

# Use of CSIA to Distinguish Between Vapor Intrusion and Indoor Sources of VOCs

**Thomas McHugh**

GSI Environmental Inc., 2211 Norfolk, #1000, Houston, Texas 77098

**Kyle Gorder**

Hill Air Force Base Environmental Restoration Branch, Hill Air Force Base, Utah 84056

**Tomasz Kuder, Richard Philp**

The University of Oklahoma School of Geology and Geophysics, 100 East Boyd Street Suite 710, Norman, Oklahoma 73019

**Stephanie Fiorenza**

BP America, 501 WestLake Park Blvd. MC 28.144A, Houston, Texas 77079

**Harry O'Neill**

Beacon Environmental Services, Inc. 323 Williams Street, Bel Air, Maryland 21014

**Joe Odencrantz**

Tri-S Environmental, 2121 Yacht Yankee, Newport Beach, CA 92660

## ABSTRACT

Indoor sources of volatile organic compounds (VOCs) are ubiquitous, resulting in detectable concentrations in indoor air, often at concentrations above regulatory screening levels. Because of these indoor sources, the detection of a site-related VOC in a potentially affected building at a concentration above the regulatory screening level does not necessarily indicate a vapor intrusion impact.

At sites where the subsurface and indoor sources of VOCs exhibit different isotope signatures, compound-specific isotope analysis (CSIA) may be used to distinguish between vapor intrusion and indoor sources of the same VOCs. Although CSIA has been validated and accepted as an effective tool for distinguishing between different sources of VOCs in groundwater, we are not aware of prior application of CSIA to identify the source of VOCs in indoor air.

In order to evaluate the utility of CSIA to distinguish between vapor intrusion and indoor sources of VOCs, we have conducted a preliminary study at Hill AFB. The results indicate that there are measurable differences in  $\delta^{13}\text{C}$  values between TCE in the subsurface at Hill AFB and indoor sources of TCE. The  $\delta^{13}\text{C}$  values for the three source area soil gas samples ranged from -25.3‰ to -24.4‰,  $\delta^{13}\text{C}$  values for four groundwater samples collected from the off-site plume ranged from -23.8‰ to -20.6‰,  $\delta^{13}\text{C}$  values for seven soil gas samples collected from above the off-site plume ranged from -23.7‰ to -5.2‰. These results show a pattern of  $^{13}\text{C}$  enrichment away from the source area. In contrast, the  $\delta^{13}\text{C}$  values for the four indoor source samples ranged from -26.6‰ to -25.5‰, lower values than any of the subsurface samples. These preliminary results support the hypothesis that CSIA of indoor air samples can be used to distinguish between vapor intrusion and indoor sources of the same VOC.

## INTRODUCTION

Hill Air Force Base, near Ogden, Utah, has been an active military facility since before World War II and has been used extensively for aircraft maintenance. Historic waste management practices associated with aircraft maintenance and other base activities have resulted in the contamination of shallow groundwater systems with trichloroethylene (TCE) and other chlorinated VOCs. Impacted groundwater has migrated across facility boundaries and into residential areas. In response to these impacts, the Air Force has conducted extensive investigation and remediation programs that include monitoring contaminant concentrations in groundwater and indoor air in neighborhoods surrounding the base. These investigations have identified a number of houses with elevated concentrations of TCE and other chlorinated solvents in indoor air.

Hill AFB is conducting an on-going indoor air monitoring program to identify off-base residences impacted by vapor intrusion of chlorinated VOCs. In lieu of collecting investigative samples from below residences (i.e., soil gas or sub-slab vapor samples) to identify potential exposure pathways, indoor air samples are collected in homes to directly determine if exposure is occurring. Samples are collected over a 24 hour period using project-dedicated Summa canisters. Residential samples are analyzed by method TO-15 for specific constituents based on contaminants detected in shallow groundwater. The primary constituent of concern for the air-sampling program is TCE, with a typical reporting limit of 0.11 ppbv ( $0.6 \mu\text{g}/\text{m}^3$ ).

