

# **Innovative, Non-Intrusive Passive Soil Gas Collection Device Maps Large Carbon Tetrachloride Plume at the DOE Hanford Site, Washington -- 10501**

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## **ABSTRACT**

Approximately 100 hectares (250 acres) were investigated as part of the passive soil gas (PSG) investigation that included multiple areas of concern. The objective of the investigation program was to rapidly identify potential source areas and guide future sampling events based on the frequency and magnitude of compounds identified in the survey. PSG sampling was the preferred technology because it does not involve intrusive activities and allowed a comprehensive data set for evaluation before more invasive techniques were implemented. Vadose zone sources were detected using a well-executed and properly conducted non-intrusive PSG survey. A two-year field investigation allowed the development of a refined conceptual site model. The results show that historical disposal operations at this DOE facility resulted in the continuing presence of residual chlorinated contamination in the vadose zone that may present a potential threat for impacting groundwater. Confirmatory site investigation techniques revealed carbon tetrachloride soil gas concentrations at a depth of approximately 35 m (115 ft), near an area that is currently undergoing site remediation. The analysis of discrete soil samples taken in regions where significant soil gas concentration exists resulted in non-detections, indicating that dense non-aqueous phase liquid sources are not present at these locations.

## **INTRODUCTION**

A cost-effective passive soil gas (PSG) technology has been employed on multiple Department of Energy sites, including Los Alamos, Sandia, Oak Ridge, and the Hanford Site. A PSG technology affords the ability to rapidly target a broad range of volatile organic compounds and semi-volatile organic compounds (VOCs and SVOCs) in the vadose zone using a non-intrusive sampling approach. The work described herein focuses on the investigations conducted at the Hanford Site to evaluate the presence or absence of carbon tetrachloride (CCl<sub>4</sub>) in order to (i) identify source areas that may contain dense non-aqueous phase liquid (DNAPL) in areas where CCl<sub>4</sub> was disposed of after use in the plutonium recovery operations at the Plutonium Finishing Plant (PFP, formerly Z-Plant) and (ii) to prioritize areas of concern for subsequent sampling and analysis in several other phases of follow-up investigation. CCl<sub>4</sub> and other organic liquids containing plutonium and other radionuclides were released into the subsurface at an area of the US DOE Hanford Site in large quantities (570,000 kg to 920,000 kg (Bratton, et. al., 2004)) from the mid-1950s to the early 1960s.

A large number of PSG sample locations, 503, were chosen for the first phase of this project. The locations were determined based on (i) the nature of past activities within the potential areas of concern after a review of historical records, and (ii) targeting those areas with high  $\text{CCl}_4$  concentrations in groundwater. The PSG samplers, each consisting of a 16 mm (5/8th inch) diameter by 51 mm (2-inch) long borosilicate glass vial containing specialized hydrophobic adsorbents, were placed open-end down in 19 mm (3/4 inch) diameter holes advanced to a four-inch depth at the selected locations and were exposed to emissions of subsurface soil vapors for three days prior to being retrieved. An alternative sampling approach is also used at other DOE facilities where 10.2 cm (four-inch) diameter stainless steel flux chambers are placed directly on the ground surface and the adsorbent traps are suspended from stainless steel stakes beneath the chambers to trap compounds emitting from the ground surface. A general overview of both methods is presented.

## **PASSIVE SOIL GAS SURVEY**

A high resolution, passive soil gas survey was performed to obtain a surficial representation of the subsurface  $\text{CCl}_4$  contamination. The environmental investigator obtained a BESURE Sample Collection Kit from Beacon Environmental Services, Inc. to collect samples and then submitted the samples to Beacon Environmental for analysis. PSG surveys are ideal for measuring a wide-range of VOCs and SVOCs in a broad range of geologic formations (Byrnes, 2009). An advantage of PSG surveys is that the method allows for long exposure times (several days to weeks) that enable the sorbents to be in contact with the organic gas or vapor in order to allow a representative soil gas sample as discussed in a standard for soil gas sampling and monitoring (ASTM D 5314-92, 2006).

