

# **Soil Vapor Reproducibility: An Analytical and Sampling Perspective**

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## **ABSTRACT**

Field duplicate samples are often requested with soil vapor surveys to evaluate the reproducibility and precision of the sampling and analytical process, as well as variation in the sample matrix. However, questions often arise with regards to differences between the primary sample and the duplicate. What is an acceptable variation, and if the variation is in exceedance, what does that indicate? Over the years, H&P Mobile Geochemistry, Inc. (H&P) has compiled a database of thousands of primary and duplicate samples that have been collected and analyzed under various conditions. The differences within the database have been evaluated with regards to sample container, analytical method, compounds present in the samples, sample depth, as well as the contamination level in the samples. The dataset has several controls, including consistent analytical methods and containers for the sample pairs, as well as consistent sampling methodology across the database. This allows for the evaluation of the data to focus primarily on the variation in the sample matrix. Understanding what sort of reproducibility can be expected for duplicate samples will better prepare consultants and regulators with the information needed to evaluate variations in sample pairs, therefore aiding in the evaluation of the survey results.

## **INTRODUCTION**

The collection of field duplicate samples is a common quality control step for many environmental sampling plans.<sup>1</sup> The intent of collecting a field duplicate is generally to assess the precision of the analytical process, evaluate the reproducibility of the sampling process, and/or to determine the sample matrix variability.<sup>2,3</sup> However, with such a broad range of intent, when differences are observed between primary and duplicate results, it can be difficult to identify the reason(s) for variation. In addition, the guidelines for acceptable variation are vague and inconsistent. This research intends to clarify the expected variation for duplicate samples, and also to identify common reasons for variations to exceed this expectation.

A field duplicate is a secondary sample collected in addition to a primary sample. Duplicates can be collected for any environmental sample matrix, but this research focuses on soil vapor specifically. For soil vapor, the secondary sample is collected from the same soil vapor probe as the primary sample, but into a separate container. The sample/duplicate sets in this research were analyzed for volatile organic compounds (VOCs).

There are technically two types of secondary samples which may be collected after a primary sample: A duplicate or a replicate. A duplicate sample is a sample collected simultaneously along with the primary sample (i.e. two passivated stainless steel summa canisters collected with a split fitting off of the soil vapor probe). A replicate sample is a sample collected sequentially after the primary sample (i.e. one summa canister is filled, then the second summa canister is filled). The distinction between soil vapor duplicates versus replicates was only made recently in the California EPA DTSC Guidance in 2012.<sup>1,2</sup> It is interesting to consider that soil vapor is the only environmental matrix for which the distinction is made between the two types of secondary samples. For example, all environmental water duplicates are technically replicates by definition, yet they are universally referred to as duplicates.<sup>3</sup> Despite the distinction between duplicates and replicates in soil vapor, the terms are often used interchangeably, and the samples serve the same quality control purpose.<sup>1,2</sup> Therefore, this research presents all duplicate and replicate data together without distinction, and refers to all secondary samples as a duplicates.

In addition to duplicate samples, this study also evaluates the differences in purge volume test samples. To understand what a purge volume test is, it is important to know that a purge volume is the calculated dead volume of the ambient air within a soil vapor probe (i.e. tubing volume, sand pack pore space, etc) that is removed or purged prior to sample collection. A purge volume test is conducted by collecting a series of three samples at varying purge volumes from the same soil vapor probe.<sup>1</sup> For example, a sample is collected after removing one purge volume from the probe, a second sample is collected after removing three purge volumes from the probe, and a third is collected after removing ten purge volumes from the probe. The intent behind conducting a purge volume test is to analyze all three purge volume test samples, compare the sample results, select the purge volume that yields the highest results for the compounds of concern, and utilize that purge volume for the remaining soil vapor probes on a particular site. Purge volume testing was recommended in California for all soil vapor investigations being conducted under CA EPA DTSC guidance up until the current guidance document, which came out in 2015.<sup>1</sup> The current guidance document removed the recommendation for purge volume testing, and replaced it with a recommendation to use a default of three purge volumes.<sup>2</sup> Although they are not true sequential samples, and therefore not true replicate or duplicate samples, the purge volume test results are used in this research because of their ability to show reproducibility from a soil vapor probe despite different purge volume amounts.