In cooperation with U.S. EPA Region 8 and the State of Utah, site-specific Mitigation Action Levels (MALs) have been developed for 10 constituents of concern. The current MAL for indoor air is  $12 \mu\text{g}/\text{m}^3$  for TCE, however, the MAL was  $2.3 \mu\text{g}/\text{m}^3$  prior to 2008. Sub-slab depressurization systems are installed to mitigate vapor intrusion in homes where detected concentrations of constituents exceed MALs, and there is no apparent interior source of the chemicals. At these residences, post-mitigation TCE concentrations significantly lower than pre-mitigation concentrations indicate that vapor intrusion is the primary source of indoor TCE (Case and Gorder 2006). Quarterly sampling is recommended for homes with detections below MALs to more closely monitor contaminant concentrations.

As part of the Hill AFB indoor air-monitoring program, TCE and other VOCs are commonly detected in indoor air. In many cases, these VOCs are not attributable to vapor intrusion. Over 25% of the TCE detections above the pre-2008 MAL in indoor air have subsequently been attributed to indoor sources of VOCs rather than vapor intrusion. For other VOCs such as PCE and 1,2-DCA, an even higher percentage of MAL exceedances are attributable to indoor sources. However, identification of the indoor VOC source has typically required multiple rounds of sampling and analysis, and in some cases an indoor source is identified only after a vapor intrusion mitigation system has been installed and has failed to improve indoor air quality. Based on this experience, improved methods to identify indoor sources of VOCs are needed.

For this project, we have evaluated the potential for using compound-specific stable isotope analysis (CSIA) to distinguish between vapor intrusion and indoor sources of VOCs. Full validation of this site assessment tool could provide a new, cost-effective method to rapidly identify residences with real vapor intrusion problems.

For this study, base personnel identified a residence (U8-8078) where indoor air sampling showed TCE concentrations of 1 to 4 ug/m<sup>3</sup> during routine monitoring conducted from 2003 to 2008. Groundwater underlying this residence is known to be impacted by TCE and at least two products known to contain TCE are being stored in the garage. Because this residence has two potential sources for the TCE detected in indoor air (i.e., TCE in the subsurface and TCE-containing products in the garage), this residence was selected for the CSIA testing program.

## **SAMPLE COLLECTION METHODS**

Air and soil gas samples were collected onto sorbent tubes using a sampling apparatus that allowed for simultaneous collection of separate volumes onto two sorbent tubes as described in USEPA Method TO-17. The glass sorbent tubes were 6 mm outside diameter, 4 mm inside diameter, 6 inches long that were fritted at one end and packed with a short bed of quartz beads, a bed of Tenax-GR, a separating bed of quartz beads, a bed of Carboxen 569, then a retaining bed of quartz beads, held in place by stainless steel gauze and a retaining spring. This adsorbent configuration choice has proved to be appropriately applicable for targeting TCE. For each location, the concentration of TCE in the sample (i.e., air or soil gas) was measured using a field GC/MS (HAPSITE) with an approximate detection limit of 1 ug/m<sup>3</sup>. The sample collection time and flow rate was then set in order to collect 100 ng to 300 ng of TCE on each sample tube. For indoor air samples, the indoor air was collected directly onto the sorbent tubes. For soil gas samples, the soil gas was collected in a Tedlar bag and then transferred from the Tedlar bag to the sorbent tube. A back-up tube was placed in series behind some tubes in order to check for break through during sample collection (no TCE was detected on any of the back up tubes, which were analyzed at a separate laboratory than the primary tubes).

