Soil Vapor Reproducibility

in Duplicate and Purge Volume Test Samples

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Soil Vapor Reproducibility

Evaluation of how soil vapor sample results obtained from the same vapor probe compare to one another.

1. **Duplicates (Quality Control Samples)**
   - Research is focused real data from 700+ samples
   - Definition, Purpose, and Evaluation of Results
2. **Purge Volume Tests**
   - What impact does purge volume have on results?
   - Real data from over 350 samples
   - Definition, Purpose, and Evaluation of Results

Duplicates: Definition

- **Field Duplicate (or Replicate)**
  - A secondary sample collected in addition to the primary sample.
  - Collected into a separate container from the same soil vapor probe.
  - Typically both are analyzed using the same analytical method.

Most commonly requested Field QC sample

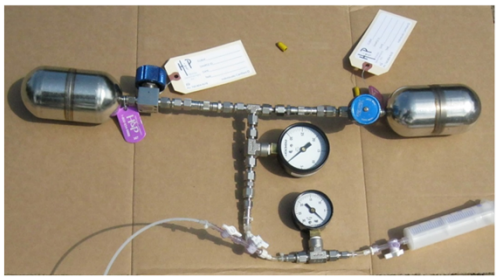
Not to be confused with Lab Duplicates

(Two analyses performed from the same container)

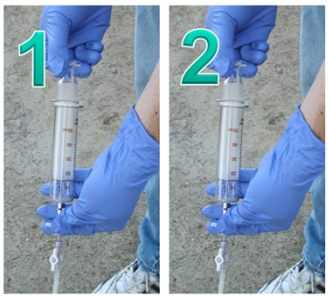
Duplicates/Replicates: Definition

The terms are often used interchangeably, so what is the difference between a Duplicate and a Replicate?

Two samples collected ***simultaneously*** are ***DUPLICATES***



Two samples collected ***sequentially*** are ***REPLICATES***



- *The distinction was only made recently (DTSC 2012)*
- *Generally applies only to soil vapor (sequential soil and water samples are still called duplicates)*
- *The terms are often used interchangeably*

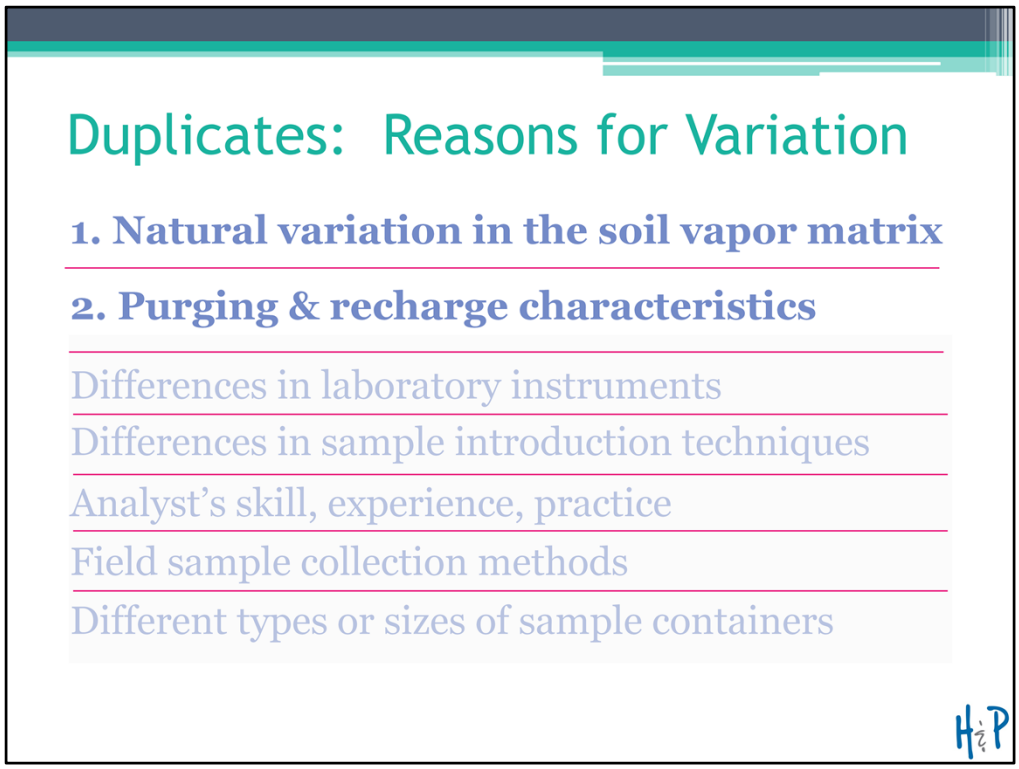
Duplicates: Purpose

Regardless of simultaneous or sequential sampling, collecting a secondary sample of any matrix can be used to:

- Evaluate reproducibility of the **sampling process**
- Assess precision of the **analytical process**
- Determine **sample matrix variability**

For this research, duplicates and replicates were evaluated together; a distinction is not made between the two and the terms are used interchangeably.

You cant assess analytical precision when you are already expecting sample variability.



What is the criteria for soil vapor and what is indicated by an exceedance? *"A replicate sample collected immediately after the original sample may not be the same due to spatial and temporal differences."*

Duplicate: Methods for Comparison

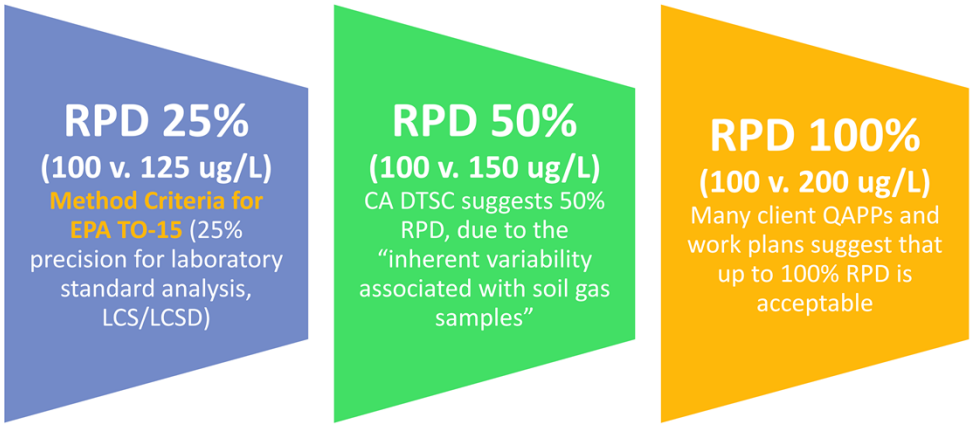
1. **Relative Percent Difference (RPD)**
   - Quantitative indicator of QA/QC for repeated measurements where the outcomes are expected to be the same:

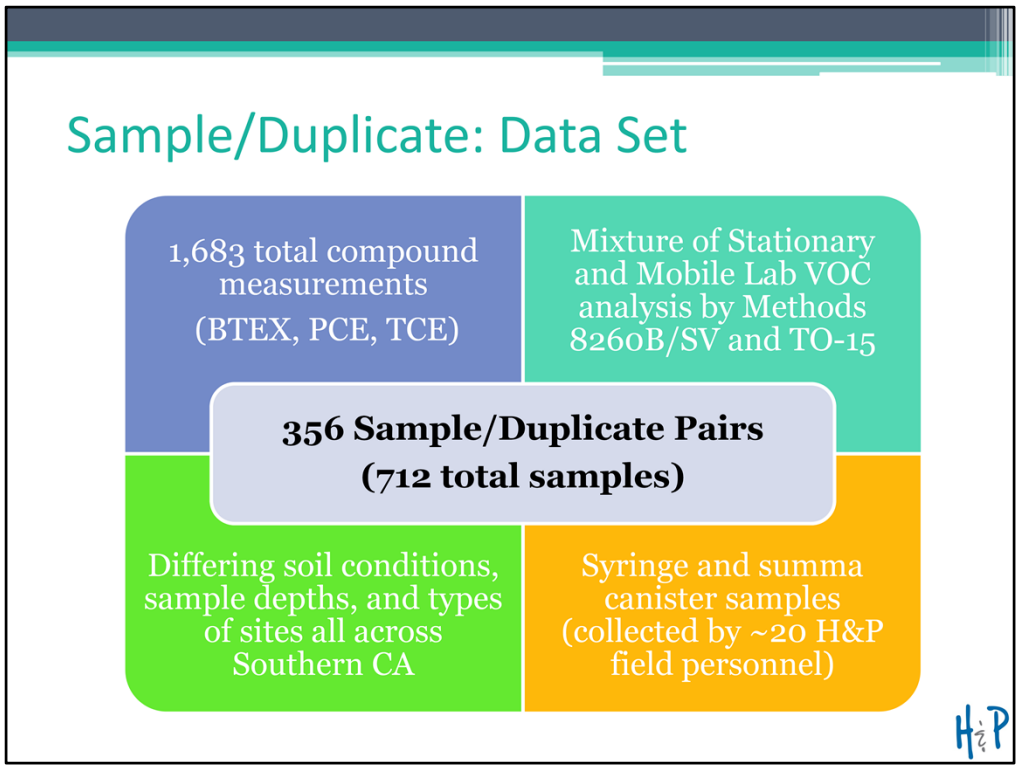
$$RPD = 100 \times \frac{(Sample - Duplicate)}{((Sample + Duplicate) / 2)}$$