## **PROJECT APPROACH**

H&P is a field sampling and analytical firm that is involved with the collection and/or analysis of more than 18,000 soil vapor samples per year, providing a rich database from which to gather information regarding the reproducibility of duplicate soil vapor samples. H&P's database of sample results from the 2014 calendar year was evaluated to determine the actual reproducibility of primary sample results and the corresponding duplicate sample results, as well as reproducibility of different purge volume test samples.

Duplicates are commonly evaluated using Relative Percent Difference (RPD)<sup>1,2</sup>, which is the absolute difference between the primary sample and the duplicate, divided by the average of the sample and the duplicate, expressed as a percent:

$$\%RPD = 100 \times [ |X1 - X2| / (X1 + X2 / 2) ]$$

where:

RPD = Relative Percent Difference

X1 = measured value of the primary sample

X2 = measure value of the duplicate sample

Because the purge volume test data contains information for three samples per set, the results were compared using percent Relative Standard Deviation (RSD) to determine the spread of the results with respect to the average of the results (instead of RPD). RSD is calculated by determining the standard deviation of the data set, divided by the average of the data set.

$$\%RSD = 100 \times \left\{ \left[ \frac{\sqrt{\sum(x - \bar{x})^2}}{N} \right] / \bar{x} \right\}$$

where:

%RSD = Relative Standard Deviation as a percent

$\sum$  = the sum of the dataset

$x$  = each value in the data set

$\bar{x}$  = mean of all values in the data set

$N$  = number of values in the data set

The H&P database yielded a total of 356 sample/duplicate pairs (712 total samples). Since the intent of the study is to determine real and expected RPD values for sample detections, the sample/duplicate sets which yielded non detect results were not included in the study, as these would bias the evaluation toward lower RPD. This provided 1,683 total compound measurements focusing on chlorinated compounds and petroleum compounds: Tetrachloroethene (PCE) and Trichloroethene (TCE), as well as Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX). The database of sample/duplicate pairs provides details for many different parameters, including a variety of certified analytical methods such as H&P 8260SV (a certified modification of EPA 8260SB for soil vapor samples), EPA TO-15, and H&P TO-15 (a certified modification of EPA TO-15 for mobile lab analysis with glass syringes). The database also provides an opportunity to evaluate the container type for sample/duplicate pairs (summa canisters or glass syringes). All samples in the database were collected using consistent and certified soil vapor sampling protocols by trained H&P field personnel. The samples were collected from 300+ various types of sites in southern California, ranging from an open field with petroleum contamination to an operating dry cleaner with solvent contamination, yielding different soil conditions and sampling depths.

In addition to the sample/duplicate pair evaluations, the study also evaluated 117 purge volume tests (351 total samples, 3 per test). The purge volume tests yielded 787 total compound measurements focusing on the same compounds as the sample/duplicate pairs (PCE, TCE, and BTEX). The parameters as described above for the sample/duplicate pairs also apply to the purge volume test comparisons.

The data were evaluated to look for real and expected RPD values, as well as any possible trends in sample container types and analytical methods with respect to individual compounds. This was accomplished by reviewing individual and combined RPDs, plotting the average RPD for each compound against the sampling container (i.e. syringes yield a different average RPD than summa canisters), and finally by plotting the average RPD for each compound against the analytical method to determine if there were trends with regards to the analytical method (i.e. using method

H&P 8260SV yielded a different RPD than EPA TO-15). The data were also evaluated to compare the compound concentrations against one another to identify any possible bias toward the primary or duplicate sample with regards to either chlorinated or petroleum compounds. The evaluation of the purge volume test results was used to demonstrate whether or not the volume of purge air that is removed from the soil vapor probe has an impact on the reproducibility of the results.

