

## **A Comparison between EPA Compendium Method TO-15 and EPA Method 8260B for VOC Determination in Soil Gas**

**Paper #46**

**Heidi C. Hayes**

Air Toxics, Ltd., 180 Blue Ravine Rd. Ste. B, Folsom, CA 95630

**Diane J. Benton**

Air Toxics, Ltd., 180 Blue Ravine Rd. Ste. B, Folsom, CA 95630

**Sarbjit Grewal**

Air Toxics, Ltd. 180 Blue Ravine Rd., Ste. B, Folsom, CA 95630

**Noor Khan**

Air Toxics, Ltd. 180 Blue Ravine Rd., Ste. B, Folsom, CA 95630

### **ABSTRACT**

Evaluations of vapor intrusion pathways of chemical contaminants often include soil gas measurements to assess the potential for indoor inhalation. No longer just a screening tool, soil gas measurements are requiring a level of quality and defensibility which should be incorporated in soil gas analytical protocols. While both EPA Compendium Method TO-15 and EPA SW-846 Method 8260B are routinely used for the analysis of Volatile Organic Compounds (VOCs) in soil gas, neither method has been validated for the soil gas matrix. To determine comparability of the two methods, the precision and accuracy of EPA SW-846 8260B are compared to EPA Compendium Method TO-15. Using reference standards prepared to simulate expected soil gas humidity levels, the two methods are compared post-collection through analysis. Additionally, real field samples are analyzed by each method to compare performance. Comparative results are generated using both GC/MS full scan and SIM mode and the limitations of each approach are discussed. Finally, recovery of VOCs through a TO-15 soil gas sampling train is evaluated at several sampling temperatures. The specific VOCs evaluated in the study are Vinyl Chloride, Benzene, Trichloroethene and Naphthalene.

### **INTRODUCTION**

In November 2002, the EPA published its *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway*. Since then, numerous states have issued guidance

documents describing various approaches to evaluating exposure to subsurface vapors entering a building. In most cases, shallow soil gas measurements are recommended to assess the potential for indoor air inhalation.

In an effort to produce high quality data for health risk assessment, the DTSC and LARWQCB issued their *Advisory - Active Soil Gas Investigations* in January 2003 which outlines a standardized approach to soil gas sampling and analysis. The advisory allows either soil gas collection with a syringe and subsequent analysis by EPA SW-846 Method 8260B or sample collection utilizing a Summa canister followed by TO-15 analysis. Neither analytical method has been validated for the analysis of VOCs in soil gas. The standard application for method 8260B is the analysis of VOCs in water or solid waste matrices and does not address the direct analysis of vapor phase samples<sup>1</sup>. Although TO-15 is applicable for vapor phase samples, the method is written for ambient air<sup>2</sup>. Relative to ambient air, soil gas typically has higher moisture content (>60% relative humidity)<sup>3</sup> and may contain significantly higher levels of VOCs.

While both methods are configured with a multisorbent concentrator and a GC/MS for compound separation and detection, several major differences exist between the 8260B and TO-15 method. One significant difference is the calibration technique utilized by each method. Method 8260B uses liquid phase standards to calibrate for vapor phase samples, while TO-15 calibration is achieved using vapor phase standards. When calibrating 8260B, liquid standards are injected in the water contained in the purging chamber of the concentrator. The VOCs are then transferred from the water into the vapor phase by purging the water with an inert gas. The vapor is collected on a sorbent, followed by desorption onto the GC/MS. The vapor phase soil gas samples are analyzed by injecting an aliquot into the purging chamber containing water.

Despite technical concerns with calibrating in a manner inconsistent with the sample matrix, using liquid phase standards for vapor phase sample analysis is a more convenient and much less costly approach than using vapor phase standards. As a result, the 8260B method has been considered the preferred approach for field applications. However, it is unclear as to extent the calibration technique affects the accuracy of the 8260B soil gas data as compared to TO-15 data.

