PASSIVE, NON-INTRUSIVE SOIL-GAS SAMPLING METHOD TO TARGET CHEMICAL WARFARE AGENT (CWA), CWA BREAKDOWN PRODUCTS, MUNITIONS AND EXPLOSIVES OF CONCERN (MECs), AND COMPOUNDS ASSOCIATED WITH THE DEMILITARIZATION OF CWA AND CHEMICAL WARFARE MATERIEL

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Beacon is the recognized leader in passive soil gas sampling

DoD ELAP and ISO/IEC 17025 Accredited Laboratory
NEFAP Accredited Field Sampling Organization
Accreditation No. 72690

PASSIVE, NON-INTRUSIVE SOIL-GAS SAMPLING METHOD TO TARGET CHEMICAL WARFARE AGENT (CWA), CWA BREAKDOWN PRODUCTS, MUNITIONS AND EXPLOSIVES OF CONCERN (MECs), AND COMPOUNDS ASSOCIATED WITH THE DEMILITARIZATION OF CWA AND CHEMICAL WARFARE MATERIEL

1.0 Background

Beacon Environmental Services, Inc. provides passive soil-gas sampling and analytical services to target a broad range of volatile and semi-volatile organic compounds (VOCs and SVOCs). The state-of-the-art sampling and analytical procedures followed by Beacon Environmental are the foundations for a highly sensitive technology to identify trace levels of compounds present in the vapor phase. Sample collection is performed by using either a subsurface sampler emplaced within an approximately one-inch diameter hole advanced to a typical depth of four inches to three feet or by using a completely non-intrusive, surface-placed flux chamber. Either sampling approach is provided through easy-to-use BESURE Sample Collection Kits™ for the client's personnel to collect the samples and ship the samplers to Beacon Environmental for analysis.

In addition to targeting standard compounds of concern in the environmental industry, such as chlorinated and petroleum hydrocarbons, Beacon Environmental has also targeted Mustard (HD) and its degradation products (1,4-dithiane and 1,4-oxathiane) in the vapor phase, as well as those compounds used in the demilitarization of HD and other chemical warfare agents and materiels (CWAs and CWMs). At an army installation where non-intrusive flux chambers were used, Beacon Environmental identified several locations where HD or nerve agents were present in the vapor phase, and also identified CWA degradation products at numerous locations. These measurements were recorded at sites where disposal reportedly would have occurred more than 30 years ago. In addition, chlorinated hydrocarbons, such as Trichloroethene (TCE) and 1,1,2,2-Tetrachloroethane (DANC), that are known to have been used in the demilitarization of HD contaminated materiels were identified as still being present.

At sites where CWAs were stored, the demilitarization and disposal of CWAs and CWMs occurred, or MECs are potentially present, a broad range of contaminants can be identified in a passive soil-gas survey with a completely non-intrusive approach. The chemicals of concern (CoC) that can be targeted are CWAs, agent breakdown products (ABPs), CWA stabilizers, explosives, fuel hydrocarbons, and other VOCs and SVOCs used in the demilitarization process. CWAs that can be targeted directly include HD, Sarin (GB), Tabun (GA), and VX. Following is Beacon Environmental's approach to safely and accurately target these contaminants. **Table 1** provides the list of specific compounds that can be targeted.

Biography of Author

Harry O'Neill is the President of Beacon Environmental Services and has managed soil gas investigations for more than 20 years working on military and commercial projects throughout the United States, as well as internationally. Mr. O'Neill has been on the forefront of the acceptance of passive soil gas sampling technologies at the national and international level and has overseen the implementation of over a thousand soil gas surveys. He is also the lead author of the recent *ASTM Standard D7758: Standard Practice for Passive Soil Gas Sampling in the Vadose Zone for Source Identification, Spatial Variability Assessment, Monitoring, and Vapor Intrusion Evaluations*.