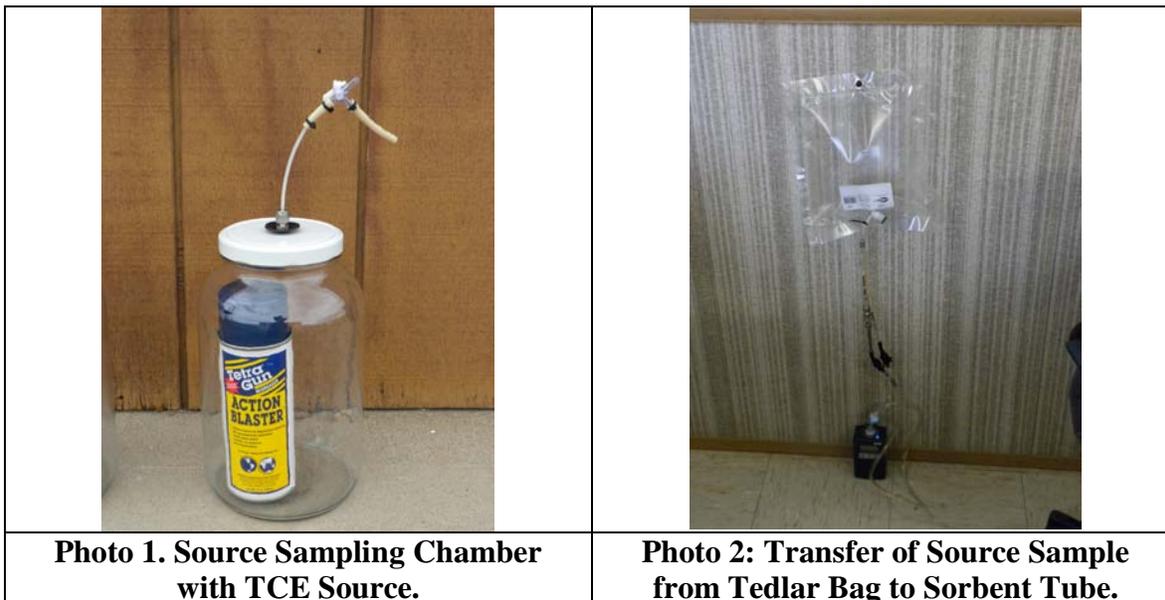
Indoor Air Samples: The sampling rate was 30 mL/min (100 ng tube) and 90 mL/min (300 ng tube) for up to 26 hours.

Soil Gas Samples: Soil gas samples were collected into Tedlar bags for initial screening by field GC/MS. If necessary, samples were diluted with nitrogen into a second Tedlar bag so that samples could be collected onto the sorbent tubes using a reasonable flow rate (>20 mL/min) and sample collection time (1 -30 min).

Source Samples: Each TCE source (unopened) was placed in a 4L glass jar with a sample port installed through the lid (see Photo 1). After 60 to 120 minutes, 500 mL of air was collected into a Tedlar from the glass jar through the sample port and the sample was screened by field GC/MS. The TCE concentration in these samples was typically > 10,000 ug/m<sup>3</sup>. Each sample was diluted with nitrogen into a second Tedlar bag so that

samples could be collected onto the sorbent tubes using a reasonable flow rate (>10 mL/min) and sample collection time (20 -30 min; See Photo 2).

Groundwater Samples: Groundwater samples were collected from monitoring wells screened at the top of the shallowest water-bearing unit. Samples were collected in 40 mL VOA vials and stored at <4°C until analysis.



## SAMPLE ANALYSIS METHODS

Compound-Specific Stable Isotope Analysis: Samples for CSIA were shipped to the laboratory of Dr. Richard (Paul) Philp at University of Oklahoma. The isotope ratios of TCE were determined by a modified PT-GC-IRMS (purge-and-trap-gas chromatography–isotope ratio mass spectrometry) protocol. For sorbent tube samples, the PT unit (Eclipse 4660, OI Analytical) was fitted with an Air-Tube Desorber Accessory (OI Analytical). The desorber replaces PT sparge vessel and permits integration of sorbent tubes into a normal PT protocol. A tube mounted in the desorber is initially flushed with He to remove absorbed moisture and O<sub>2</sub>, then the tube is heated and VOCs are purged to the sample concentrator's trap. VOCs collected on the concentrator's trap are transferred without split onto GC-IRMS. The tube desorption parameters are similar to those of TO-17. A detailed description of the standard PT-GC-IRMS method are available elsewhere (Kuder et al., 2009, Supporting Information).

A modified approach was necessary to analyze the indoor air samples, due to high concentrations of unidentified VOCs that could not be chromatographically resolved from TCE. In standard method, GC separation on single, non-polar phase column is sufficient. For the indoor air samples, 2-D GC separation was necessary, utilizing a polar phase (DB-Wax) and a non-polar phase (DB-MTBE) in a sequence. For the 2-D separation, a heartcut of the polar DB-Wax column effluent with the compound of

interest was trapped on liquid nitrogen, and then the heartcut was separated on the non-polar DB-MTBE column. This transfer results in no measureable loss of mass. 2-D separation is often successful in resolving extremely complex mixtures of compounds, because relatively few compounds have identical retention times on polar and non-polar GC columns. The PT-GC interface used at the OU facility (Kuder et al., 2009, Supporting Information) permits 2-D GC without additional hardware modification.

