

A Comparison of EPA Methods 8260B and TO-14A/15 for the analysis of VOCs in Soil Gas: Application to Upward Vapor Intrusion Risk Studies

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ABSTRACT

The determination of Volatile Organic Compounds (VOCs) in soil vapor (gas) is necessary in order to obtain empirical data to enter into risk models for upward vapor intrusion. Several EPA Methods are currently being used to furnish the regulatory community with this information. Two of the most commonly used are EPA Method 8260B (from SW-846) and the two similar ambient air methods EPA TO-14A and TO-15. None of the methods were originally designed to apply to soil vapor and as such all are being modified by analytical chemists and laboratories in order to make them amenable to the soil vapor matrix.

A comparison of the methods will be presented that shows the similarities and the differences between the two procedures. The protocols for sampling of soil vapor, the analytical instrumentation used, standardization and calibration procedures, range and detection limits will be contrasted along with those modifications necessary to apply the written methods to soil gas. The advantages of each of the three methods along with the assumptions and weaknesses inherent in each method will be presented with the objective of utilizing all three in a complementary fashion. Finally, parallel analysis of soil vapor samples by EPA 8260B and TO-15 performed in the author's laboratories will be presented to support the theoretical conclusions.

INTRODUCTION

Vapor intrusion

There exists in the U.S. and abroad a growing concern regarding the increased health risk from subterranean pollutants finding their way into living and workspaces. This process, termed vapor intrusion (VI), is currently the focal point of new types of studies by a variety of environmental scientists. The degree to which VI will affect individuals is the final objective of toxicologists, geologists, engineers and other workers in the field.

Vapor Intrusion has been studied, at least to a limited degree for some time. The concern for the household intrusion by Radon gas, first described in the mid 1980s, brought to light this pathway for adverse health effects. Since then the concern has expanded to include intrusion from a variety of pollutants. Groundwater plumes from petroleum spills, dry cleaning operations and pesticide applications are just some examples of possible sources of both subsoil contamination and the resultant vapor intrusions.

EPA Methods

In order to assist the environmental scientists and engineers grappling with the problem of vapor intrusion, the analytical chemical laboratories have had to keep pace with the demands for chemical analysis data. Owing to the obvious properties of the majority of compounds of concern, namely that they have appreciable volatility, the applicable analytical procedures are volatile organic methods. Historically, the method of choice for volatile organic analysis has been gas chromatography/mass spectrometry (GC/MS) in the form of EPA Method 8260B (the current version dated 12/1996 is denoted by “B”) which has been in use in some form for over twenty-five years. This method has been the workhorse of the environmental laboratory since the inception of the U.S. E.P.A.

Written originally by the EPA Office of Solid Waste, the EPA 8000 series methods state that they are applicable to a “wide variety of solid waste matrices...including air sampling trapping media, ground and surface water, aqueous sludges...soils and sediments”. Since then various other branches of EPA have slightly modified procedures for specific uses. Thus came about the “600” series methods (for industrial effluents) and the “500” series (for drinking water). In another form, this procedure formed the basis of the “Superfund” Contract Lab Program, which resulted in the intensive nationwide cleanup from that program. The general technique of the method, however, remains the same, purge and trap GC/MS for volatile organic compounds.

On a later yet parallel course EPA Office of Research and Development (ORD) created a series of methods for the determination of pollutant compounds in ambient air referred to as the Toxic Organic (TO) methods. The volatile organic GC/MS version began with Method TO-14 first published in 1989. The most recent and comprehensive version is currently EPA Method TO-15 and was published in January of 1999. These methods were developed and intended for low concentrations of organics as would be found in “everyday” places such as homes, offices all the way down to quite pristine rural environments.

Soil Vapor/Soil Gas Analysis

Prior to the current concern of upward vapor intrusion, much site investigation had been done using soil vapor (gas) analysis most often performed in the field by mobile laboratories. The mobile laboratories were able to take advantage of modern and rugged instrumentation to bring the same quality analytical techniques into the field as were in use in the stationary facilities. In addition, as opposed to drilling or excavating to obtain groundwater or soil samples, the use of “direct push” probe trucks and the subsequent

analysis of soil vapor samples was generally more efficient and made a far smaller impact on site operations. Many locales developed protocols for site assessment investigations using soil vapor as the only technique necessary for regulatory compliance. These regulations were generally concerned with contaminant concentrations well within the capability of the EPA 8000 series. Hence it was quite natural and convenient for the mobile laboratories to adapt current groundwater procedures to the analysis of the soil vapor. As an example, the author's mobile laboratories have been performing soil vapor analysis by EPA Methods for more than fifteen years and Method 8260 for ten years.

