A Dirty Secret:
Duplicate Variability in Summa Canister Samples for Vapor Intrusion Investigations

GSI ENVIRONMENTAL




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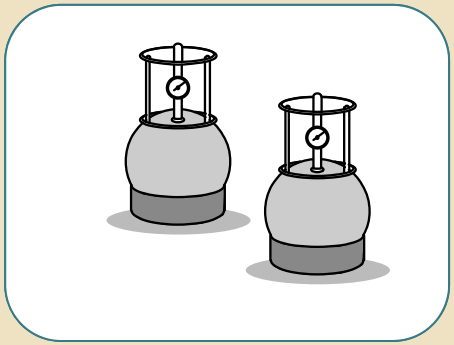
9 April 2018

CONTENTS OF PRESENTATION



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INFORMATION FROM FIELD DUPLICATES?

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PURPOSE: EVALUATE SAMPLING PRECISION

DIFFERENCES BETWEEN SAMPLES REFLECT:

- **Sample collection**
  - Matrix variability
  - Sample container
  - Sample handling
- **Laboratory analysis**
  - Analytical precision
  - Laboratory contamination
  - Instrument carryover

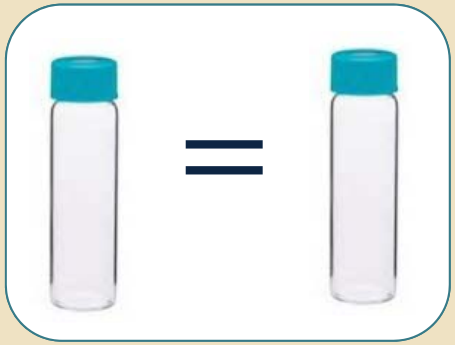
AIR SAMPLE:
Reusable Container

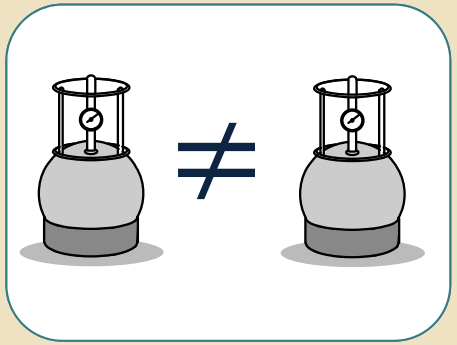
WATER SAMPLE:
Disposable Container

KEY POINT: **If I do the same thing twice, do I get the same answer?**

MOTIVATION FOR THIS STUDY

- Observations and hypothesis formed from personal project experience





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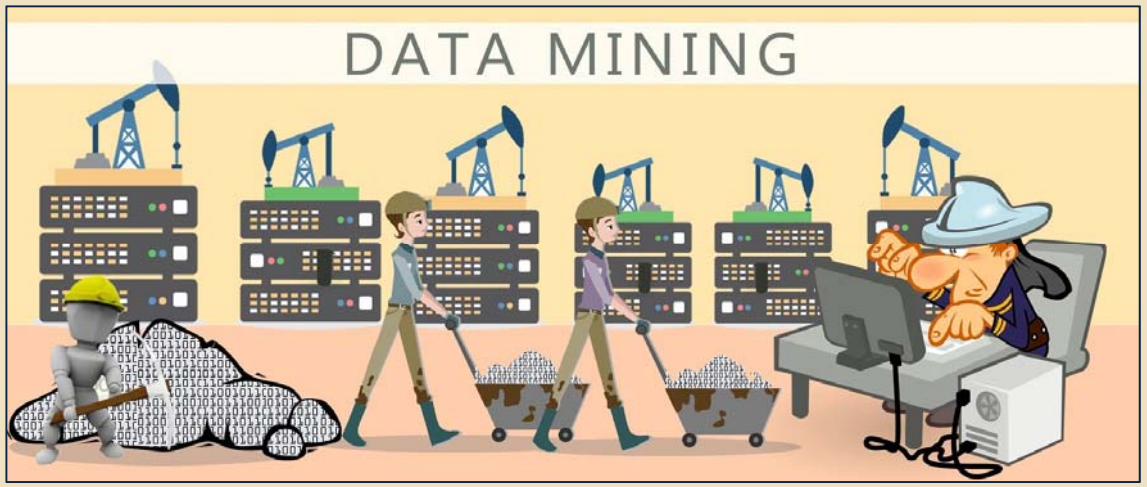
PROJECT GOALS