PSG surveys are a powerful and efficient tool if the appropriate quality controls are included in the technology design. This includes both the uniformity in the construction of the sampler as well as in the level of QA/QC used during the analysis of the samples. At a minimum, controls should be in place to ensure that (i) the appropriate hydrophobic adsorbents are used to target the compounds of concern, (ii) porous materials are not included in the sampler which may act as a competing adsorbent, (iii) an identical amount of adsorbent is used for each sampler, (iv) internal standards and surrogates are included with each analysis, and (v) that a multi-point calibration curve is performed with the low point of the curve at or below the method's reporting limit. Historically, other PSG methods have been considered screening technologies and have not adhered to a high level of quality control in both the design of the sampler and analysis of the samples. The BESURE method, however, does adhere to each of these requirements resulting in quantitative data that accurately depicts not only the source areas but also the lateral extent of contamination even when present at low concentrations. Strict adherence to these criteria brings advanced PSG testing to a level III/IV tool for quantitative assessment as opposed to a screening tool/semi-quantitative method as defined by the EPA (1988).

The BESURE PSG sampler consists of a borosilicate glass vial pre-wrapped with wire for installation and retrieval of the sampler, shown in Figure 1. Each sampler contains two sets of adsorbent cartridges to adsorb compounds in soil gas. The adsorbent materials used are hydrophobic, with low-affinity for water vapor that makes them effective even in water saturated conditions. An ample and identical amount of specialized adsorbents are contained within each

cartridge to allow for a dynamic range of collection with reproducible results. In accordance with ASTM D 5314-92, no porous materials, such as polytetrafluoroethylene (PTFE), which can act as a competing adsorbent, are used within the sampler. The sampler is compact, allowing for installation in a variety of conditions and in small diameter holes.



Figure 1. BESURE PSG Sampler

BESURE samplers are most often installed in an approximately one-inch diameter hole that is between four-inches and three-feet in depth. Holes may be advanced to greater depths when necessary; however, the samplers need only be suspended in the upper portion of the hole because compounds in soil gas that enter the hole will migrate up to the sampler. Samplers typically are exposed in the field for three (3) to 14 days, with the length of time dependent on the site conditions, the depth contaminants are expected to be present, the expected contaminant concentration, and the overall objectives of the survey.

One person can install up to 100 samplers per day with a standard shallow installation when asphalt or concrete are not present on the ground surface, which requires drilling through the impervious surfacing. When asphalt and/or concrete are present, a two-person team can install on average 50 samplers per day using a hammer drill (with an approximately one-inch diameter drill bit). For retrieval of the samplers, one person can easily retrieve 100 samplers per day regardless of whether asphalt or concrete surfacing is present. The ability to collect samples rapidly and at a shallow depth reduces the overall field costs, while also minimizing the health risk to site workers and the amount of waste generated.

BESURE PSG samples are analyzed by Beacon Environmental using thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) instruments following EPA Method 8260B, modified for the introduction of samples by thermal desorption and to target a broad range of compounds including VOCs and SVOCs. PSG results are based on a higher level of QA/QC than can be achieved with other field screening methods and specifically are based on a five-point initial calibration with the lowest point on the calibration curve at or below the practical quantitation limit of each compound. Internal standards and surrogates are included with each analysis – per EPA Method 8260B – to provide proof of performance that the system was operating properly for each sample and to provide consistent reference points for each analysis, which enables an accurate comparison of measured quantities. Trip blanks are analyzed with

each batch of samples and because two sets of adsorbent cartridges are provided in each sampler, duplicate or confirmatory analyses can be performed for any of the sample locations if requested.

Tabular results are provided in both hard copy and electronic copy along with color isopleth maps showing the distribution of selected compounds identified in the survey and targeted by the client. As an option, tentatively identified compounds (TICs) can be reported and complete data packages, including Contract Laboratory Program (CLP) summary forms, can be provided when necessary.