2. **Plot the results against one another**

Sample/Duplicate: RPD Criteria

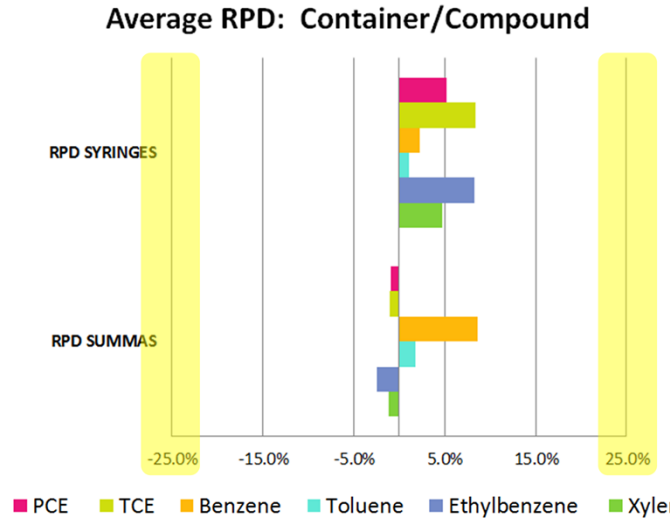
Very few guidance documents provide suggestions for primary and duplicate evaluations





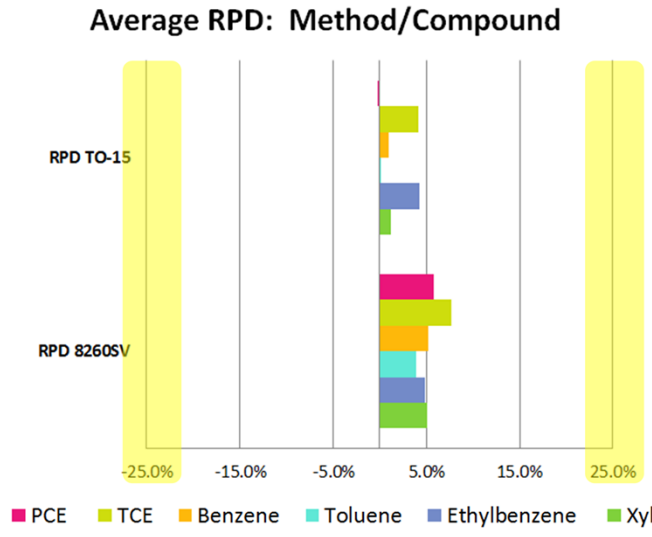
Data set explanation

RPD: Container Evaluation



- The average RPD for each compound was evaluated against the sample container to identify any trends…
- **However, all RPDs were low (good) and well within analytical precision.**

RPD: Method Evaluation



- The average RPD for each compound was also evaluated against the analytical method to identify any trends…
- **Again, all RPDs were low (good) and also well within analytical precision.**

RPD: Results of Complete Data Set

Overall Average RPD for all compounds combined (PCE, TCE, BTEX)*:

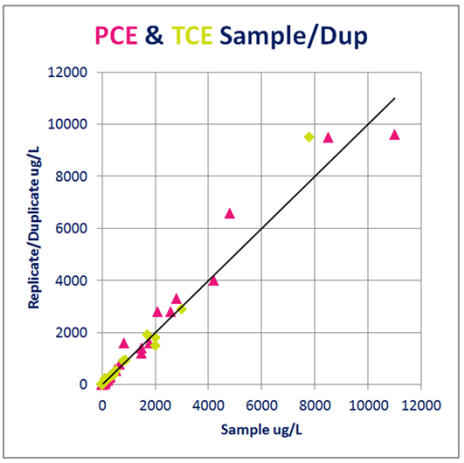
4.1 %

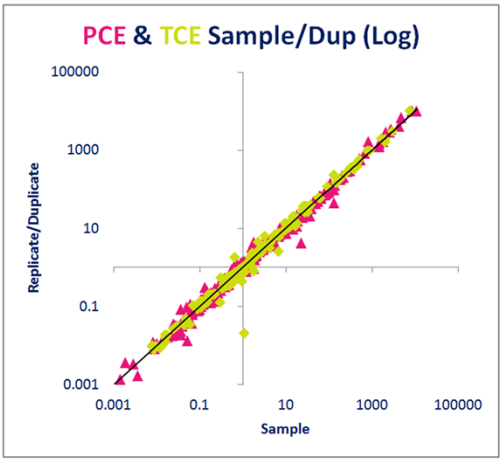
From 1,683 total compound measurements from 712 samples

Despite looking for trends in sample container types and analytical methods, the results of the evaluations were similar and within analytical precision

NEXT: How do the results actually plot against one another?

Sample/Dup Evaluation: PCE & TCE



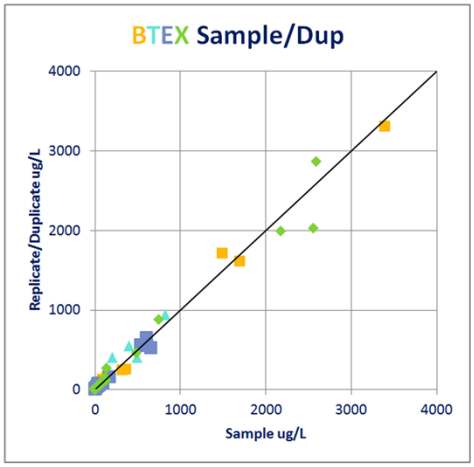


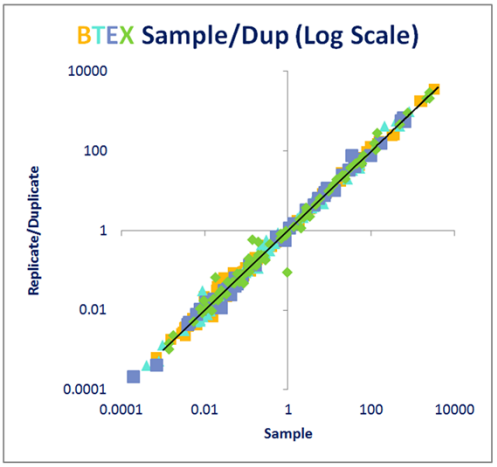
◆ TCE

▲ PCE

Outliers are within the precision of the analytical method.

Sample/Dup Evaluation: BTEX





- Benzene
- Toluene
- Ethylbenzene
- Xylenes

No bias toward the first or second sample being higher or lower

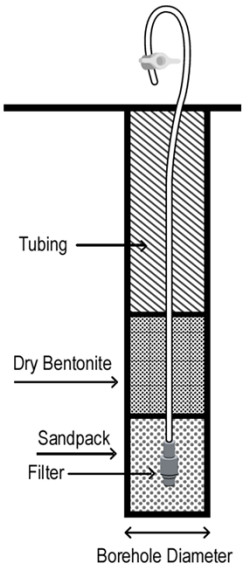
Sample/Dup Evaluation: Results

- Results plot along the 1:1 line
  - No bias toward the first or second sample for either Chlorinated compounds or Petroleum Compounds
- Syringe versus summa results had similar RPD (within method criteria)
  - Sample container did not show a significant impact

Does the volume of soil vapor that is removed from the probe really matter?