Human Health Risk

Once the focus shifted from simply underground or groundwater contamination to human health risk in the home and workplace, the concentrations at which one must measure the pollutants began to drop. The application of slope factors of 10^{-4} to 10^{-6} for risk calculations and the desire to sample indoor air (with detection limits in the low ppbv range) dictated either additional modifications to EPA8260 or the use of the TO Methods. The latter were, of course, already in use for indoor air. Their use in soil vapor had not been fully utilized.

It is the purpose of this paper to compare the two methods as they apply to vapor intrusion studies and to show how they are complementary not mutually exclusive.

THE METHODS IN DEPTH

Similarities

As mentioned in the introduction both EPA Method 8260B and TO-15 are GC/MS methods. Specifically they are high resolution gas chromatography (HRGC) combined with low resolution mass spectrometry (LRMS). As such they immediately have many features in common. Current instrumentation favors less expensive benchtop quadrupole or ion trap GC/MS systems (such as the Agilent 5973N or Varian Saturn systems). Fused silica capillary columns of 20-60 meters in length with an inner diameter of 0.18-0.32 mm provide the GC separation.

The two GC/MS methods also have other features in common. These are:

- Use of common MS tuning compounds and parameters
- Uses Internal Standards for accuracy
- Uses Surrogate(s) for QC
- Multipoint Initial Calibration (ICAL) with linearity checks,
- Daily Calibration Verification
- Varying sample size permitted

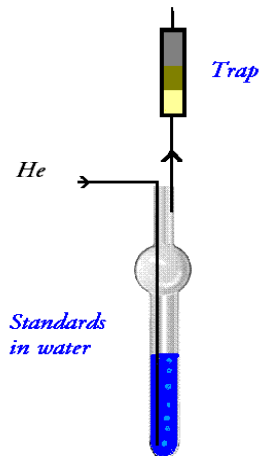
The net effect of the above is that the acquisition of data beginning with the gas chromatograph to its final reduction and reporting is virtually identical for both methods.

The final similarity to be noted is the most important. Both methods collect and concentrate compounds through the use of a multiadsorbent trap. This trap, which is designed to exclude water and preferentially hold organic compounds is the single feature in the preparation of samples which makes these methods virtually the same for most compounds.

Differences I

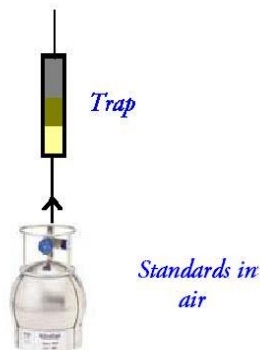
Where the two methods diverge comes from the fact that they were initially intended to treat different matrices (liquids/solids for 8260 and vapor for the TO methods). As such, sample preparation and handling are slightly different for the two. For Method 8260B, the sample preparation technique is actually a separate method number. (For water EPA 5030B) This technique, called purge and trap involves the stripping of volatile organics from a water solution using an inert (usually He) gas. The purge gas is bubbled through the water sample, the volatile compounds are transferred to the vapor phase and are swept out of the water and deposited on the aforementioned multisorbent trap.

Figure 1: Schematic of EPA 8260 concentration by Purge and Trap



In Method TO-15 the sample is initially contained in an inert canister or some other appropriate container for holding vapor. To begin the analysis, the canister is connected in series to the multisorbent trap. Using either a positive pressure in the canister or, alternatively a vacuum pump on the opposite side of the trap to pull vapor into the trap, the compounds are concentrated on the trap in a similar manner to the 8260 method. Irrespective of the matrix (vapor or water) the end result is that both methods have resulted in the organic compounds being deposited on the multisorbent trap.

Figure 2: Schematic of TO-15 concentration by trapping



The possible differences between the two methods come from the transfer of compounds from the water solution to the vapor phase. In the case of the TO-15 method the compounds are assumed to already be in the vapor phase. In the case of purge and trap, complete quantitative transfer from the water solution to the vapor phase may or may not occur. In other words, if one places 100 ng of a compounds in the water solution and purges the solution, one may not get 100 ng transferred to the trap during the purge and trap step. Recovery of compounds from the water is compound dependent and may not be 100%, whereas in the TO-15 method it is assumed to be 100%. (N.B. this assumption it is an issue for future study).