Another significant difference between 8260B and TO-15 is the applicable calibration range. While 8260B typically can achieve reporting limits of about 100 ppbv using a standard quadrupole GC/MS full scan and approximately 5 ppbv using SIM mode, TO-15 can achieve sub-ppbv reporting limits using GC/MS full scan and pptv reporting limits in the SIM mode. As the shallow soil gas screening levels often require ppbv reporting limits, the selection of the method and the detector mode (full scan vs. SIM) may impact the data usability and interpretation.

The third major difference lies not in the analytical technique, but in the sample collection requirements of each method. While 8260B samples are collected via syringe directly at the head of the soil gas probe, collection of a TO-15 soil gas sample typically requires a sampling train consisting of a transfer tube, particulate filter, and flow

controller. The impact of the sampling train on VOC recovery, specifically Naphthalene, may be important in selecting the appropriate analytical method.

## APPROACH

To evaluate the significance of these differences and compare the precision and accuracy of EPA Compendium TO-15 to EPA SW-846 8260B, three studies were performed. In the first study, a humidified vapor phase reference standard was prepared at two different concentrations. Parallel analysis was performed via TO-15 and 8260B to compare performance from post-collection through analysis. The second study compared TO-15 and 8260B soil gas VOC measurements from the analysis of real field samples. In the third study, the impact of the TO-15 soil gas sampling train on VOC recoveries was evaluated.

Vinyl Chloride, Benzene, Trichloroethene (TCE) and Naphthalene were evaluated in each of the comparison tests. This set of compounds varies significantly in their vapor pressures, and each is a common compound of concern on contaminated sites. Benzene and Naphthalene are often associated with petroleum hydrocarbon spills or leaks, while TCE and Vinyl Chloride are common VOCs of concern on sites contaminated with chlorinated solvents. Additionally, Naphthalene was selected based on California's newly adopted cancer unit risk value<sup>4</sup>, prompting the need to measure Naphthalene in the soil gas for health risk determination. Table 1 is the list of the target VOCs along with their CAS number, vapor pressure, and boiling point.

**Table 1.** VOC Physical Data.

Compound	CAS #	Vapor Pressure 25°C	Boiling Point
Vinyl Chloride	75-01-4	3200 Torr <sup>2</sup>	-14 °C
Benzene	71-43-2	76.0 Torr <sup>2</sup>	80.1 °C
Trichloroethene	79-01-6	20.0 Torr <sup>2</sup>	87.0 °C
Naphthalene	91-20-3	0.086 Torr <sup>5</sup>	218 °C