## NON-INTRUSIVE SURFACE FLUX CHAMBERS

To collect soil-gas samples using 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, which never come into contact with the soil, are placed in borosilicate vials for return transport to the laboratory.

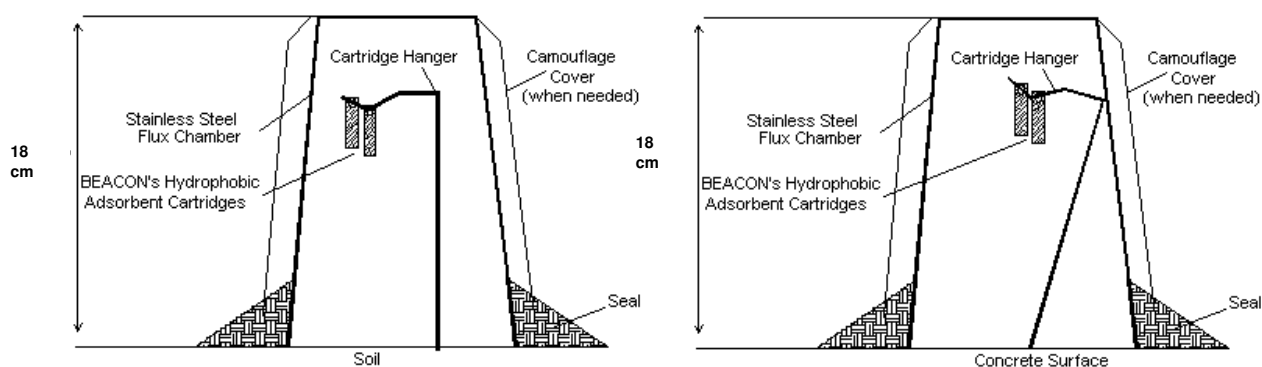


Figure 2. Nonintrusive Surface Flux Chamber

## FIELD INVESTIGATION SUMMARY

An extensive non-intrusive, PSG survey was conducted to provide a current picture of soil gas conditions, fill in data gaps, and investigate previously identified hot spots. The typical application sequence is to place the passive samplers on a pre-defined grid. After a 72-hr collection period, the cartridges are retrieved and analyzed in a laboratory using thermal desorption and gas chromatography/mass spectrometry (TD-GC/MS) instrumentation. Based on the compounds detected and a comparison of their relative mass on a spatial basis, the technology is able to identify underground volatile organic contaminants (including  $\text{CCl}_4$ ) and help target areas for follow-up investigation. A field test plan that described the survey location, personnel, safety issues, and survey procedures was prepared and submitted to Hanford

personnel for review. The planned survey location coordinates for each sample point were extracted from a GIS base map and then loaded into a Trimble Pathfinder Pro-XRS Global Positioning System (GPS) unit.

The objective of the passive soil gas survey was to identify  $\text{CCl}_4$  source areas in the vadose zone, to delineate the lateral extent of contamination, and to increase the spatial resolution of hot spots. The initial application sequence was to place the samplers on a pre-defined coarse grid with spacing of about 50 meters. In areas where soil gas highs were recorded, a refined grid was established on about a 20-m spacing to confirm and repeat some of the more important measurements. This approach refined and verified the potential  $\text{CCl}_4$  source regions for subsequent intrusive investigation. Coarse grid studies were therefore deployed to investigate known and suspected  $\text{CCl}_4$  waste disposal sites or potential source locations of DNAPL contamination. After results were obtained from the initial deployment, the data were analyzed to identify areas warranting a refined grid investigation. The coarse grid survey followed by a more refined grid survey added more structure to the data and provided higher resolution in the spatial dimension. This graded approach provided data to efficiently focus on vadose zone locations that should be further investigated by invasive technologies in subsequent tasks.