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Table 1
Target Compound List

Total Petroleum Hydrocarbons (TPH)

VOCs
1,1,1-Trichloroethane
1,1-Dichloropropene
Carbon Tetrachloride
Benzene
Dibromomethane
1,2-Dichloropropane
Trichloroethene
Bromodichloromethane
Methyl methacrylate
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,2-Trichloroethane
Toluene
1,3-Dichloropropane
Dibromochloromethane
1,2-Dibromoethane (EDB)
Tetrachloroethene
1,1,1,2-Tetrachloroethane
Chlorobenzene
Ethylbenzene
p & m-Xylene
Bromoform
Styrene
1,1,2,2-Tetrachloroethane
o-Xylene
1,2,3-Trichloropropane
Isopropylbenzene
Bromobenzene
n-Propylbenzene
2-Chlorotoluene
4-Chlorotoluene
1,3,5-Trimethylbenzene
Pentachloroethane
tert-Butylbenzene
1,2,4-Trimethylbenzene
sec-butyl Benzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
n-Butylbenzene
1,2-Dibromo-3-chloropropane
Hexachloroethane

SVOCs
Naphthalene
1,2,4-Trichlorobenzene
Hexachlorobutadiene
1,2,3-Trichlorobenzene
2-Methylnaphthalene
Acenaphthylene
Acenaphthene
Fluorene
Anthracene
Phenanthrene
Carbazole

Explosives/Nitroaromatics
Nitrobenzene
2-Nitrotoluene
3-Nitrotoluene
4-Nitrotoluene
1,3-Dinitrobenzene
Dinitrotoluenes
1,3,5-Trinitrobenzene
2,4,6-Trinitrotoluene

Chemical Warfare Agents
HD
GB
GA
VX

ABP and CWA Stabilizers
Thiodiglycol
1,4-Oxathiane
1,4-Dithiane
Diisopropyl methylphosphonate (DIMP)
Diisopropyl carbodimide (DIPC)
Tributylamine
Dissopropylaminoethanol
Dicylcohexyl carbodimide

Note: The compound reporting quantitation level (RQL) is typically 25 nanograms (ng) and the RQL for TPH is 2,500 ng. Actual detection limits are lower.

2.0 Survey Design

The survey design varies depending on the amount of historical and other site information that is available prior to initiating the passive soil gas (PSG) survey. Typically an unbiased grid is established across the site with additional biased sample locations to target specific features. The spacing between sample locations is dependent upon the expected depth of the CoC, the soil type, and the size of the area to be investigated. Global positioning system (GPS) equipment is used to collect the sample location coordinate data.

Each PSG sampler contains two or more adsorbent cartridges for collection of the CoCs; the exact number of cartridges is determined by the targeted range of compounds. The adsorbents used are hydrophobic, which allows the samplers to be effective even in water-saturated or high moisture conditions. Following retrieval, the PSG Samplers are shipped to Beacon Environmental for analysis. Beacon Environmental performs the analysis for ABPs, CWA stabilizers, explosives, fuel hydrocarbons, and VOCs/SVOCs using one of the adsorbent cartridges from the sample location. Analyses for CWAs are performed by a subcontracted surety laboratory using separate adsorbent cartridges collected at each location.

A comprehensive survey report is provided by Beacon Environmental that includes results in tabular form as well as on color isopleth maps showing the distribution of compounds identified in the investigation (see **Figure 1** below).