## RESULTS AND DISCUSSION

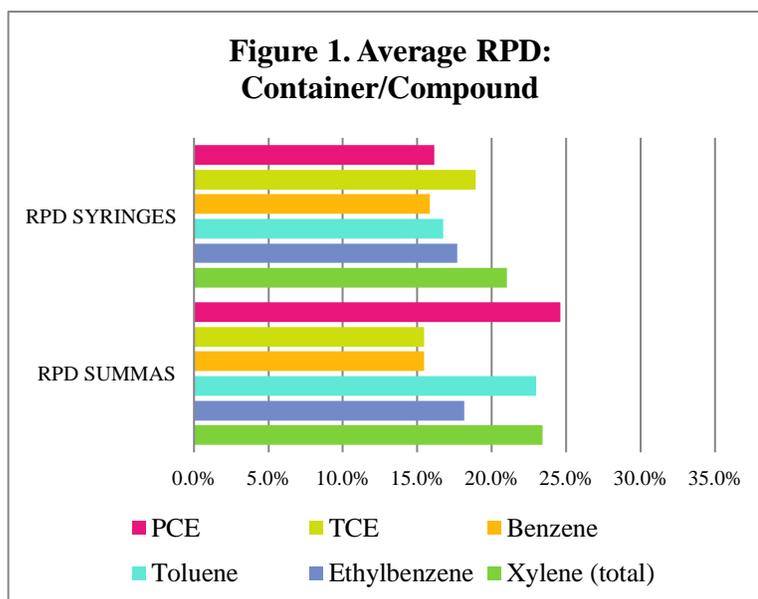
In order to evaluate the RPD values in the database, it was necessary to assess criterion in the industry with regards to an expected and acceptable RPD value for a primary and duplicate sample set. However, while many guidance documents suggest collecting a duplicate as a quality assurance sample, very few guidance documents provide suggestions for an acceptable RPD. CA DTSC suggests a 50% RPD, due to the “inherent variability associated with soil gas samples.”<sup>1,2</sup> Analytical method criteria, such as H&P 8260SV and EPA TO-15, have built in requirements for 25%-30% precision for the laboratory standard analysis (laboratory control standard versus the laboratory control standard duplicate).<sup>4,5</sup> Still, many project quality assurance plans have acceptance criteria for an RPD up to 100% for duplicate samples.

The sample/duplicate RPD results were evaluated using these RPD values as a guideline, with 25%-30% being the most stringent per common analytical methods<sup>4,5</sup> and 100% being the most lenient based on observed expectations from the environmental community.

### Container Evaluation

#### *Average RPD*

The average RPD for each compound was evaluated against the two types of sample containers included in the study: Air tight glass syringes (50mL-100mL) and batch certified summa canisters (400mL-1L). The evaluation indicated that the difference in average RPD values was not significant enough to identify any trend with regards to syringe samples versus summa canister samples. Additionally, it was observed that all compound average RPD values were within 25%-30% (which is within analytical precision).



#### *Detailed RPD for Summa Canisters versus Syringes*

Looking further at the dataset, the minimum and maximum RPD values were considered for each compound with respect to container type. The table below shows the selected compounds PCE, TCE, Benzene, as well as the Combined Total VOC evaluations. There were observed outliers

in the dataset, but the median and average RPD values were within 25%-30% analytical precision.

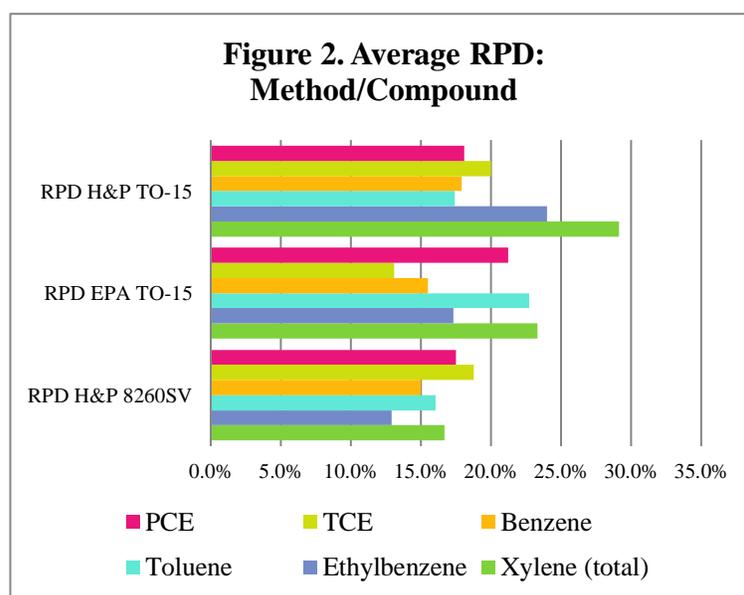
**Table 1. Detailed RPD Evaluation of Compounds versus Container**