## Comparison Test - Reference Standards

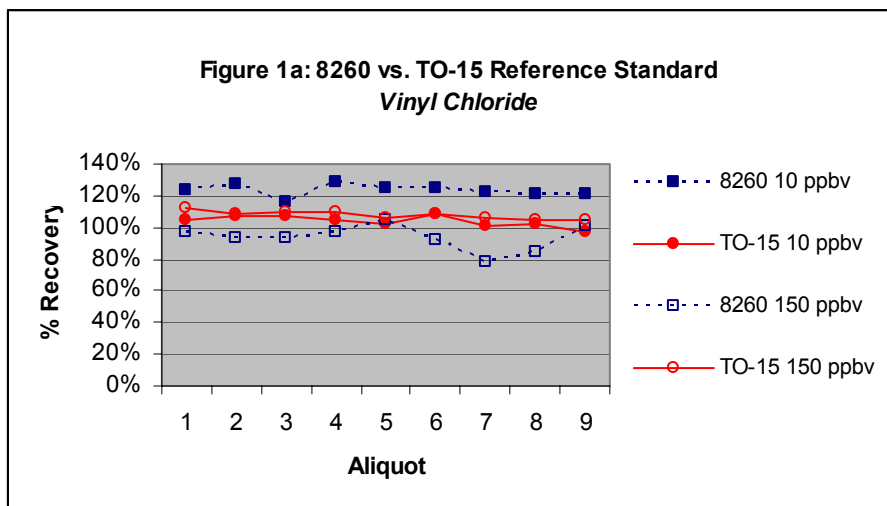
### *Testing Protocol*

Two reference standards containing Vinyl Chloride, Benzene, TCE and Naphthalene were prepared in Summa canisters. One reference standard was prepared at 10 ppbv and a second standard was prepared at 150 ppbv for Vinyl Chloride, Benzene, and TCE and 30 ppbv for Naphthalene. Standards used to prepare the reference standards were NIST certified vapor phase standards supplied by Scott Specialty Gases. Since soil gas generally has moisture content of over 60% relative humidity (RH), the reference standard was prepared at a RH of 70%. To provide sufficient volume for completion of this validation test, a 15 L Summa canister was used and pressurized to 15 psig with zero air.

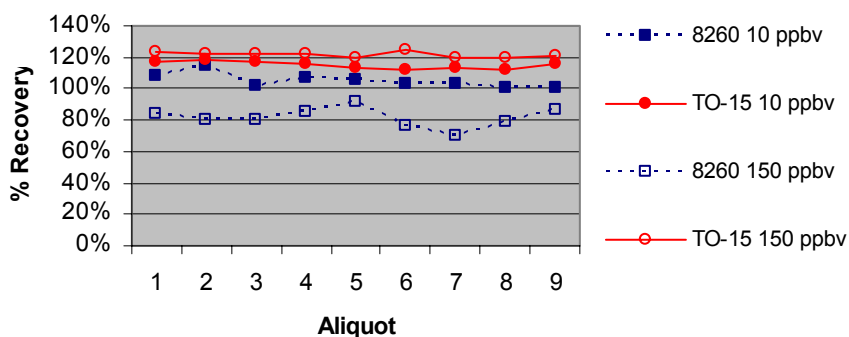
Nine aliquots were withdrawn from each standard via a clean, leak-free gas-tight glass syringe equipped with a luer lock with on/off exit valve. Immediately after withdrawing the aliquot, the exit valve was closed and the syringe body wrapped in aluminum foil. The aliquot was then injected into the 8260B unit within 30 minutes to simulate approximate time between collection in the field and analysis. This represents the recommended hold time by the DTSC document. Each aliquot was analyzed by 8260B on a Tekmar Purge and Trap and Agilent 6890/5973 GC/MS. In order to achieve the required sensitivity, the 8260B method was run in the Selected Ion Monitoring (SIM) mode.

Nine 1 L cleaned and certified Summa canisters were sampled from each reference standard and filled to ambient pressure. A regulator was attached to the 15 L soil gas standard along with a toggle switch to transfer to the collection canister. After collection, canisters were pressurized to 15 psig with nitrogen and analyzed by TO-15. Canisters were analyzed on the laboratory's standard concentrator using Agilent 6890/5973 GC/MS in the full-scan mode. Analysis occurred 3 days after collection of the canister; consistent with the recommended 3-day hold time in the DTSC document.

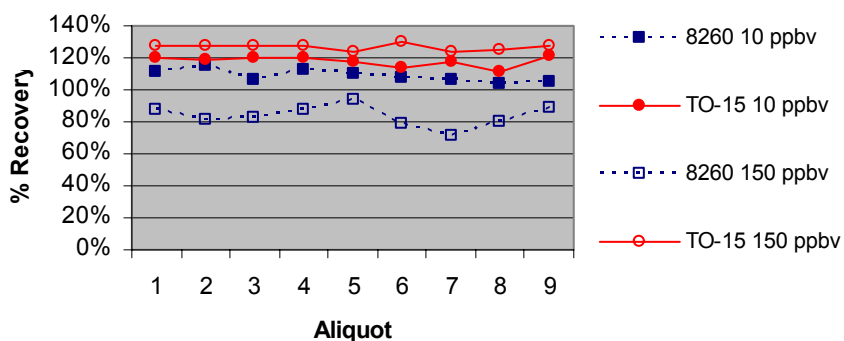
Collection of each 1 L canisters and each syringe aliquot was alternated to minimize bias due to the change in pressure of the standard canister. Results from the comparison test for the two reference standards are summarized in Figures 1a-1d.