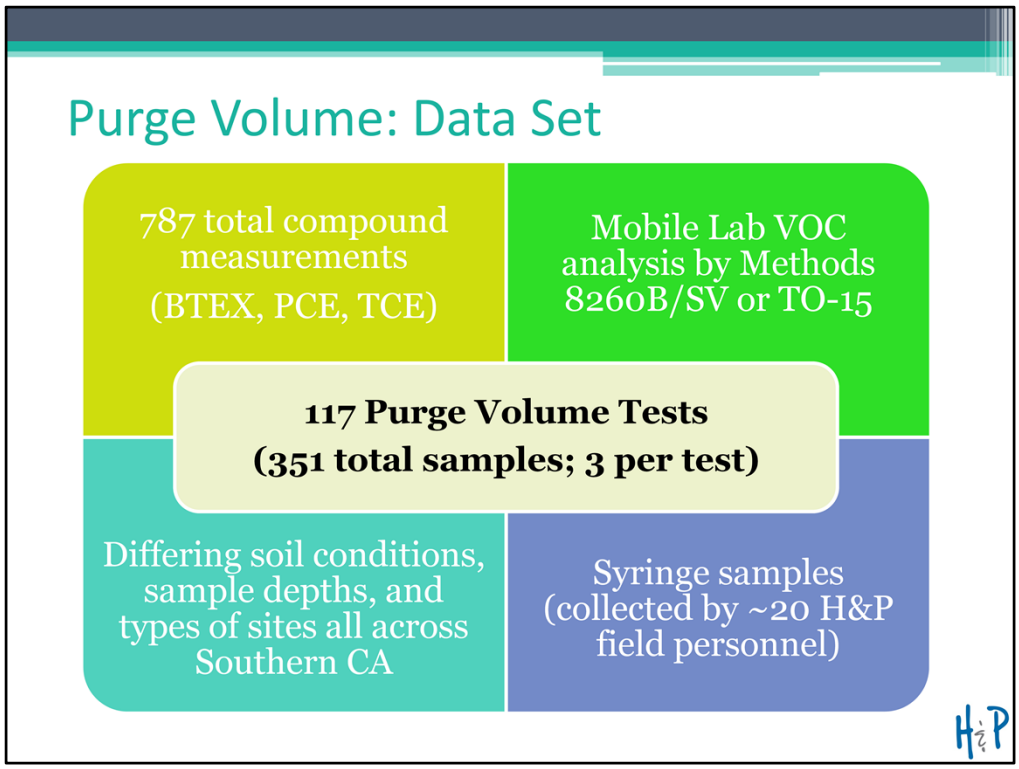
Purge Volume

A **Purge Volume** is the volume of the vapor probe tubing and filter, as well as the pore space of the sand pack (and possibly the pore space of dry bentonite)



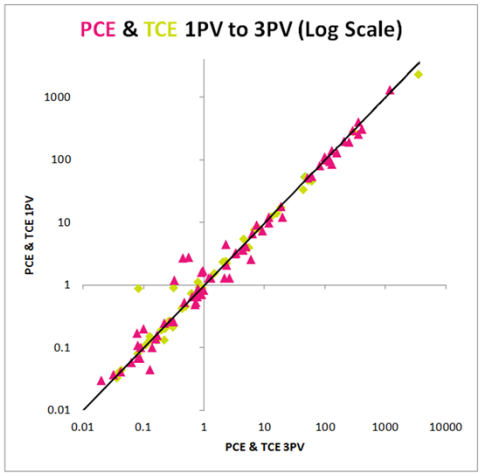
A Purge Volume Test

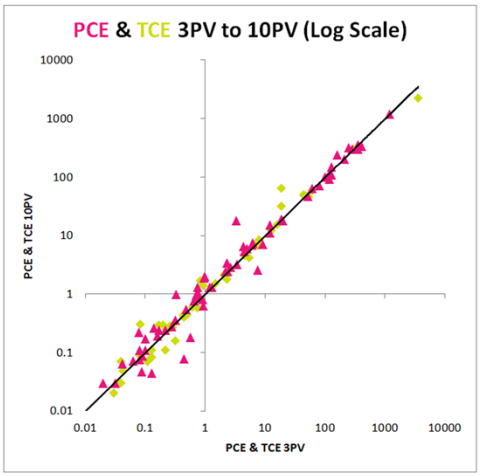
1. Calculate the purge volume, then collect three samples using different purge volumes: 1 volume, 3 volumes, and 10 volumes (e.g. 100 cc / 300 cc / 1,000 cc)
2. Compare the results of the three samples and choose the purge volume sample that yields the highest target compound concentrations