RPD (%)	PCE Summa	PCE Syringe	TCE Summa	TCE Syringe	Benzene Summa	Benzene Syringe	Total VOC Summa	Total VOC Syringe
Minimum	0	0	0	0	0	0	0	0
Maximum	120.0	139.5	80.2	192.9	85.7	66.7	75.5	102.5
Median	16.2	10.4	9.5	11.2	8.4	11.5	19.6	12.7
Average	24.6	16.2	15.5	18.9	15.5	15.8	22.2	17.7

## Analytical Method Evaluation

### Average RPD

The average RPD for each compound was evaluated against the three analytical methods included in this study: H&P 8260SV (a certified modification of EPA 8260SB for soil vapor samples), EPA TO-15, and H&P TO-15 (a certified modification of EPA TO-15 for mobile lab analysis with glass syringes). The evaluation observed that 8260SV had a slightly lower RPD than either of the TO-15 methods, but the average RPDs were within the 25%-30% expectation of analytical precision.



### Detailed RPD for 8260SV versus the TO-15 methods

Looking further at the dataset, the minimum and maximum RPD values were considered for each compound with respect to analytical method. The table below shows the selected compounds PCE, TCE, Benzene, as well as the Combined Total VOC evaluations. There were observed outliers in the dataset, but the median and average RPD values were within 25%-30% analytical precision.

**Table 2. Detailed RPD Evaluation of Compounds versus Analytical Method**

RPD (%)	PCE A	PCE B	PCE C	TCE A	TCE B	TCE C	Benz A	Benz B	Benz C	Total VOC A	Total VOC B	Total VOC C
Min	0	0	0	0	0	0	0	0	0	0	0	0
Max	139.5	76.9	82	192.9	80.2	88.1	66.7	85.7	59.5	97.8	75.5	102.5
Median	11.8	13.0	9.6	11.5	7.4	9.1	11.3	8.2	11.8	12.4	17.6	15.9
Avg	17.5	21.2	18.1	18.8	13.1	20.0	15.0	15.5	17.9	17.3	20.3	21.8

A = H&P 8260SV B = EPA TO-15 C = H&P TO-15

## Overall Evaluation of RPD

### Average RPD for All Studied Compounds

The combined average RPD for all 1,683 compound measurements from 712 samples was determined to be 18.7%, which indicates that, on average, primary samples and their duplicates can be expected to have reproducibility within 25%-30% analytical precision.

### Detailed RPD for all Compounds

Below is a detailed evaluation of the RPD values for the dataset as a whole, including BTEX, PCE, TCE, and the combined total VOC values for all sample containers and analytical methods. The evaluation shows that despite outlying occurrences of RPDs greater than 100%, the average and median RPD values were within 25%-30% analytical precision.