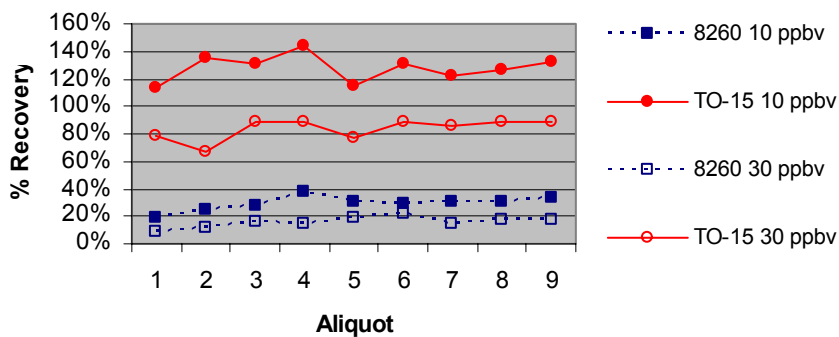
**Figure 1b: 8260 vs. TO-15 Reference Standard**  
*Benzene*



**Figure 1c: 8260 vs. TO-15 Reference Standard**  
*Trichloroethene*



**Figure 1d: 8260 vs. TO-15 Reference Standard**  
*Naphthalene*



## ***Discussion of results***

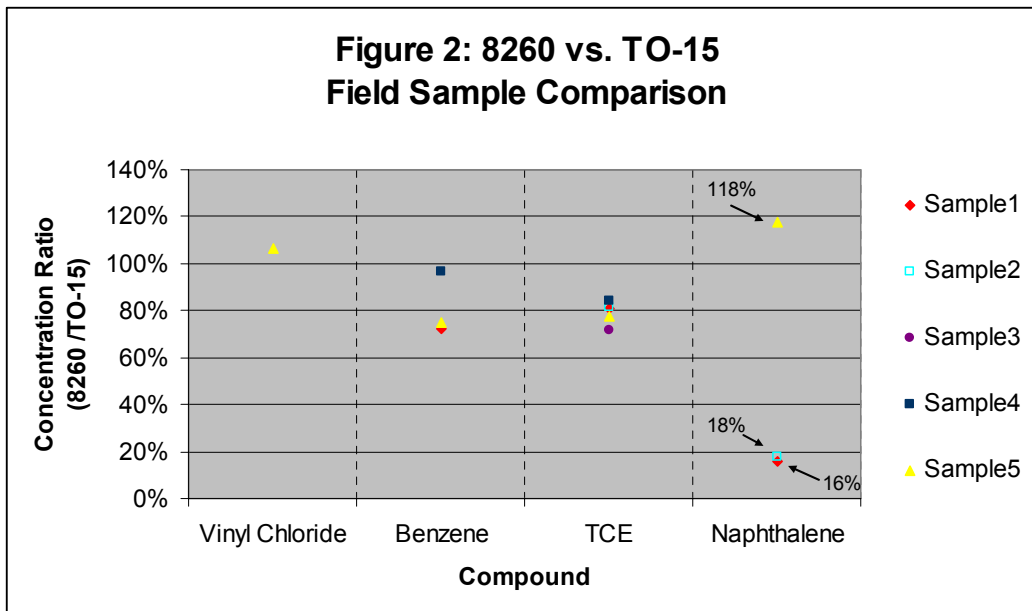
Recoveries of Vinyl Chloride, Benzene, and TCE were within method accuracy limits of 70-130% for both 8260B and TO-15 analysis at both the 10 ppbv and 150 ppbv concentrations. Naphthalene did not meet the method accuracy limits for the 8260B aliquots with average recoveries for the 10 ppbv and 30 ppbv standards of 29% and 16% respectively. In contrast, average Naphthalene recoveries for TO-15 were within standard method acceptance limits of 128% and 84% for each standard. Precision for each compound and each method was generally below 10% relative standard deviation (RSD). Naphthalene exhibited higher %RSD for 8260B with 18% and 24% RSD for the 10 ppbv and 30 ppbv standards respectively.