TO-17: The back-up tubes installed in series behind the 300 ng sample tubes were shipped to Beacon Environmental Services in Bel Air, Maryland. These samples were analyzed for TCE by USEPA Method TO-17.

## RESULTS AND DISCUSSION

Laboratory Control Samples: In order to evaluate the effect of sorbent tube samplers on the measured  $\delta^{13}\text{C}$  values, laboratory control samples were analyzed directly as TCE vapor samples and sorption and desorption from sorbent tubes (see Table 1)

**Table 1: Results of Compound-Specific Stable Isotope Analysis of Laboratory Control Samples**

Sample Type	Corrected $\delta^{13}\text{C}$ TCE (‰) <sup>(1)</sup>
TCE Spiked Tube	-30.4
TCE Spiked Tube	-30.7
TCE Spiked Tube	-30.5
TCE Spiked Tube	-31.0
TCE Spiked Tube	-30.4
TCE Spiked Tube	-30.8
TCE Spiked Tube	-30.9
TCE Spiked Tube	-31.0
TCE Spiked Tube	-30.7
TCE Spiked Tube	-30.9
TCE Spiked Tube	-30.6
TCE Vapor	-30.6
TCE Vapor	-30.7
TCE Vapor	-30.8
TCE Vapor	-31.0

Note: The TCE used for the laboratory control samples has a  $\delta^{13}\text{C}$  value of -30.7‰, based on independent laboratory measurements. The Corrected  $\delta^{13}\text{C}$  values = laboratory measured  $\delta^{13}\text{C}$  value + bias correction. The bias correction (-0.6) is the difference between the average  $\delta^{13}\text{C}$  value for the TCE spiked tubes and the known  $\delta^{13}\text{C}$  value of -30.7‰ for the laboratory TCE standard. When comparing the results from this study to results reported in other studies, the corrected  $\delta^{13}\text{C}$  values should be used.

For the laboratory control standards, the TCE-spiked sorbent tubes showed a slightly higher corrected  $\delta^{13}\text{C}$  value compared to the direct inject of vapor phase TCE (-30.1‰ vs. -30.4‰,  $p=0.04$ ). This difference (bias) was replicable and can be accounted for by proper QA/QC procedures. The analytical bias was small compared to the variations in  $\delta^{13}\text{C}$  values typically observed in field samples due to the fractionation effects associated with biodegradation and other transformation reactions.

**Table 2: Results of Compound-Specific Stable Isotope Analysis of Environmental Samples**

Sample ID	Corrected $\delta^{13}\text{C}$ TCE (‰) <sup>(1), (2)</sup>	Comments
<b>Source Area Soil Gas Samples</b>		
SG-2	-24.5, -24.3	
SG-3	-25.3, -25.4	
SG-4	-24.6	
<b>Groundwater Samples from Off-Site Groundwater Plume</b>		
Clearfield	-28.3J	
Sunset 2, MW-10	-21.6	
Sunset 2, MW-12	-20.6	
Layton	-22.3	
<b>Soil Gas Samples from Above Off-Site Groundwater Plume</b>		
Layton Green	-5.2	Depth = 8 ft bgs, approx. 7 ft above GW table.
Layton Blue	-18.5	Depth = 10 ft bgs, approx. 5 ft above GW table.
Layton 2 Blue	-20.6	Depth = 12 ft bgs, approx. 3 ft above GW table.
Layton 3 Blue	-19.4	Depth = 14 ft bgs, approx. 1 ft above GW table.
Layton Yard Yellow	-15.7	Depth = 10 ft bgs, depth to GW table not measured.
Sunset 2, MW-5	-1.3	Depth = 8 ft bgs, approx. 2 ft above GW table.
Clearfield 2 Blue	-23.7J	Depth = 7.5 ft bgs, approx. 1 ft above GW table.
<b>Potential Indoor Sources of TCE</b>		
SOURCE 1	-25.5	Tetra Gun Action Blaster: Aerosol spray can (contains TCE) purchased from local retail store.
SOURCE 2	-26.3, -26.2	Rusty Duck Gun Cleaner: Aerosol spray can (contains TCE) from residence other than U8-8078.
SOURCE 3	-26.6, -26.7	Zep 45: Aerosol spray can (contains 40 to 50% TCE) from the garage of U8-8078.
SOURCE 4	-26.6, -26.6	Zep X OUT II Spot and Stain Remover: Aerosol spray can (contains TCE and PCE) from the garage of U8-8078.
<b>Indoor Air Samples (U8-8078, above GW plume &amp; with Suspected Indoor Sources)</b>		
INDOOR AIR 1	-26.8	
INDOOR AIR 2	-26.6	

