANIC COMPOUNDS

   An important goal in the PSG sampling program was to delineate the spatial distribution of soil gas to determine locations of possible sources of VOCs and SVOCs for additional investigation and to identify areas with potential vapor intrusion risks. The results of this investigation are limited to a presentation and analysis of eight compounds that will first entail a detailed examination of the distribution of detections from the reporting limit to the maximum mass analyzed on a compound-by-compound basis. The second portion of this section will be the results of source identification for several different compounds or compound groupings.

FIGURE 1.   Passive soil gas sample locations.

   A detailed analysis of the detections of eight compounds was performed to illustrate the variability of soil gas impacts across the sampled area and to examine the effect of reporting limits on the interpretation of passive soil gas survey results. The most detected compound over the sampled area was tetrachloroethylene (PCE) with 173 detections from the 324 sample locations, which is a relative frequency of detection of 53.7%. Figure 2 is a summary of histograms for compounds detected across the investigation area as defined by the relative number of detections over a mass range defined by natural logarithmic integers. The relative number of detections is simply the number of detections over a natural logarithm integer divided by the total number of detections for

that compound. As an example, there were 41 detections of benzene in the natural logarithmic integer of 3, which when divided by the total number of detections (59) is equal to 0.694. A summary of the natural logarithm integers for the detected masses of each compound in nanograms (ng) is shown in Table 1.

Table 1. Summary of Corresponding Mass Ranges to Logarithm Cycles

Natural Logarithm Integer	Detected Mass Range (ng)
1	2.7-7.4
2	7.4-20.1
3	20.1-54.6
4	54.6-148
5	148-403
6	403-1,097
7	1,097-2,981
8	2,981-8,103
9	8,103-22,026
10	22,026-59,874

The histograms are presented in order from most detected to least detected compound from the eight chosen for detailed analysis. There are four chlorinated compounds: PCE,Chloroform (Chlor), 1-1-1 trichloroethane (TCA), trichloroethylene (TCE) and four petroleum hydrocarbon compounds: BTEX (which is the summation of benzene, toluene, ethylbenzene and xylenes), benzene (Ben), naphthalene (Nap), and Methyl-t-butyl ether (MTBE). The reporting limit for the chlorinated compounds was 5 ng, while the RL for the petroleum hydrocarbon compounds was 25 ng because the petroleum hydrocarbons are often found to be ubiquitous at low measurements in urban environments. Therefore, the four chlorinated compounds have distributions in the natural logarithmic ranges of 1 and 2, while the four petroleum hydrocarbon compounds have distributions beginning in the range of 3 because the RL for these compounds is 25 ng. All of the chlorinated compounds had between 56% and 62% of their detections between the lower reporting limit of 5 ng and the upper end of the natural logarithm mass range of 2 (20.1 ng). The petroleum hydrocarbon compounds detections in natural logarithm mass range of 3 ranged from 41% to 69% bounded by the lower reporting limit of 25 ng and the upper end of the natural logarithm mass range of 3 (54.6 ng). A discussion of the influence of the reporting limit will be discussed in a subsequent section. The chlorinated compounds detections in natural logarithm mass range of 3 ranged from 19% to 28% bounded by the mass ranges that encompass natural logarithm range 3 (See Table 1). The remaining distributions from natural logarithmic ranges of 4 to 10 are governed by the total number of detections in a given range and the total number of detections as defined by each compound's reporting limit. The purpose of performing an analysis of the distribution of detections is to both understand the influence of the reporting limit and to aid in the determination/delineation of source areas.
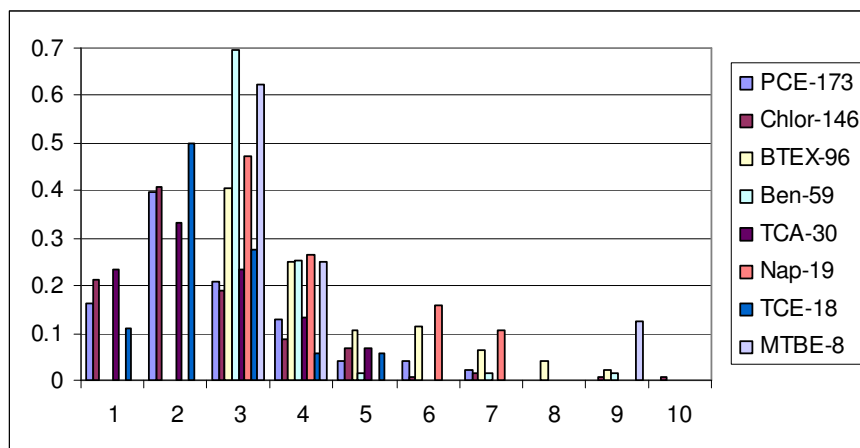
FIGURE 2. **Histograms for eight compounds as defined by the relative number of detections over a mass range defined by natural logarithmic integers.** Number of detections listed next to each compound. Petroleum hydrocarbon compound reporting limit of 25 ng and chlorinated compounds reporting limit of 5 ng.