The net effect is that during the 8260 calibration procedure one may be actually analyzing a smaller amount and assuming that it is larger number. This would lead to a high bias in the calculation of compounds in a vapor relative to the TO method.

Most compounds currently of interest to vapor intrusion studies, however, are well recovered from the purge and trap procedure. Table 1. shows a study in 2001 of 40 compounds showed high recoveries above 75% for all compounds with most recoveries in the 90% for the conditions of the study.

Table 1. Percent recovery of selected compounds by purge and trap.
From Kang-Jin Lee et.al. bull. Korean Chem.Soc.2001, vol22, No.2

| | | | |
|----------------------|-----|------------------------|----|
| 1,1-DCE | 73 | Ethylbenzene | 88 |
| Methylene chloride | 100 | m,p-xylene | 90 |
| Trans-1,2-DCE | 86 | bromoform | 95 |
| 1,1=DCA | 92 | styrene | 98 |
| MEK | 84 | o-xylene | 97 |
| Chloroform | 100 | 1,1,2,2-TCA | 96 |
| 1,1,1-TCA | 81 | isopropylbenzene | 98 |
| 1,2-DCA | 100 | bromobenzene | 87 |
| benzene | 97 | 2-chlorotoluene | 78 |
| Carbon tetrachloride | 85 | n-propylbenzene | 95 |
| 1,2-DCPA | 96 | 4-chlorotoluene | 95 |
| TCE | 91 | 1,3,5-trimethylbenzene | 94 |

| | | | |
|----------------------|-----|------------------------|-----|
| Dichlorobromomethane | 91 | tert-butylbenzene | 96 |
| cis-1,3-DCPE | 100 | 1,2,4-trimethylbenzene | 96 |
| trans-1,3-DCPE | 100 | 1,3-dichlorobenzene | 74 |
| Toluene | 91 | sec-butylbenzene | 96 |
| 1,1,2-TCA | 99 | 1,4-Dichlorobenzene | 100 |
| Dibromochloromethane | 83 | p-isopropyltoluene | 92 |
| PCE | 87 | 1,2-dichlorobenzene | 94 |
| Chlorobenzene | 90 | n-Butylbenzene | 96 |

Of the 40 compounds listed above only 3 have recoveries less than 80%. That means that only those three compounds would have errors greater than 20% when compared with TO-15. A 20% error between methods essentially means the methods are identical for the analysis of a particular parameter.

Water soluble compounds.

Although there is no liquid water solution involved, water is an issue with the TO methods. In order to achieve the low detection limits, larger samples must be concentrated on the multisorbent trap. Even in dry climates, this can result in the deposition of large amounts (relative to the target compounds) of water vapor in the analytical system. Compounds which have appreciable water solubility can be trapped and remain in the water phase and not analyzed by the TO system. For this reason Method TO-14 was replaced by TO-15, which contains various methods for dealing with the water vapor problem and hence was able to analyze compounds with some solubility. These same compounds are the ones which do not have quantitative transfer in the purge and trap analysis. Examples are the fuel oxygenates and higher ketones. In our laboratory we have studied the purging efficiency of oxygenates and found them to be on the order of 50% or more. This relates to a difference between EPA 8260B and TO-15 of roughly a factor of 2 or less. Given the widely varying parameters that are used in vapor intrusion, it is clear that a factor or at most 2 times is likely not significant.