Note: 1) The TCE used for the laboratory control samples has a  $\delta^{13}\text{C}$  value of -30.7‰, based on independent laboratory measurements. The Corrected  $\delta^{13}\text{C}$  values = laboratory measured  $\delta^{13}\text{C}$  value + bias correction. The bias correction (-0.6) is the difference between the average  $\delta^{13}\text{C}$  value for the TCE spiked tubes and the known  $\delta^{13}\text{C}$  value of -30.7‰ for the laboratory TCE standard. When comparing the results from this study to results reported in other studies, the corrected  $\delta^{13}\text{C}$  values should be used.

2) Two values are results from duplicate samples collected from the same location. J = value qualified as estimated due to low sample mass.

For approximately 50% of the samples, back-up sorbent tubes were used in series behind sorbent tube collected for CSIA. These back-up tubes were analyzed for TCE by Beacon Environmental Services in Bel Air, Maryland in accordance with USEPA Method TO-17. TCE was not detected in any of the 18 back-up tubes analyzed at a detection limit on 0.4 ng to 0.6 ng.

## SUMMARY

Active Sorbent Tubes: The results indicate that sorbent tubes can be used to collect vapor phase samples for CSIA, including samples with low concentrations of the target VOC (1 to 4 ug/m<sup>3</sup>). The indoor air samples were found to contain a number of other organic compounds, some of which co-eluted with TCE when using a standard GC separation. This observation was consistent with TO-15 analysis of indoor air samples, which typically results in the detection of dozens of petroleum hydrocarbons and other VOCs (McHugh, personal communication). However, University of Oklahoma was able to obtain a clean TCE peak using an enhanced GC method. Because CSIA requires a clean compound peak, similar enhanced separation methods may commonly be required for indoor air samples and other samples that are likely to contain several organic compounds. For “complex” samples, it may be important to collect an additional sample for preliminary analysis in order to determine the best way to obtain a clean peak for the target compound. Additional laboratory validation work is being conducted evaluate potential fractionation effects associated with variations in sampling conditions such as sample volume, humidity, and other factors.

Carbon Isotope Ratios: The results indicate that there are measurable differences in  $\delta^{13}\text{C}$  values between TCE in the subsurface at Hill AFB and indoor sources of TCE. The  $\delta^{13}\text{C}$  values for the three source area soil gas samples ranged from -25.3‰ to -24.4‰,  $\delta^{13}\text{C}$  values for four groundwater samples collected from the off-site plume ranged from -23.8‰ to -20.6‰,  $\delta^{13}\text{C}$  values for seven soil gas samples collected from above the off-site plume ranged from -23.7‰ to -5.2‰. These results show a pattern of  $^{13}\text{C}$  enrichment away from the source area. In contracts, the  $\delta^{13}\text{C}$  values for the four indoor source samples ranged from -26.6‰ to -25.5‰, lower values than any of the subsurface samples. The  $\delta^{13}\text{C}$  values for the indoor air samples collected from U8-8078 (26.6‰ and 26.8‰) closely matched the  $\delta^{13}\text{C}$  values for the two indoor sources identified in the house (26.6‰ and 26.7‰) indicating that these two indoor sources were the most likely source of the TCE being detected in indoor air. These preliminary results support the hypothesis that CSIA of indoor air samples can be used to distinguish between vapor intrusion and indoor sources of the same VOC. Additional work is being conducted to develop a fully validated method for use of CSIA to distinguish between vapor intrusion and indoor sources of VOCs.

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## KEY WORDS

Vapor Intrusion, Compound-Specific Stable Isotope Analysis, CSIA, TCE