- Quantify variability through more rigorous analyses
  - Identify differences in data quality for water vs air samples
  - Identity factors associated with poor data quality

KEY QUESTION: **Is duplicate variability greater for vapor samples than for water samples? If so, why?**

CONTENTS OF PRESENTATION

1. INTRODUCTION
2. METHODS
3. RESULTS
4. CONCLUSIONS



FIELD DUPLICATE STUDY

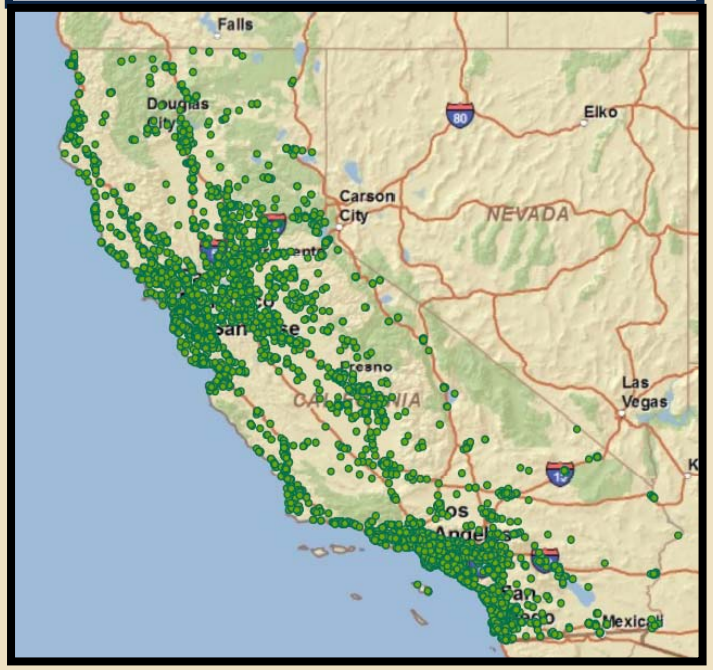
STATE WATER RESOURCES CONTROL BOARD
GEOTRACKER

GeoTracker Database

- Data management system for cleanup sites in California

- 65,000+ sites
- 30,000+ sites w/ electronic data
- Electronic data from 2001 and after

30,000+ SITES W/ ELECTRONIC DATA



KEY POINT: **GeoTracker provides unique resource for data mining.**

DATASET

	Vapor
#Sites	400
#Samples	>1,400
Timeframe	2003 - 2016
#Concentration Results	>52,000

KEY POINT: **Normal and duplicate results paired up and compared to evaluate variability.**

QUANTIFYING DIFFERENCES IN PAIRED DATA

Typical Method: Relative Percent Difference

$$RPD = \frac{|C1 - C2|}{AVERAGE(C1, C2)} \times 100\%$$

Alternate Percent Difference (APD)

$$APD = \frac{|C1 - C2|}{MIN(C1, C2)} \times 100\%$$

KEY POINT: **APD used to better resolve large differences between results.**

Note: Detection limit was substituted for non-detect results.

WHY APD?

Sample Results		Calculations	
Result 1	Result 2	RPD	APD
1	1.3	26%	30%

KEY POINT: **Large differences between results approach an RPD of 200%, but get bigger for APD. APD used as basic method to evaluate dataset.**