It is unclear as to the cause of the low Naphthalene recoveries for the 8260B runs. Loss may be occurring either through adsorption onto the glass syringe surface used to load the aliquot or through loss in the purge and trap concentrator. The low vapor pressure of Naphthalene increases its adsorption to unheated and active surfaces translating to low recovery. In contrast to 8260B, vapor phase samples are introduced into the TO-15 concentrator through heated stainless steel lines having a quantifiable advantage for low vapor pressure compounds.

## **Comparison Test – Field Samples**

### ***Testing Protocol***

Five soil gas samples collected in 1 L and 6 L Summa canisters representing various matrix composition and concentrations were analyzed by TO-15 GC/MS full scan and 8260B GC/MS full scan and SIM. Several samples contained high levels of VOCs and a heavy fuel pattern. Not all compounds were detected in each sample. Results from the comparison test for field samples are summarized in Figure 2. The 8260B concentration for each compound was divided by the TO-15 concentration to yield a concentration ratio. Ratios less than 100% indicate a low bias for the 8260B result when compared to TO-15.



### *Discussion of results*

Evaluation of the 8260B and TO-15 field sample data indicates good comparability for Vinyl Chloride, Benzene, and TCE with 8260B results recovering 70-130% relative to TO-15 data. Three samples contained detectable levels of Naphthalene. Two of the field samples exhibited low recovery (16% and 18%) when compared to TO-15 results which is consistent with the reference standard comparison test. One sample, Sample 5, did not follow the same trend and recovery of Naphthalene (118%) was comparable between 8260B and TO-15.

Several of the field samples were analyzed by GC/MS SIM for 8260B and GC/MS full scan for TO-15. The resultant chromatograms clearly demonstrate the limitations of the SIM mode when compared to full scan. Figures 3a and 3b are chromatograms of the same sample. Figure 3a represents the 8260B SIM run and Figure 3b represents the TO-15 full scan run. TCE is highlighted in both chromatograms to serve as a reference marker. The high concentrations of the petroleum hydrocarbons relative to TCE in the full scan run are negligible relative to the TCE peak in the SIM analysis.

Figure 3a:

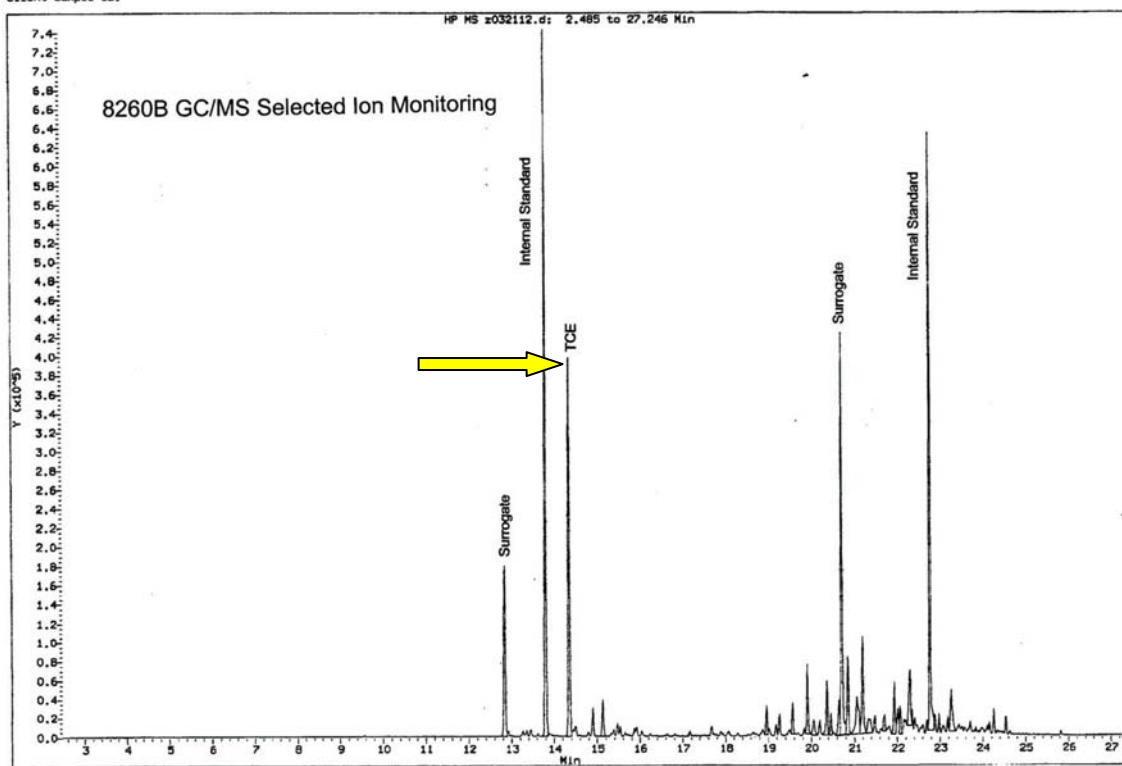
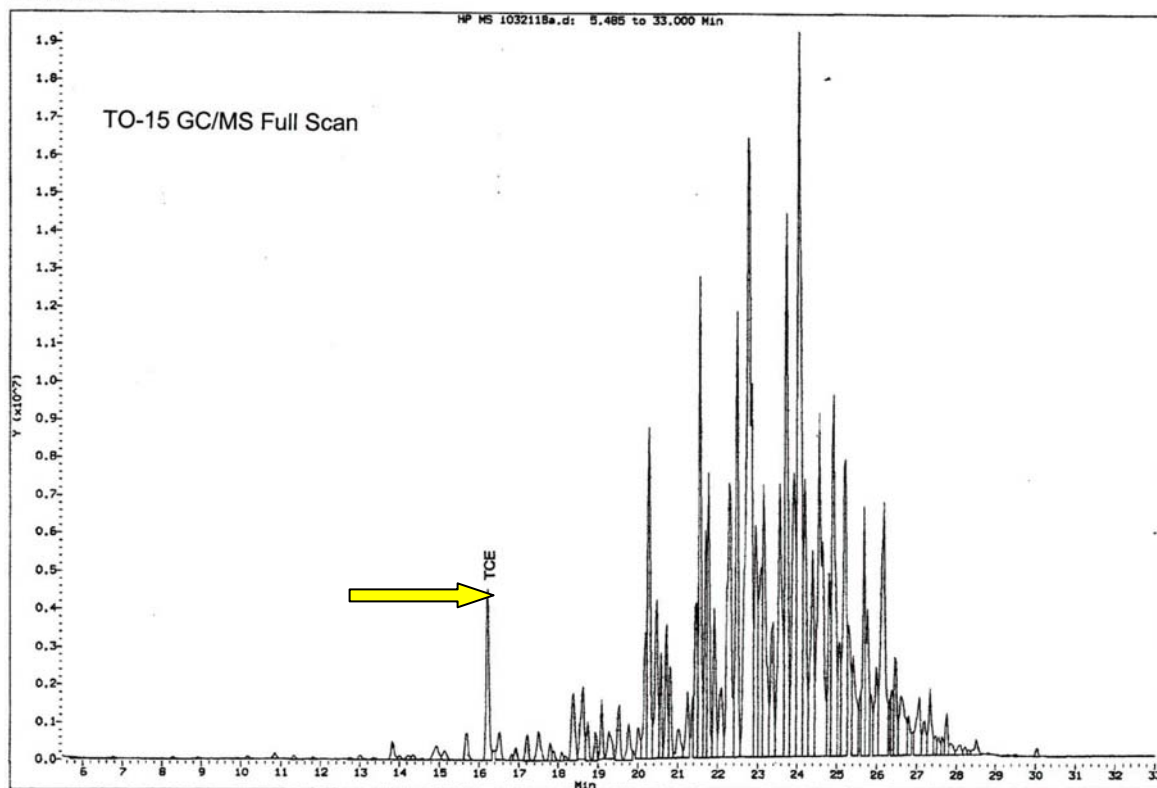