The soil gas samplers were deployed in the field by a two-person field crew. The GPS unit was used to locate each planned sample point (with sub-meter accuracy) as well as to survey the final location of any sample points that had to be shifted to avoid vegetation or manmade obstacles. The soil gas samplers were deployed and collected following the standard field procedures prepared by Beacon Environmental. All of the samplers were deployed in 10-cm (4-in) deep holes that were backfilled with native soil and marked with a pin flag. The soil gas samplers were left in place for a minimum of three days and were then retrieved (DOE (2006), Bratton et al 2006 and Bratton et al 2007). The investigation included multiple deployments from August 2003 through February 2005. A total of 503 passive soil gas samples were obtained in the entire investigation and the results are presented in a subsequent section of this paper.

The fieldwork was completed with no accidents, injuries, illnesses or near miss incidents. The PSG samplers were shipped overnight to an off-site laboratory dedicated to the analysis of PSG samples using TD-GC/MS techniques. The reported quantitation level for  $\text{CCl}_4$  was 25 nanograms. The spatial distribution of  $\text{CCl}_4$  was mapped within the areas of concern and served as the primary means for selecting locations for the other phases of the investigation.

## **FIELD INVESTIGATION RESULTS**

The soil gas samples and trip blanks were shipped under chain-of-custody to the analytical laboratory for analysis of VOCs by EPA Method 8260B. A total of twelve different contaminants were reported and  $\text{CCl}_4$  was the most frequently detected compound. Laboratory QA/QC procedures included standards, surrogates, and blanks appropriate to EPA Method 8260B (Modified). Field work, analyses, and reporting were done in accordance with BEACON's Quality Assurance Program Plan. The results for  $\text{CCl}_4$  are presented in Figure 3 and shows the spatial variability of  $\text{CCl}_4$  across the site. Several hot spots that were discovered and the areal extent around these hot spots are well-delineated over a large area. The investigation resulted in pinpointing future invasive sampling efforts and helped evaluate the possibility of

other undocumented or unknown source regions not associated with the major disposal sites. The regions where the passive soil gas results indicated  $\text{CCl}_4$  contamination were evaluated with direct push techniques to determine active soil gas concentrations and collect soil samples for laboratory analysis.

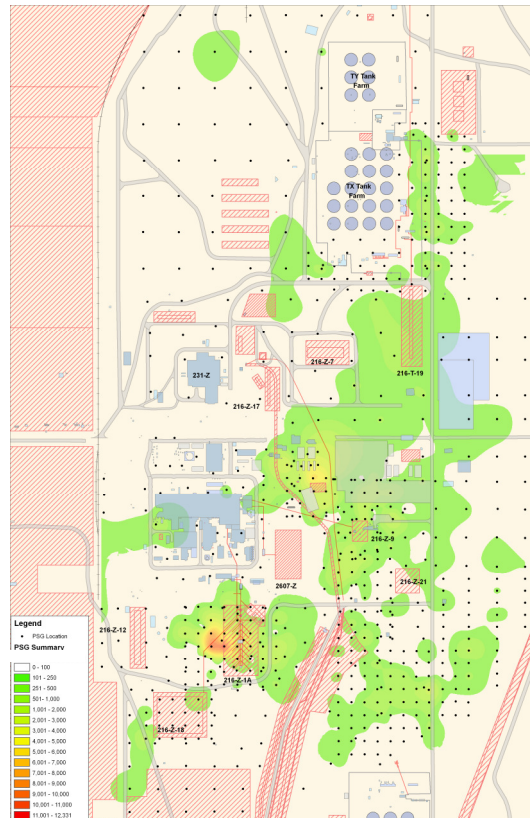


Figure 3. All passive soil gas results. Highest  $\text{CCl}_4$  in red and a linear scale down to light green.

The vertical distribution of  $\text{CCl}_4$  in soil gas was measured at several locations after the passive soil gas surveys were completed. Active soil gas samples were pulled for analysis at approximately 1 m (3.3 ft) intervals in all follow-up investigation locations using a cone penetrometer. Location P10A, which produced the second highest  $\text{CCl}_4$  passive soil gas sampler mass, is located near the entrance to the PFP, in a passive soil gas hot spot (Bratton et al, 2006). Figure 4 shows the vertical profile of  $\text{CCl}_4$  to a depth of 115 ft below ground surface (bgs) at location P10A. Active soil gas concentrations exceed 10 ppmv at a depth of 80 ft bgs to a maximum of 119 ppmv at 102 ft bgs. There are several fine-grained layers at the depth intervals where the  $\text{CCl}_4$  was found and the passive soil gas sampling program guided the investigators to several locations where similar vertical distributions of  $\text{CCl}_4$  in soil gas were obtained.