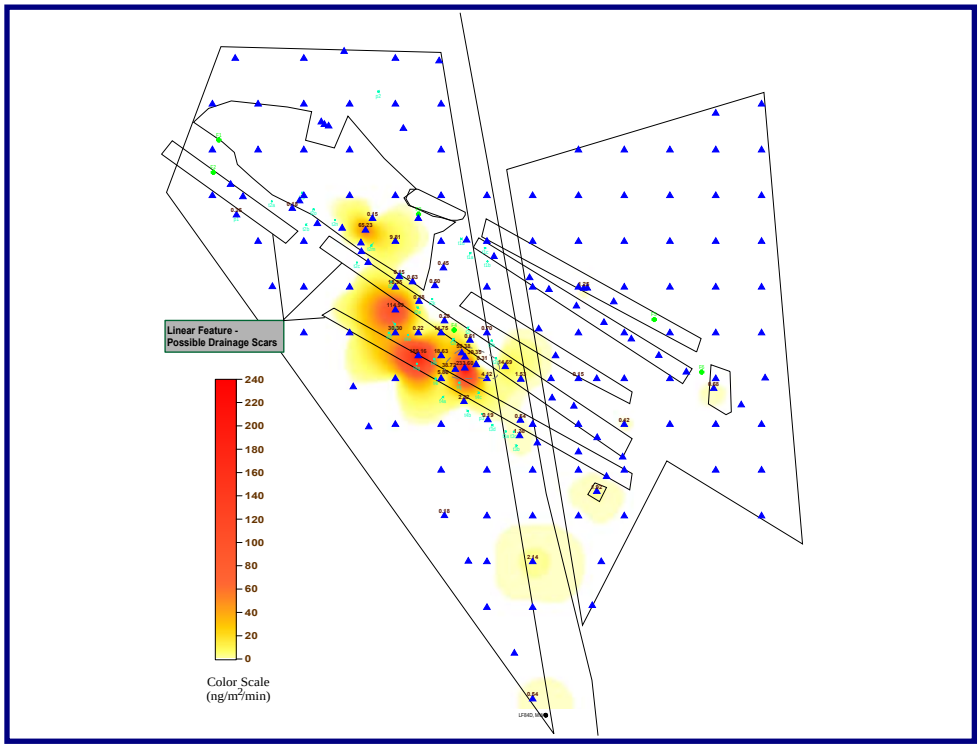

Figure 1 – Example Color Isopleth Map

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3.0 Soil-Gas Sampling Procedures

To perform the soil-gas investigation, BEACON provides BESURE Sample Collection Kits™ with all the materials necessary to collect the requested number of soil-gas samples. BEACON offers two sampling approaches: a completely non-intrusive method and also a minimally intrusive method where the PSG Samplers are installed in the ground to a depth as shallow as four-inches. The procedures for each of these methods, which have been evaluated formally and implemented on government test sites, are described below.

To collect soil-gas samples using the **Non-Intrusive Surface Flux Chambers**, the sampling team prepares the sample location as necessary and removes two or more laboratory-conditioned adsorbent cartridges containing hydrophobic adsorbent from a borosilicate glass vial. The adsorbent cartridges are then hung from a stainless steel hanger, and this sampler assembly is positioned immediately above the ground surface at the designated location. The stainless steel flux chamber is then lowered over the sampler assembly, open end down, and the chamber is surrounded with a collar of sand or local soil. The chamber can be covered with a camouflage cloth that is secured with a small additional amount of sand or soil. **Figure 2** provides a diagram of the Surface Flux Chambers. During retrieval, the adsorbent cartridges are placed in borosilicate vials for transport.