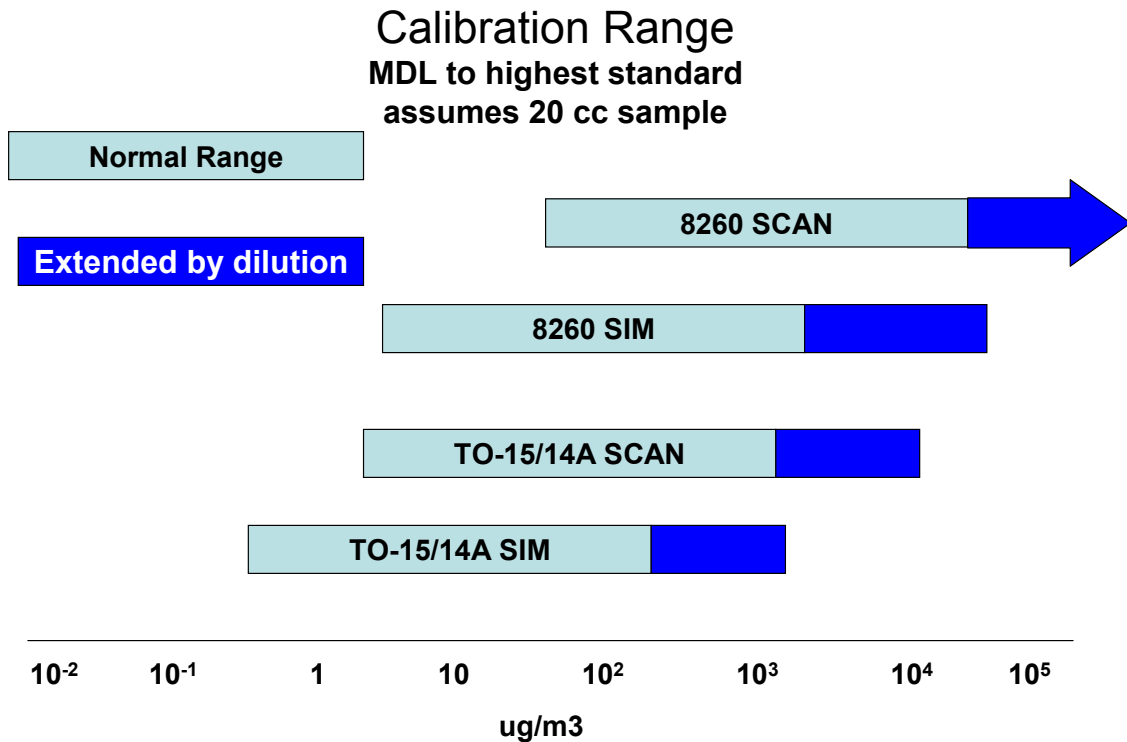
Extremely water soluble compounds may be a different story. Compounds such as ethanol, 1,4-dioxane, acetone, MEK and TBA are better handled by TO-15 if they are of interest. Their extreme water solubility make them difficult to analyze even by 8260.

Differences II

Another area in which the two methods differ, when applied to vapor samples, is that of the range of concentrations to which they are applied. The typical GC/MS conditions for 8260 involve the use of small capillary column and a split injection. Because of the need to rapidly desorb from the multiadsorbent trap, split ratios of 20:1 to 50:1 are used so that the P&T apparatus has sufficient flow. In contrast, TO-15 uses cryogenic focusing of the trapped compounds and no split is generally used. When compared to TO-15, EPA Method 8260B is, in effect, operating in a different range of concentrations, roughly one to two orders of magnitude higher. Figure 3. shows the relative ranges for the two methods, assuming the same sample size is used for both methods. The methods are

further subdivided into full GC/MS Scanning mode and selected ion monitoring mode (SIM). Also represented in the dark blue in the additional range possible for each method through the dilution of sample to smaller sample size, which is possible for both methods.