The significance of the reporting limit is the next topic of discussion in this paper. In order to illustrate the impact of the reporting limit, the four petroleum hydrocarbons in the previous section are compared with a reporting limit of 5 and 25 ng. The number of detections dramatically rises when the reporting limit is lowered from 25 ng to 5 ng. A summary is: BTEX from 96 to 323, Benzene from 59 to 314, Naphthalene from 19 to 39, and MTBE from 8 to 60. There were detections at 99.6% of locations for BTEX and 96.9% of locations for benzene at a reporting limit of 5 ng. It is fair to conclude that these aromatic hydrocarbons are ubiquitous in this urban area at low concentrations. Naphthalene and MTBE are clearly not ubiquitous, however, 25 ng is sufficient in this instance to ascertain potential source areas. The distribution of detections is summarized in the histograms in Figure 3 for the four petroleum hydrocarbon compounds for both reporting limits. There is a substantial difference in the distributions for all the compounds, and occurrences in the natural logarithmic ranges of 1 and 2 are not likely to be representative of discrete source areas.
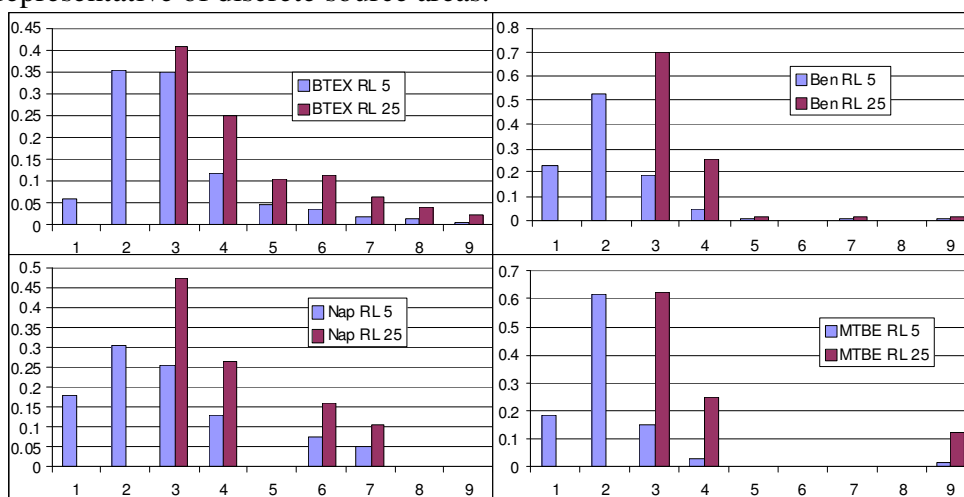

Figure 3. **Histograms for selected petroleum hydrocarbons with two different reporting limits: 5 ng and 25 ng.**

All the detections in the 5 to 25 ng range of the petroleum hydrocarbon compounds are included in the histograms presented in Figure 4. The reporting limit for all compounds is 5 ng. BTEX is now the most frequently detected compound group over the sampled area, with 323 detections from the 324 sample locations or a relative frequency of detection of 99.6%. The frequency of occurrence order has changed now for all the compounds as a result of the change in the reporting limit for the petroleum hydrocarbons.
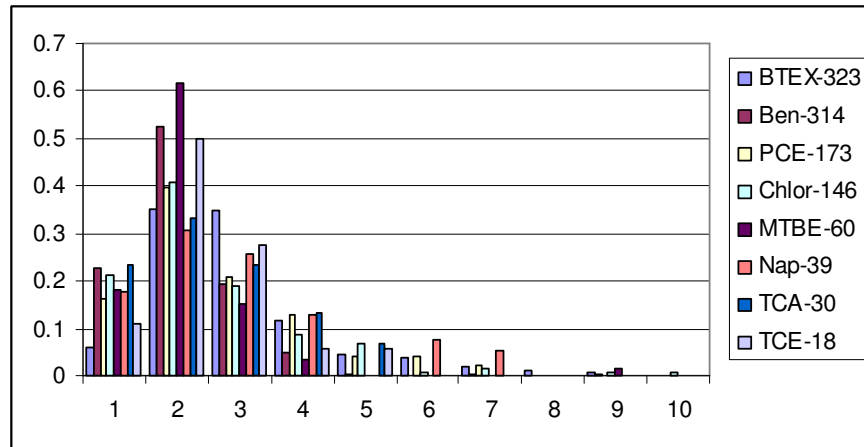