Figure 3b:





While SIM provides increased sensitivity by setting the detector to observe only a specific mass, or a selection of specific masses, the detector is also “blind” to many other compounds whose ions are not monitored. Not only does SIM limit the full characterization of a soil gas sample, the lack of complete mass ion data available using full scan mode may result in inaccurate compound identification and/or quantification. In the example sample shown above, target compounds eluting in the fuel pattern in the SIM run may exhibit erroneous ion ratios or a positive bias attributed to the “invisible” matrix. Without the power of the full scan spectra to identify the interfering ions, the possibility of false positives, high bias, or false negatives increase especially when analyzing soil gas samples from uncharacterized sites. SIM mode of detection should not be employed by the analytical laboratory during the site characterization phase.

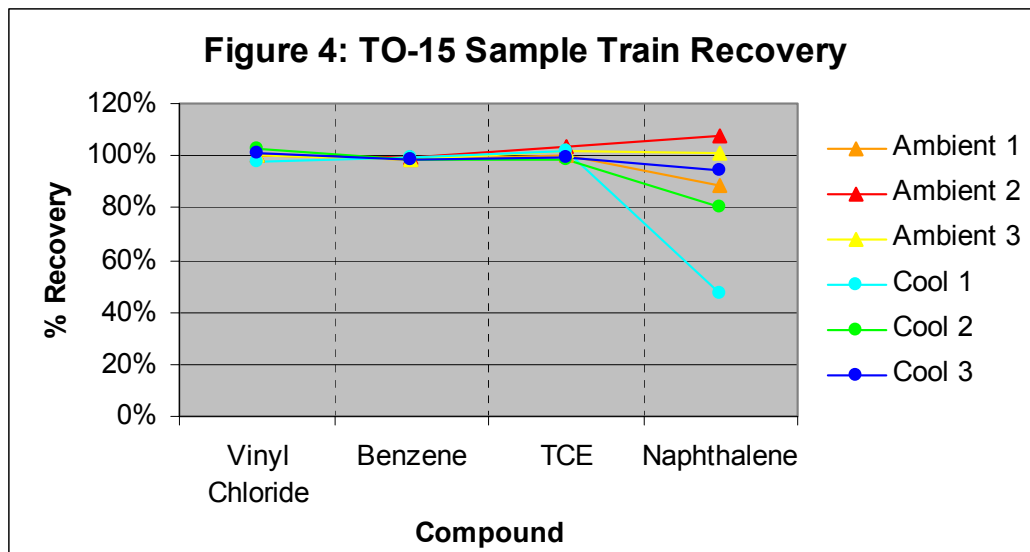
## **Sample Train Recovery Test**

### ***Testing Protocol***

Recovery of Vinyl Chloride, Benzene, TCE, and Naphthalene through a typical TO-15 soil gas sampling train was evaluated at several temperatures. A 7.5 ppbv standard containing the target VOCs and 70% RH was prepared to serve as the sample source. A total of six sampling trains were assembled prior to sampling. Consistent with procedures outlined in the DTSC ASGI guidance, a flow controller set at approximately 175 mL/minute was utilized in the train. Using compression fittings, 2 feet of ¼” Teflon tubing was attached to the sample source and connected to a 2 micron particulate filter and flow controller. The flow controller was then connected to a clean and evacuated 1 L canister. The collection canister valve and the source canister valves were opened to commence sampling. When the collection canister reached approximately 5 in Hg vacuum, the valves were closed and the collection canister was pressurized to 15 psig with nitrogen and analyzed by TO-15.