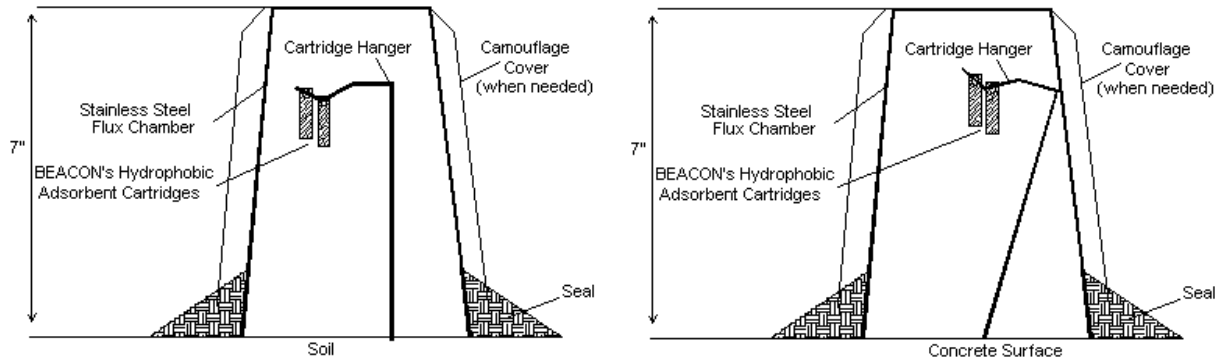

Figure 2 – Nonintrusive Surface Flux Chamber

To collect soil-gas samples using the **Minimally Invasive Sampling Method**, a 3/4" diameter hole is made to a depth of four inches using a hammer and a metal stake provided in the Field Kit. As an option, a slide hammer, hand auger, hammer drill, or other comparable equipment can be used to advance an approximately one-inch diameter hole to a greater depth. The PSG Sampler (which contains a minimum of two hydrophobic adsorbent cartridges) is installed in the hole and covered with soils to seal the sampler in the ground. The sampler is shipped to the site with a length of wire that is wrapped around the vial and twisted around the shoulder of the vial to expedite retrieval from the ground. During retrieval, the adsorbent cartridges from these samplers are transferred to separate clean transport vials prior to shipment. It is not necessary to use ice or preservatives during shipment; however, the samplers are sealed and shipped under established chain-of-custody procedures. **Figure 3** shows a PSG

Figure 3
PSG Subsurface Sampler

Sampler for subsurface installation as it looks when received in the Field Kit.

With either sampling approach, the adsorbent cartridges are exposed to subsurface gas for three to 14 days depending on the objectives of the investigation and the compound concentrations that are expected to be present. Beacon Environmental assists in planning of the sampling event so that the highest level of sensitivity and accuracy can be achieved.

Following the exposure period, the cartridges are retrieved and placed in clean borosilicate transport vials for shipment. When targeting CWA, as well as degradation products and other compounds used in the demilitarization of CWA, four adsorbent cartridges are collected at each location. At each sample location, two cartridges are placed in a transport vial that is to be sent to the surety laboratory to target CWAs and two cartridges are placed in a separate transport vial to be sent to Beacon Environmental to target ABPs, CWA stabilizers, explosives, fuel hydrocarbons, and VOCs/SVOCs. Trip blanks, which remain with the other samples during preparation, shipment, and storage, are included at a typical rate of five percent of the total number of field samples. Samples are shipped under established chain-of-custody procedures inside of a BESURE Sample Collection Kit™ with a unique identification on the tamper proof seal.

Based on BEACON's experience, a two-person field team can install over 100 surface flux chambers per day. When using the subsurface Samplers, one person can install over 100 Samplers per day. The amount of days required to complete the installation and retrieval procedures is dependent upon the number of personnel deployed for the execution of the fieldwork, weather conditions, and health and safety considerations.

4.0 Screening of Equipment for CWA by Chemical Surety Laboratory

When necessary, the clean borosilicate transport vials containing the adsorbent cartridges exposed in the field can be screened by a chemical surety laboratory prior to being shipped to Beacon Environmental. If for some reason CWA is identified on a vial, that vial and any others containing adsorbent cartridges from the same sample location will not be sent to BEACON. If no CWAs are identified, the samplers will be sent to BEACON. However, because the transport vials never come into contact with the ground at the site, CWA has not been nor is expected to be identified during the screening process.

5.0 Analytical Procedures

A chain-of-custody accompanies the field samples at all times from the time the samples are collected until final analysis. Field kits are shipped with tug-tight custody seals to ensure that samplers are not tampered with during transport (see **Figure 4**). Once samples are received at the laboratory, the sample custodian receives the samples and logs the samples into the laboratory's Sample Receipt Log per the company's *Quality Assurance Project Plan for the Analysis of Passive Soil-Gas Samples*.

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Figure 4 – BESURE Sample Collection Kit™

Beacon Environmental's laboratory is maintained in a safe and secure manner at all times. The facility is locked when not occupied and is monitored for fire and unauthorized access. Beacon Environmental personnel escort all visitors at all times while inside the facility. Neither soil nor water analyses are performed at Beacon Environmental, so no solvents are stored or used. This ensures that a clean laboratory environment is maintained for trace analysis of compounds.

Analysis of the samples for VOCs, SVOCs, ABPs, CWA stabilizers, explosives, and fuel hydrocarbons is performed by Beacon Environmental following an internal method based on EPA Method 8260C that is modified for the introduction of the sample by thermal desorption and to target a broad list of compounds including both VOCs and SVOCs. Analysis of the samplers for CWAs is performed by a surety laboratory following established methods routinely used by the laboratory to target CWAs on adsorbent tubes for purposes of air monitoring.