Figure 4.   Histograms for eight compounds as defined by the relative number of detections over a mass range defined by natural logarithmic integers. Number of detections listed next to each compound. Petroleum hydrocarbon compound and chlorinated compound reporting limit 5 ng.

The examination of the frequency of detections over the various mass ranges revealed the occurrence of compounds over the investigation area varied widely. The range and frequency of detections for each of the compounds with the 5 ng reporting limit were used to calculate the exceedence probability of the detections (the probability that a certain value is going to be exceeded). Figure 5 shows the mass of the detections for the compounds over wide range of exceedence probabilities and can be used for comparing the estimated mass of the different compounds for a fixed probability of exceedence. An exceedence probability analysis of the compounds of interest at a site can be used as a tool to assist in the establishment of sources areas or regions of interest at a site. For comparison purposes, the benzene distribution is shown with a reporting limit of 25 ng. There is a 5% probability of exceeding 66 ng (314 detections) with a reporting limit of 5 ng as opposed to 153 ng (59 detections) with a reporting limit of 25 ng.
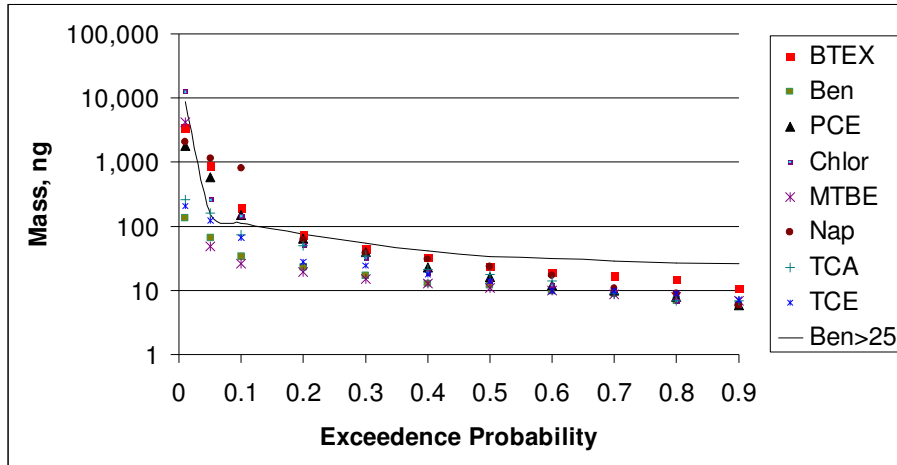
Figure 5.   Exceedence probability distribution for all compounds. Reporting limit of 5 ng unless otherwise noted (Ben>25, reporting limit of 25 ng).

The final data interpretation exercise focused on fitting continuous theoretical probability distribution functions to the detections on a compound-to-compound basis. In modeling solute transport, the variability in a soil property can be characterized by fitting a probability distribution function, indicated by one or more goodness of fit tests, to the property (Cooke et al 1995). Three goodness of fit tests (Kolmogorov-Smirnov, Anderson-Darling and Chi-Squared) were used in this study to determine which of the 60 possible distribution functions fit the data sets. The distribution fitting options define which particular distribution is the best fit to the data (EasyFit Distribution Fitting Software, 2010). Table 2 provides a summary of probability distribution functions for the chlorinated (5 ng reporting limit) and petroleum hydrocarbon compounds (5 and 25 ng reporting limits) that had the best fit to each of the twelve data sets.