Figure 3. Calibration ranges for EPA Methods



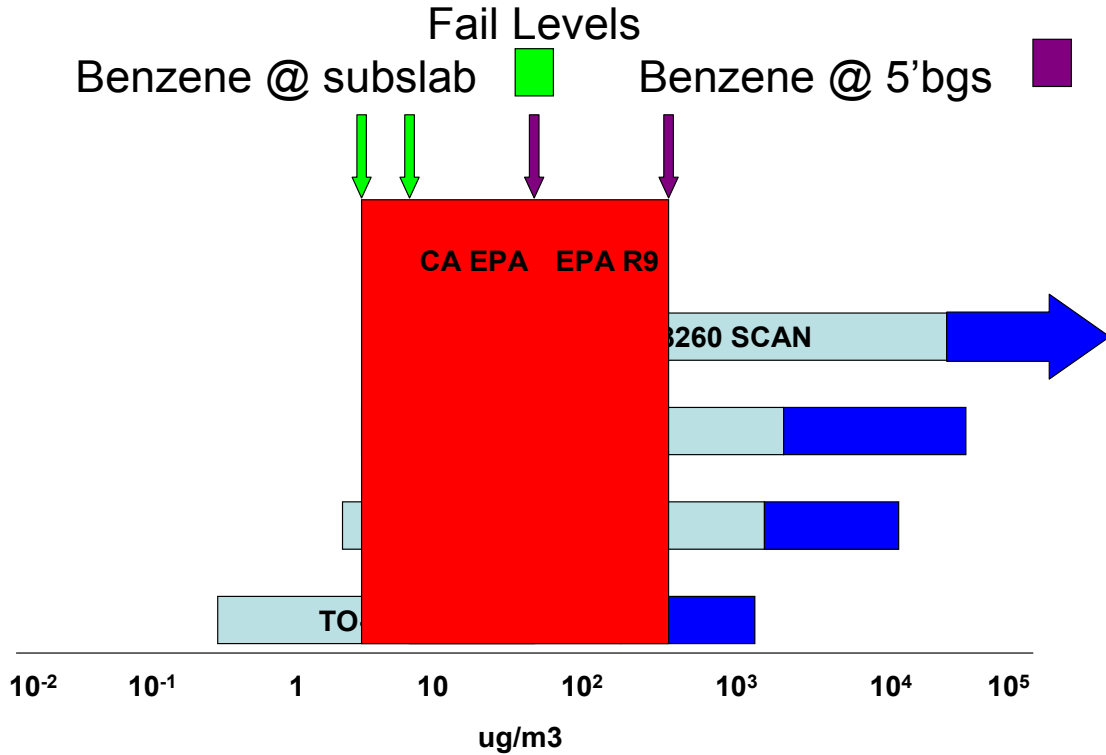
Assume for a moment that one expects to find compound concentrations at or above 1000 ug/m³. From figure 3. we see that if we chose TO-15, we would be operating in a range where every sample would likely have to be diluted prior to analysis and this assumes a relatively small sample for a TO-15 analysis. In addition to the time consumed by the laboratory in performing dilutions, there are also other concerns, such as contamination of sampling vessels and the analytical equipment. On the other hand if one chooses Method 8260B, the analysis would be operating in a convenient range for the equipment to handle. Thus one may choose which method to use dependent on expected concentration.

Choice of Method

A second reason one may wish to choose between the two methods is convenience. The availability of hardware such as sampling canisters and laboratory time may be a factor. For example, there are numerous companies offering on site testing using EPA method 8260, but few doing method TO-15 in the field setting. Figure 4. shows a possible application for that approach. In this figure we have the same ranges for the two methods as were shown above. Superimposed are the CA-EPA and federal EPA fail levels for

vapor intrusion at two levels below ground, subslab and 5ft bgs. For the 5 foot sample it is clear from the figure that both TO-15 and EPA8260B can analyze at the regulatory limit. Therefore, it may be advantageous both from an convenience standpoint and possibly from a fiscal standpoint to choose one method over the other.

Figure 4. EPA and CA-EPA fail levels for benzene subsurface



Finally, the selection of methods might actually be dictated by regulatory requirements. Figure 5. shows the fail levels for vapor intrusion subsurface this time for TCE. If one is following the CA-EPA guidance, the figure shows that the sensitivity is such that Method 8260 can be used to analyze soil vapor samples from 5' bgs as well as from the subslab. However, the significantly more stringent levels for the U.S. E.P.A are below 8260 in the scan mode. Here one must use either SIM, TO-15 or both. The level for subslab is reachable only by TO-15 in SIM mode with a larger sample size than 20 cc.

Comparitive Data

The authors' laboratories have more than 15 years experience analyzing soil vapor samples. Currently we perform between 5 and 10 soil vapor surveys every week. In addition we perform EPA Method TO-15 both in house and in a specially designed field laboratory. We thus have the ability to very closely compare the two methods as to their efficacy. Table 2. lists comparative results on a recent project. Non detected compounds have been eliminated from the data for clarity. One can see that at this level both methods correlate quite well. There is virtually no difference in the results from either

method. Even PCE which has the highest deviation (52%RSD) is well within what one can expect from two different labs performing two different methods. Compared to the wide range of approximation used in VI, this small deviation is not significant.