Adsorbent cartridges sent to Beacon Environmental are analyzed using thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) instrumentation. Samples can be analyzed for the VOCs, SVOCs, ABPs, CWA stabilizers, explosives, and fuel hydrocarbons listed on **Table 1**. As an option, TICs additionally can be reported for each sample, with the results based on the closest internal standard to the TIC.

Quantitative results for the compounds from 1,1,1-Trichloroethane to 2-Methylnaphthalene are based on an initial five-point calibration. Quantitative results for the heavier, later-eluting SVOCs, the ABPs, CWA stabilizers, and explosive compounds are based on a minimum of a three-point calibration. A bromofluorobenzene (BFB) tune is performed daily and a method blank is run following the daily calibration. Internal standards and surrogates are included with each sample analysis. The laboratory's reported quantitation level for each of the targeted compounds is 25 nanograms; however, the actual detection limits are lower and, as an option, all measurements above the method detection limits can be reported. Because multiple adsorbent cartridges are included within each Sampler, field sample duplicates may be analyzed from any locations selected.

Analyses of the samples that are performed by Beacon Environmental's laboratory use state-of-the-art instruments that are listed below.

- Agilent Gas Chromatograph/Mass Spectrometer,
- Markes Unity thermal desorber,
- Markes UltrA autosampler, and
- Markes Mass Flow Controller Module.

Note: The Markes International thermal desorption instruments outperform other older thermal desorption equipment, which cannot target as broad a range of compounds with as much sensitivity or accuracy.

Samples targeting HD, GB, and GA are analyzed by the surety laboratory using thermal desorption gas chromatography/mass spectrometry (GC/MS) instruments, following an established internal operating procedure (IOP). Samples targeting VX are analyzed by the surety laboratory using liquid chromatography/mass spectrometry (LC/MS) instruments following an established IOP.

One adsorbent cartridge is analyzed from each sample location for each target group of compounds; the second cartridge for each method is stored for 30 days for duplicate or confirmatory analysis. Other specific analytes may be targeted if requested prior to analysis.

6.0 Reporting

Following analysis and a thorough data review, a comprehensive survey report is provided that contains:

project objectives,
the plan of investigation,
the QA/QC program and findings,
laboratory data (in nanograms),
data converted to emission flux rates ($ng/m^2/min$) if surface flux chambers are employed,
color isopleth maps showing the distribution of detected compounds,
field procedures,
laboratory procedures,
Field Deployment Reports, and
Chain-of-Custody documentation.

Beacon Environmental requests that a CAD drawing of the site is provided with coordinate data for each location to facilitate creation of color isopleth maps. BEACON can provide the color isopleth maps as layers for use with CAD software or provide data files of the contours for use with GIS software. Beacon Environmental will provide post survey support to assist in interpreting the data, when requested.

7.0 Experience and References

Beacon Environmental project managers have collected passive soil gas samples from more than 1,000 projects across the United States, as well as internationally. Beacon Environmental has

worked on projects at Department of Energy facilities (including the Hanford Reservation, Los Alamos National Laboratory, and Oak Ridge National Laboratory) and at Department of Defense facilities (including Aberdeen Proving Ground, MD; Yuma Proving Ground, AZ; Camp Bullis, TX, and Deseret Chemical Depot, UT). Beacon Environmental has identified Mustard and its degradation products in soil gas and has been used to cost effectively locate contamination at sites where the demilitarization and disposal of chemical warfare materials and unexploded ordnance occurred. Because these sites received CWM and UXO, a non-intrusive sampling technology was essential to reduce the risk to the site workers and expedite the collection of samples across large areas.

In addition, BEACON has extensive experience in sampling for a wide range of compounds in soil gas and has performed bench scale tests on a variety of adsorbents to determine which adsorbent is best suited for targeting chemical warfare agents (CWAs) and their degradation products.

Following is a list of project managers who have employed Beacon Environmental to provide passive soil gas services on sites where CWAs, CWMs, or UXOs were targeted or of concern:

Mr. Rick Logsdon
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Mr. Tony Magliocchino
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Ms. Susan Trussell
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