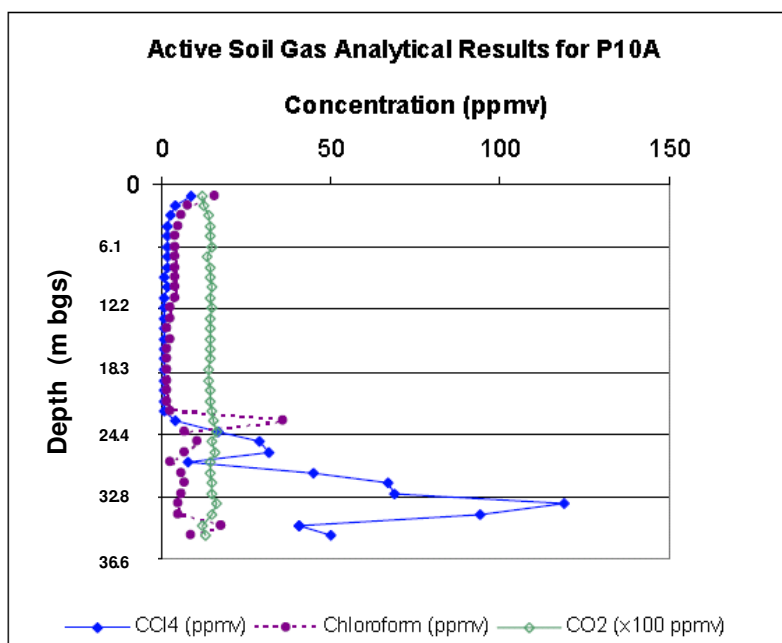


Figure 4. Active soil gas vertical profile at location P10A.

There were forty-two locations where follow-up cone penetrometer holes were installed. There were 60 soil samples taken in the deeper regions where the fine-grained materials were located that were considered to be potential sources of dense-non-aqueous phase liquid (DNAPL). Laboratory analysis of the soil samples identified no  $\text{CCl}_4$  or chloroform contamination above the quantitation limit of 2.5 ug/kg (Bratton, 2007) at these locations where PSG and active soil gas measurements indicated vapor concentrations above background. This testing confirmed the absence of any DNAPL sources at these locations. The necessity of targeting compounds in soil gas is clearly demonstrated because the detections of  $\text{CCl}_4$  at passive soil gas sampler locations helped the investigators delineate both the lateral and vertical extent of  $\text{CCl}_4$  in the vapor phase in the vadose zone.

## CONCLUSIONS

The use of an advanced, high resolution PSG technology at the Hanford Site allowed the investigators to determine the aerial extent of the  $\text{CCl}_4$  vadose zone plume, further examine previously defined hot spots and to fill in data gaps. The following summarize the conclusions from this paper.

- The PSG technique enables the assessment of the  $\text{CCl}_4$  plume in order to ascertain the location of hot spots and to provide sufficient plume definition for determining the locations for subsequent areas of investigation.
- The PSG technique allowed a low-cost and non-obtrusive investigatory tool that provided a reliable data set for the assessment of vadose zone gas distribution across a wide area.

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- The PSG survey results over the course of time allowed the investigation to focus on compounds whose distributions are key indicators of the performance evaluation of a treatment system/strategy.
- The passive soil gas investigation revealed several source areas that were subsequently investigated by measuring the vertical distribution of  $\text{CCl}_4$  whereby appreciable soil gas concentrations were found at depth.
- The analysis of discrete soil samples taken in regions where significant soil gas concentration exists generally resulted in non-detections, indicating that DNAPL sources of  $\text{CCl}_4$  are not present at these locations.

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