Figure 5. EPA and CA-EPA fail levels for TCE subsurface

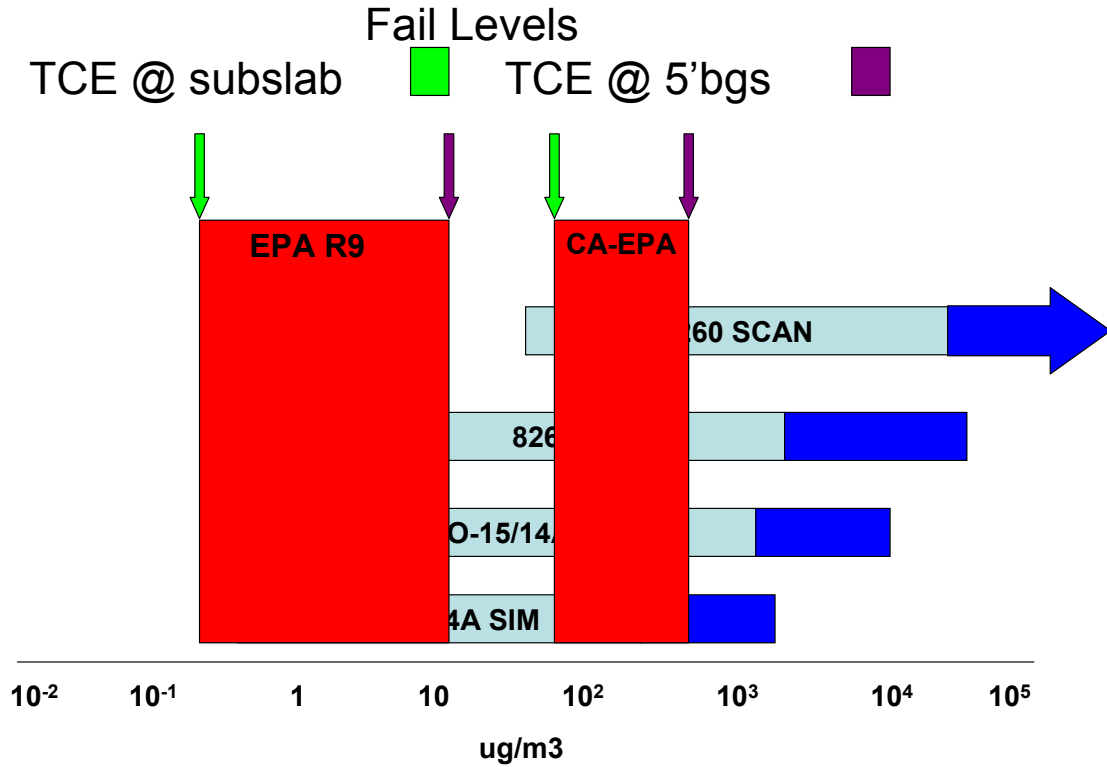


Table 2. Comparative Results EPA TO-15 vs. EPA 8260B on one project

| Sample | TO-15 PCE | 8260 PCE | TO-15 TCE | 8260 TCE | TO-15 c12DCE | 8260 c12DCE | TO-15 t12DCE | 8260 t12DCE | TO-15 F-113 | 8260 F-113 |
|---------------|--------------|-------------|--------------|-------------|-----------------|----------------|-----------------|----------------|----------------|---------------|
| SV1 | 128 | 88 | 42 | 31 | <1 | <1 | <1 | <1 | 1.6 | 1.1 |
| SV2 | 399 | 280 | 134 | 100 | 4.4 | 3.7 | 1.7 | 1.4 | 3.4 | 2.7 |
| SV3 | 95 | 46 | 40 | 31 | <1 | <1 | <1 | <1 | 1.7 | 1.6 |
| SV4 | 541 | 330 | 75 | 60 | <1 | <1 | <1 | <1 | <1 | <1 |
| SV5 | 169 | 110 | 70 | 65 | 1.5 | 1.7 | <1 | <1 | 3.4 | 3.1 |
| SV6 | 234 | 150 | 138 | 110 | 3.6 | 3.2 | <1 | <1 | 4.8 | 4.1 |
| SV7 | 108 | 54 | 25 | 17 | <1 | <1 | <1 | <1 | 3.1 | 2.1 |
| SV8 | 250 | 120 | 120 | 74 | 4.7 | 3.5 | <1 | <1 | 9.9 | 4.8 |
| AVG %Diff. | 52 | | 28 | | 13 | | 19 | | 28 | |

Average % Diff across all compounds = 38%

Conclusions

EPA Method 8260 and TO-15 offer complementary techniques with which to measure soil vapor in support of vapor intrusion (VI) studies. For all but the most water soluble compounds at low levels method 8260B is can adequately measure to meet the needs of the VI worker. In addition, EPA Method 8260B has been performed for years in the field and can continue to offer compliance with regulatory requirements for tracer compounds, purge volume tests and other field decision making.

EPA Method TO-15 is suitable and advisable when DL requirements are too low to be met with the 8260 method and or one or more of the target compounds are not amenable by 8260. It also can serve as an additional level of quality control for the other method when EPA 8260B is performed in the field.