CONTENTS OF PRESENTATION

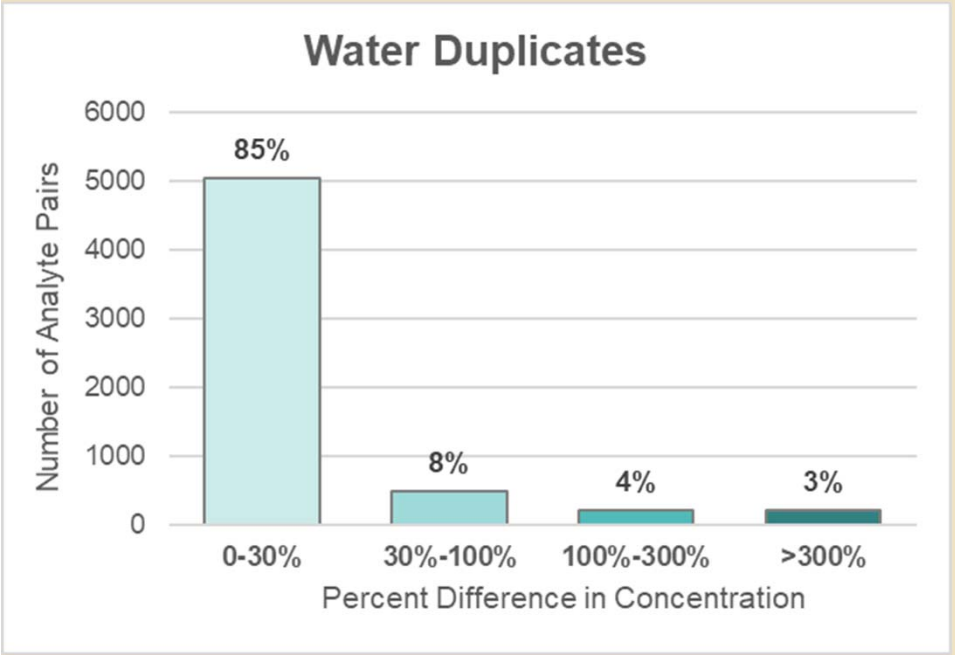
DATA PAIRS:
GROUPED INTO BUCKETS

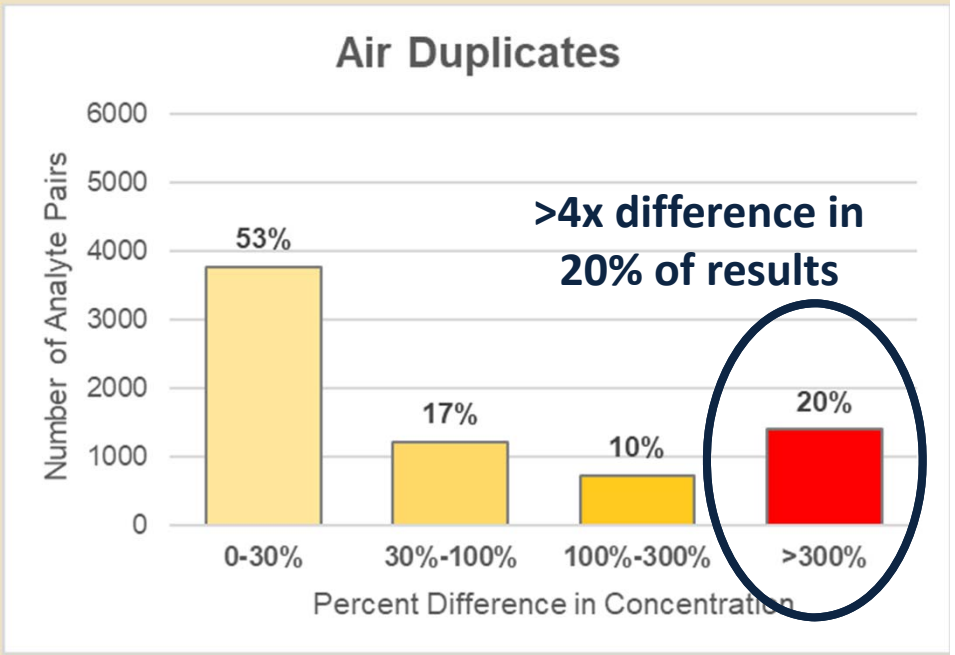
DATA PAIR	GROUNDWATER	VAPOR
Both Non-Detect	92% (72,080)	87% (45,433)
One-Detects	1% (599)	3% (1,606)
Two-Detects	7% (5,364)	10% (5,483)

KEY POINT: **Different groups of samples were used to answer different questions.**

IS THERE A DIFFERENCE BETWEEN GW AND VAPOR PAIRS?