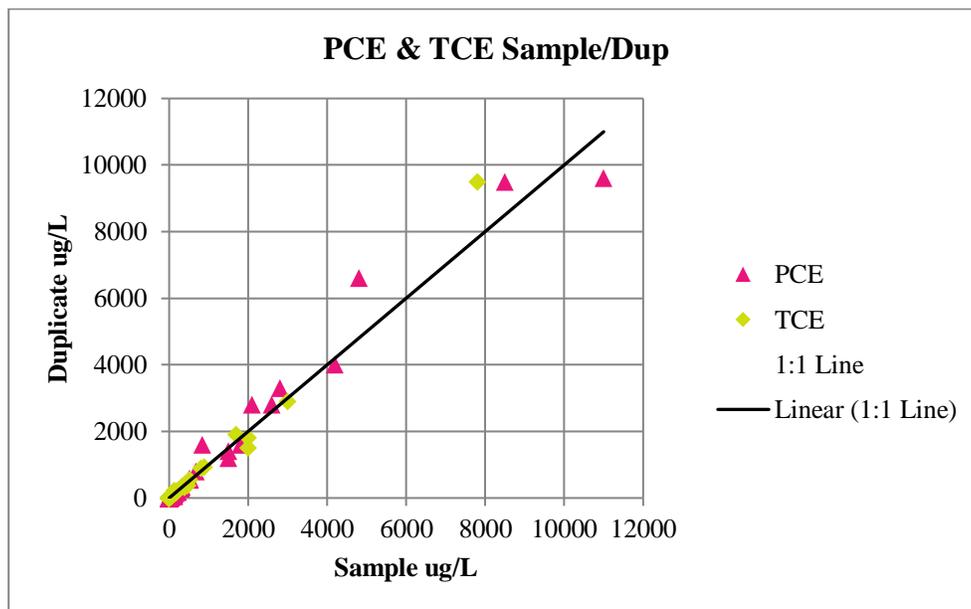
**Table 3. Detailed RPD Evaluation of Complete Data Set**

RPD (%)	PCE	TCE	Benzene	Toluene	Ethylbenzene	Xylenes	Total VOC
Minimum	0	0	0	0	0	0	0
Maximum	139.5	192.9	85.7	108.5	77.8	168.0	102.5
Median	11.8	10.8	11.2	13.3	12.5	13.8	13.6
Average	18.3	18.2	15.7	19.5	18.4	21.8	18.7

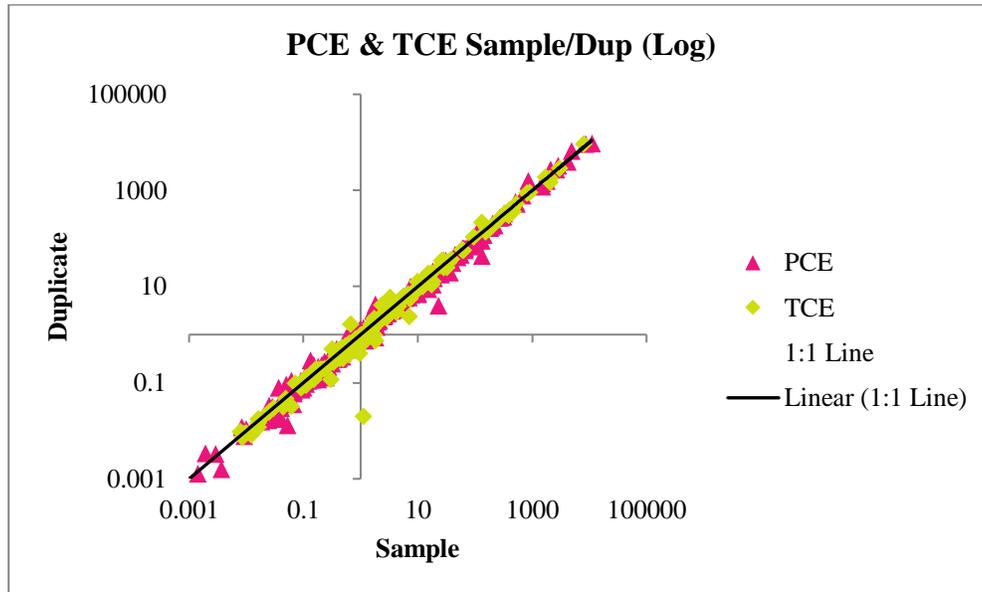
## Direct Comparison of Chlorinated Compounds

The results for the chlorinated compounds (PCE & TCE) for each sample/duplicate set were plotted to visualize the reproducibility of the duplicate sample. Below is a standard plot as well as a log scale plot (to better observe the low level detections, where a majority of the measurements lie). The figures below include a 1:1 trend line as a point of reference for interpretation.