A total of six sampling trains were assembled and used for sample collection. Three of the six trains were operated at ambient temperature, and three were stored in a refrigerator prior to use. An infrared temperature sensor was used to measure the surface temperature of the flow controller assembly before and after sample collection. The average temperature of the ambient sample trains was approximately 23°C. The average initial temperature for the cooled trains before sampling was 10°C and after sampling was approximately 18°C. The Teflon tubing quickly equilibrated to ambient temperature after removal from the refrigerator.

A control sample was prepared by transferring the sample source directly to a 1 L canister and pressurizing to 15 psig. The measured concentrations of the control sample were used to calculate the recovery through the sampling train. The results are summarized in Figure 4.



### ***Discussion of results***

Recoveries of Vinyl Chloride, Benzene, and TCE demonstrated excellent precision through all six sampling trains. Recoveries of Vinyl Chloride, Benzene, and TCE were between 98% and 103%. The recoveries of Naphthalene exhibited more variability and lower recoveries than the other target VOCs. Recoveries ranged from 89% to 108% for the ambient trains and 47% to 94% for the cooled sampling trains. The lower Naphthalene recoveries through the sampling trains are most likely due to adsorption to the surfaces of the train. As expected, lower temperatures exacerbate the adsorption effects.

### **CONCLUSION**

Despite the differences between the methods, the data suggests that EPA Compendium TO-15 and EPA SW-846 8260B generate statistically comparable results for Vinyl Chloride, Benzene and TCE at the concentrations evaluated. Naphthalene proved more problematic for both methods. The comparison tests of the analytical methods indicated that soil gas analysis by 8260B resulted in unacceptably low recoveries compared to TO-15. However, when the sample train was included in the TO-15 evaluation, additional variability and, in some cases, low recovery of Naphthalene was observed in the small data set collected. Although recovery of Naphthalene through the sampling train was erratic and temperature dependent, the data suggested that TO-15 generally outperformed 8260B. Additional studies on Naphthalene recovery through the sampling train are recommended to better understand and predict its behavior.

Based on the test results, TO-15 and 8260B comparability can only be extended to Vinyl Chloride, Benzene, and TCE under the conditions studied. In particular, further tests need to be performed to evaluate comparability for analytes with increasing polarity and water solubility. The bias of the 8260B liquid phase calibration for vapor phase

compounds may be more significant for polar compounds such as alcohols, ethers, and ketones. Because 8260B performance is not validated using vapor phase standards during calibration or soil gas analysis, questions regarding the defensibility of soil gas measurements are inherent in the analytical approach. Conversely, validation of each soil gas result is built into the TO-15 method with vapor phase calibrations, method detection limit studies, second source verifications, and daily calibration checks.

The reporting limit requirements for the soil gas investigation should also be considered in the selection of the analytical method. In order to meet low ppbv reporting levels, the standard Method 8260B quadrupole MS typically utilizes the SIM mode. When operating in SIM mode, the MS detector should be considered a “glorified FID”. Although SIM is a powerful tool in increasing detector sensitivity, SIM also limits the data acquired by the MS resulting in less characterization of the site and possible inaccurate results if the sample matrix is complex. In these situations, TO-15 GC/MS full scan provides equivalent or better reporting limits than 8260B without the limitations of SIM.

## REFERENCES

1. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods: Method 8260B, Revision 2*, U.S. Environmental Protection Agency, Washington, D.C. 1996; SW-846.
2. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-15, Second Edition*, U.S. Environmental Protection Agency: Research Triangle Park, NC January 1999; EPA 600/625/R-96/010b.
3. *Annual Book of ASTM Standards*, Volume 04.08, West Conshohocken, PA 2001; ASTM D5134-92 (2001).
4. Denton, J.E., Memorandum- Adoption of Unit Risk Value for Naphthalene, Office of Environmental Health Hazard Assessment: Sacramento, CA August 2, 2004.
5. *CRC Handbook of Chemistry and Physics*, 70th edition, Weast, Robert C, ed. Boca Raton, FL: CRC Press Inc. p. D-214-216.