- **YES!**





KEY POINTS:

- **Large differences more common in vapor pairs.**
- **Initial results confirmed anecdotal observations that vapor samples are more variable than groundwater samples.**

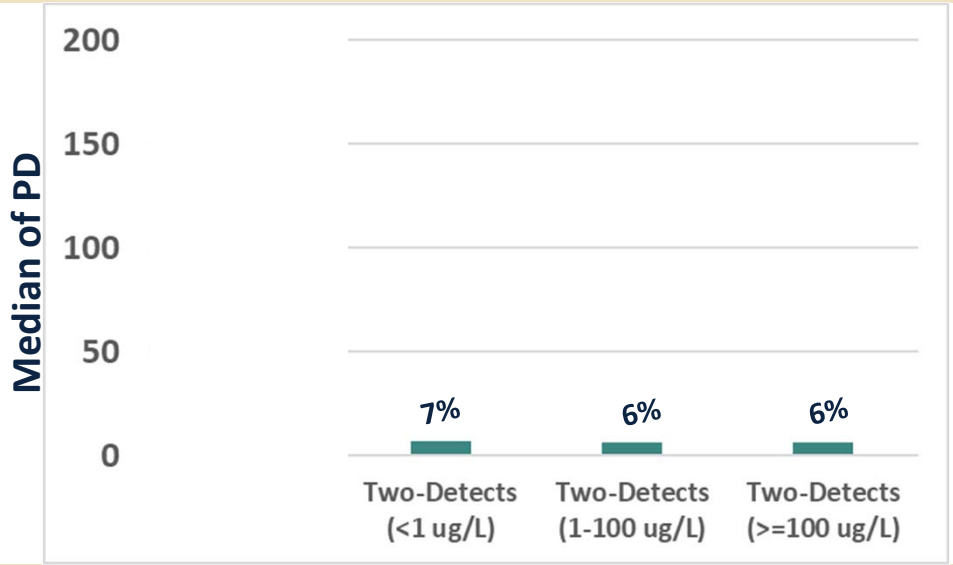
Note: Evaluation of one- and two-detect groups. Detection limit substituted for non-detect results.

DOES CONCENTRATION MATTER?

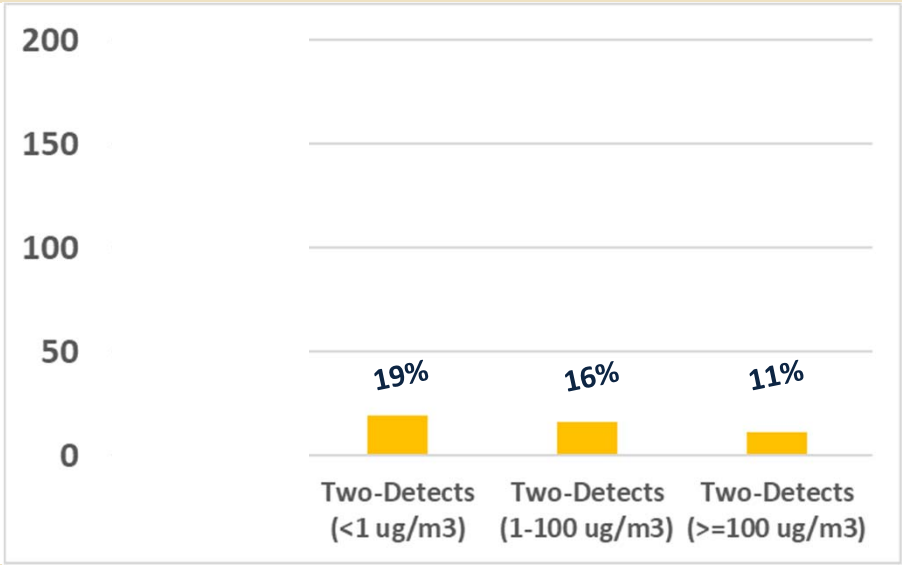
Not Really

DOES CONCENTRATION MATTER?