Table 2. Summary of Probability Distribution Function Analysis

Reporting Limit	Compound	Values	--------------Goodness of Fit Test--------------		
			Kolmogorov-Smirnov	Anderson-Darling	Chi-Squared
25 ng	BTEX	96	Log-Logistic (3P)*	Frechet (3P)	Frechet (3P)
	Ben	59	Log-Logistic (3P)	Gen. Pareto	Gen. Extreme Value
	Nap	19	Pearson 5 (3P)	Pearson 5 (3P)	Pearson 5 (3P)
	MTBE	8	Burr (4P)	Levy (2P)	NA
5 ng	PCE	173	Pearson 5 (3P)	Frechet (3P)	Frechet (3P)
	Chlor	146	Frechet (3P)	Frechet (3P)	Frechet (3P)
	TCA	30	Fatigue Life (3P)	Lognormal (3P)	Beta
	TCE	18	Frechet (3P)	Burr	Log-Gamma
5 ng	BTEX	323	Burr (4P)	Burr (4P)	Burr (4P)
	Ben	314	Frechet (3P)	Frechet (3P)	Frechet
	MTBE	60	Burr (4P)	Burr (4P)	Burr
	Nap	39	Inv. Gaussian (3P)	Pearson 5 (3P)	Pearson 5

Note: (3P-three parameter and 4P-four parameter)

The probability distribution function that fit the data sets best overall was a Frechet type which falls into the category of an extreme value distribution (Shao, et al 2004). The Frechet probability distribution fit 11of 12 of the data sets in the top five of 60 possibilities with an average of 2.6 rank or top 4% (with one exception of MTBE reporting limit of 25 ng, which had only eight detections and insufficient data). The individual highest ranked probability distribution function for each compound can be used to estimate investigation scenarios and to perform sensitivity/stochastic simulations to examine possible outcomes for future site investigations in similar settings.

SOURCE AREA DELINATIONS

The final portion of this work is an examination of the higher passive soil gas measurements over the investigation area as indications of potential source areas. The authors choose to focus on six compounds (or compound groupings) to illustrate the spatial variability of potential sources. Figure 6 provides an accounting of those areas where releases of target compounds may have occurred or where higher vapor intrusion risks are present for these six compounds overlain on the same base map. The areas were identified by examining the spatial distribution of each of the compounds from prepared contour maps in conjunction with the histograms and the prepared exceedence probability plots. There are multiple potential source and/or vapor intrusion risk areas identified across the investigation area, which is consistent with the numerous potential historical release areas known to have been present. The source areas are scheduled to be investigated further with several different intrusive methods at a limited number of locations relative to the passive soil gas investigation.
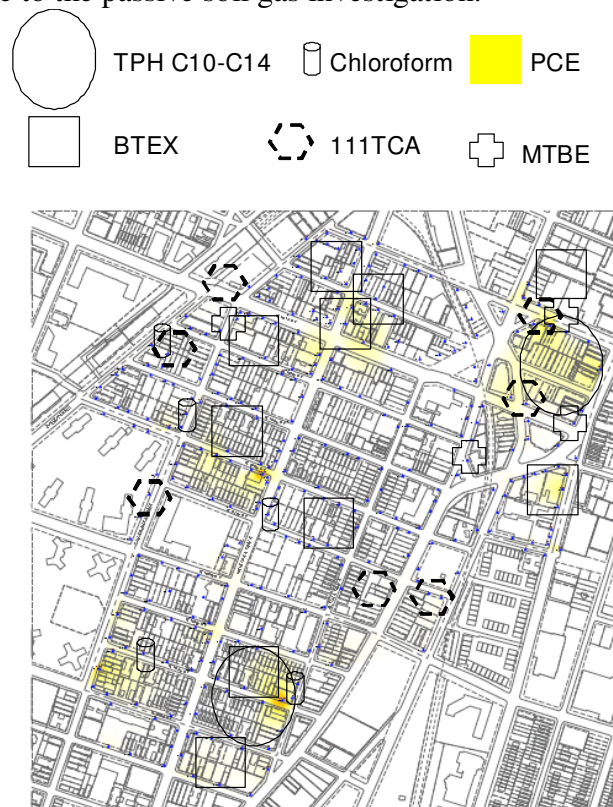

Figure 6. Source location map identified from passive soil gas survey.

CONCLUSIONS

The following summarize the research completed in the study and are not in any particular order of importance.

- The results of an extensive PSG survey conducted in public rights of way resulted in the discovery of multiple potential source areas and/or areas that pose a vapor intrusion risk.
- A detailed statistical examination of the mass detection distributions from eight compounds demonstrated the relevance of the reporting limit and showed the variability with the development of detailed histograms.
- Using the established reporting limits from the survey, PCE was the most frequently detected compound at the site (173 detections) and chloroform the second (146 detections).
- The effects of having a low reporting limit for ubiquitous compounds was demonstrated by lowering the normal reporting limit of 25 ng to 5 ng that resulted in 323 detections or an occurrence rate of 99.6% for BTEX.
- Probability distributions functions were fitted to the detections for the eight compounds and the Frechet probability distribution was the best fit.

ACKNOWLEDGEMENTS

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