Data set explanation

Purge Volume Evaluation: PCE & TCE



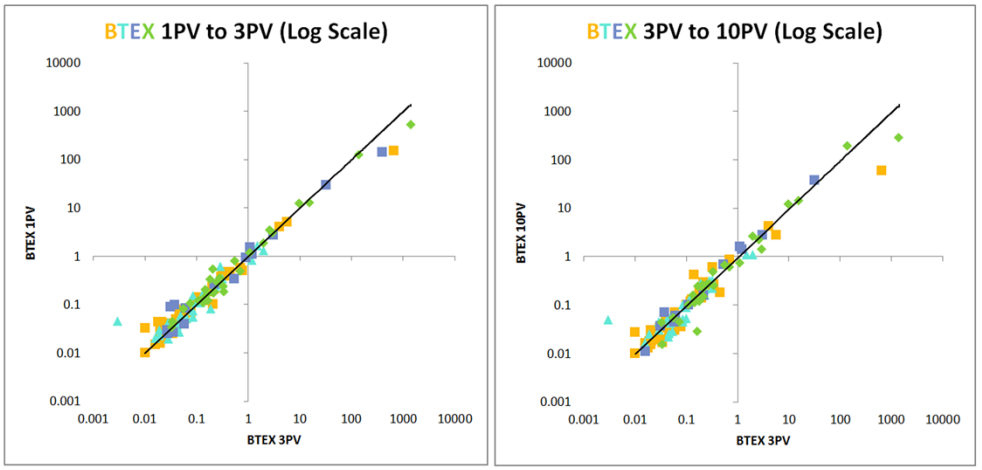


◆ TCE

▲ PCE

No significant bias toward one, three, or ten purge volumes.

Purge Volume Evaluation: BTEX



- Benzene
- Toluene
- Ethylbenzene
- Xylenes

Again, no significant bias toward one, three, or ten purge volumes.

Purge Volume Evaluation: Results

1. Similar to the duplicate samples, the Purge Volume Test sample results plot along the 1:1 line

Default to 3 Purge Volumes?

Forego the purge volume test and instead remove a default of 3 purge volumes of air from the probe prior to sample collection?

2. Evaluations yielded similar results for both chlorinated and petroleum compounds.

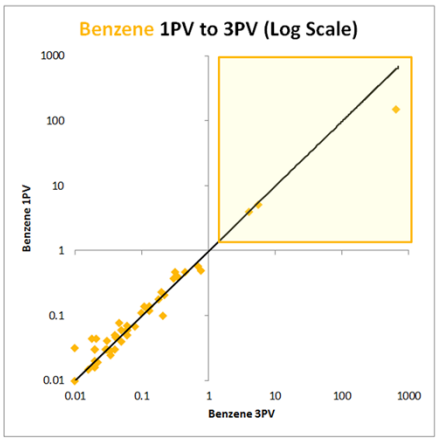
Since this is the PVI Tract…

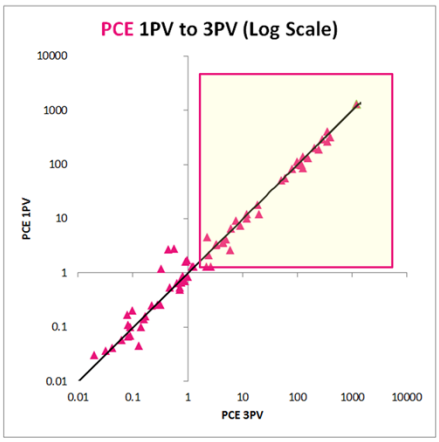
In all of the evaluations, Chlorinated compounds (PCE/TCE) behaved similar to Petroleum compounds (BTEX) in terms of reproducibility…

But there was one "trend" that appeared…

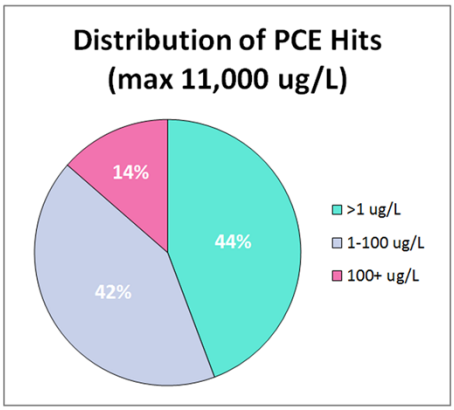
Since this is the PVI tract…

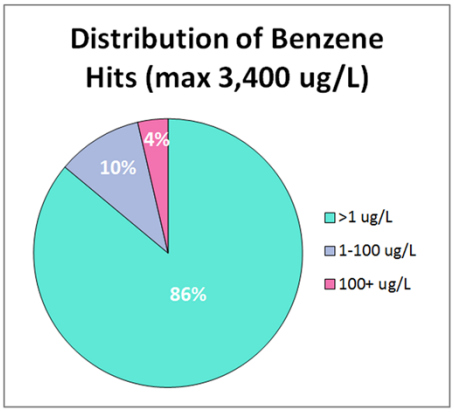
The distribution of Benzene hits in the upper quadrant was considerably less than those of PCE hits…