**Figure 3. Sample/Duplicate Comparisons for Chlorinated Compounds**



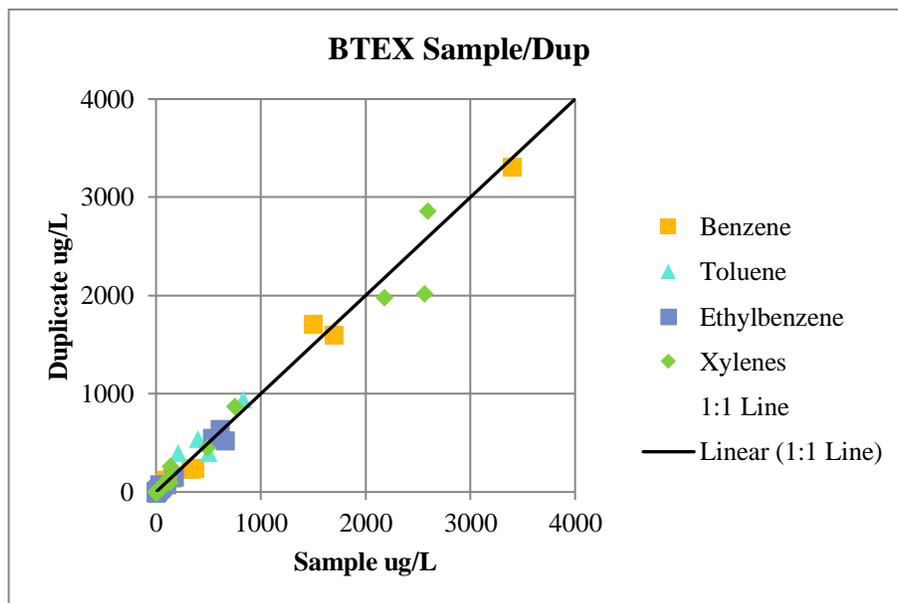
**Figure 4. Log Scale Sample/Duplicate Comparisons for Chlorinated Compounds**



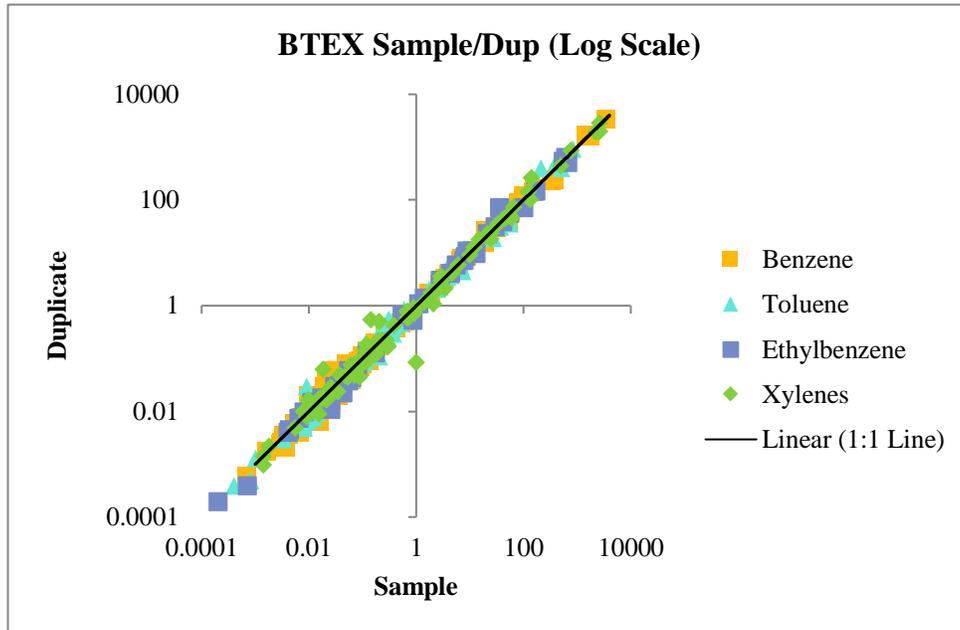
### Direct Comparison of Petroleum Compounds

The petroleum compound (BTEX) results for each primary/duplicate set were also plotted to visualize the reproducibility of the duplicate sample. Below is a standard plot as well as a log scale plot (to better observe the low level detections, where a majority of the measurements lie). The figures below include a 1:1 trend line as a point of reference for interpretation.

**Figure 5. Sample/Duplicate Comparisons for Petroleum Compounds**



**Figure 6. Log Scale Sample/Duplicate Comparisons for Petroleum Compounds**



## Purge Volume Evaluation

### *Average RSD for all Studied Compounds*

The 787 total compound measurements collected from the 351 purge volume samples (117 purge volume tests) were compared using %RSD rather than %RPD. The combined average RSD for all compound measurements in the purge volume test samples was 23.8%, which indicates that, on average, three samples collected with varying purge volumes can be expected to have a spread within 25%-30% analytical precision.

### *Detailed RSD for all Compounds*

Below is a detailed evaluation of the RSD values for the purge volume dataset as a whole, including PCE, TCE, BTEX, and the combined total VOC values for all purge volume tests. The evaluation shows that despite outlying occurrences of RSDs greater than 100%, the average and median RSD values were within 25%-30% analytical precision.

**Table 4. Detailed RSD Evaluation of Purge Volume Tests**

<i>RSD (%)</i>	<b>PCE</b>	<b>TCE</b>	<b>Benzene</b>	<b>Toluene</b>	<b>Ethylbenzene</b>	<b>Xylenes</b>	<b>Total VOC</b>
<i>Minimum</i>	0	0	0	0	7.3	7.4	0
<i>Maximum</i>	131.8	97.7	111.8	78.8	61.7	80.2	131.8
<i>Median</i>	16.1	10.4	18.5	19.6	19.2	22.0	18.9
<i>Average</i>	24.2	19.4	22.0	24.3	25.2	27.8	23.8

## SUMMARY

The goal of the research was to determine observed and expected RPD values for sample/duplicate sets in soil vapor samples. The observed RPD values were evaluated by comparing the RPD of common target compounds to container type, analytical method, and overall performance. The observed RPDs ranged from 0% (perfect match) to almost 200% (with the duplicate being three times the primary sample). However, the median RPD and the average RPD values were between 13.1% and 24.6%. Based on this observation, a realistic expectation for an average RPD value for soil vapor sample/duplicate sets should be within 25%-30% analytical precision. Even when collecting samples with anticipated changes in results due to different purge volume amounts, the observed RSD values fell within 25%-30% analytical precision.

Reasons for variation<sup>3</sup> above 25%-30% analytical precision can be attributed to differences in:

1. Laboratory instruments
2. Sample introduction techniques
3. Skill and experience of the chemist
4. Field sample collection methods
5. Skill and experience of the sampling technician
6. Type and size of sample containers
7. Purging and recharge characteristics of the soil vapor matrix
8. Natural variation in the soil vapor matrix

Each sample/duplicate pair used in the study was analyzed with the same instrument, the same sample introduction technique, and by the same chemist. In addition, each sample/duplicate pair was collected by the same sampling technician, using the same size and type of container, with the same certified field sample collection methodology. The purge volume test evaluation demonstrated that there is not large variation due to purging and recharge characteristics. In effect, the study set eliminated all but one of the typical reasons for variation, which is natural variation in the soil vapor matrix.

The dataset shows good correlation between the sample/duplicate pairs within analytical precision (25%-30% RPD) in a majority of cases, indicating that with sampling and analytical differences eliminated, natural variation in the soil vapor matrix does not have a large impact on the differences between primary samples and their duplicates.

This information leads to the conclusion that with proper sampling and analytical techniques, RPDs should be expected to be within 25%-30% (or within analytical precision). Therefore, when variations above 25%-30% do occur in a soil vapor investigation, the analytical and sampling effects should be examined before assuming it is natural variation in the soil vapor matrix.

## ACKNOWLEDGEMENTS

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## KEYWORDS

Soil Vapor, Soil Gas, Duplicate, Replicate, Reproducibility, Natural Variation, Sampling Methodologies, Environmental Sample Variation