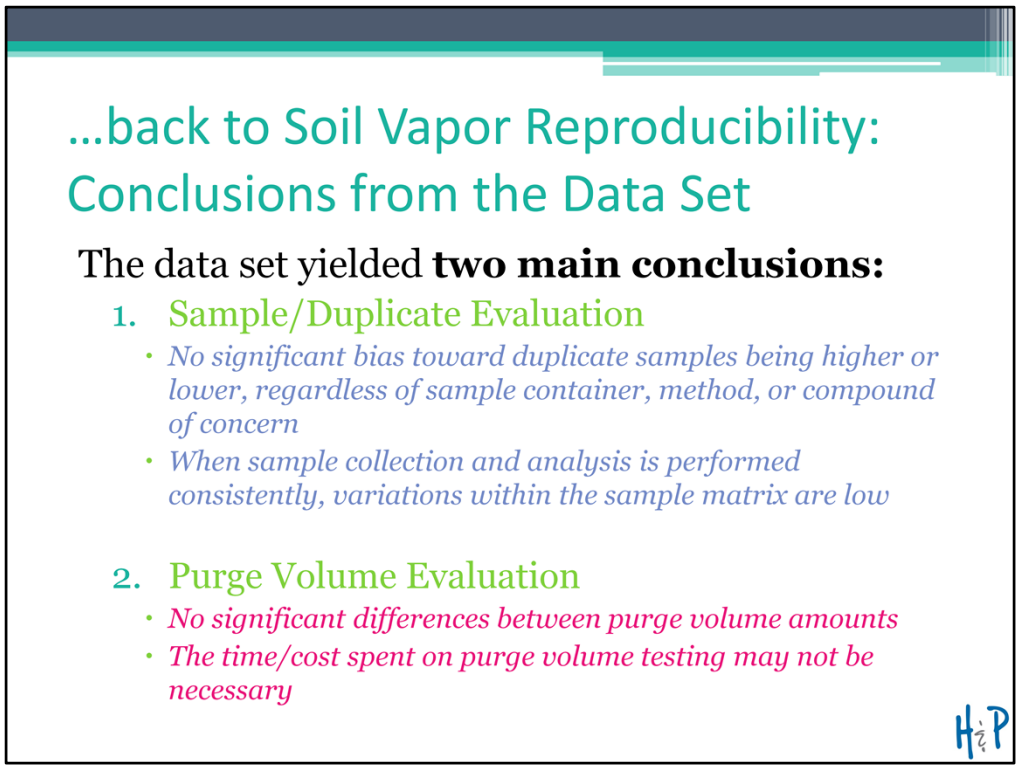


Since this is the PVI tract…





Benzene hits above 1.0 ug/L are few and far between when compared to PCE, possibly providing further evidence that **bioattenuation** is occurring



In researching and looking for trends in this data set, two main points became very obvious: 1. There is no significant bias toward duplicate samples being higher or lower in concentration, regardless of sample container, method, or compound of concern. 2. Evaluation of purge volume tests did not show a large difference between purge volumes, indicating that purge volume testing may not worth the cost or time in the field.

Soil Vapor Reproducibility: Conclusions

In conclusion, let's revisit the purposes behind evaluating Soil Vapor Reproducibility:

1. Evaluate the sampling process	• Results with low RPD indicate that the sampling is being performed consistently • Important to have experienced and well trained technicians/chemists collecting the samples
2. Evaluate the analytical process	• Results with low RPD indicate that the analytical instrument is working properly and yielding consistent results • Important for the lab to have all other QA/QC checks in place and working
3. Estimate variability in the matrix	• Variability, although it can be seen on a sample by sample basis, is not significant when looking at a large data set • Neither Chlorinated or Petroleum compounds exhibit a rising or falling trend with increases in sample or purge volume

Questions or Comments?

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References:
CA DTSC Guidance (2012 ASGI)
EPA Method TO-15

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