GW: Median of Percent Differences



Vapor: Median of Percent Differences



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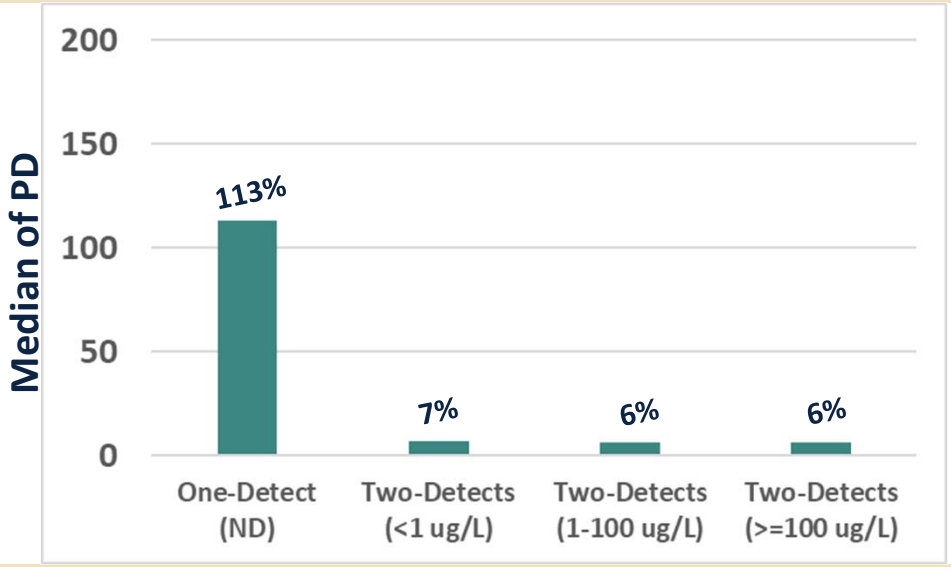

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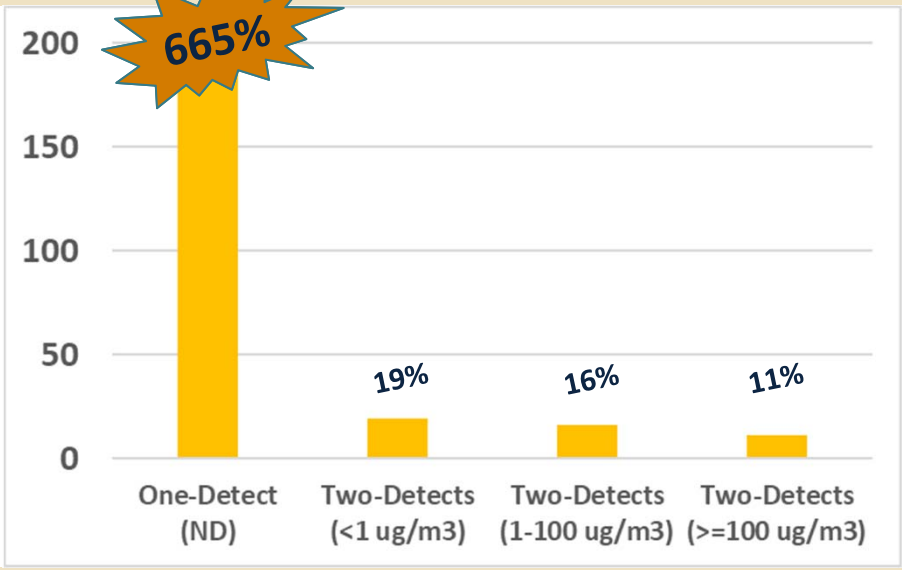

KEY POINT:

- **Good analytical precision across concentration ranges.**
- **Duplicate variability was higher for one-detect analyte pairs.**
- **Implies difference not due to analytical precision.**

Note: Evaluation of one- and two-detects, grouped into concentration range buckets by the lowest value in the pair. Detection limit substituted for non-detect results.

HIGH VARIABILITY IN ONE-DETECT PAIRS

- **Apparently caused by "sample contamination"**
  - **Sampling process, container, sample prep in lab, carry-over contamination during analysis**
- **Seen for GW and vapor, but worse for vapor**

	GROUNDWATER	VAPOR
Median PD	113%	665%
How Common are 1-D Pairs?	10% of pairs	23% of pairs
Container		

KEY POINT: **Sample contamination issues are more significant for vapor samples than for water samples. One key difference: re-use of containers for vapor.**

WHAT IS THE IMPACT OF "SAMPLE CONTAMINATION?"

DATA EVALUATION ASSUMPTIONS:

PAIR TYPE	MOST LIKELY EXPLANATION
Two-Detects	■ Chemical IS present at sample point
Both Non-Detects	■ Chemical NOT present at sample point
One-Detects	■ Chemical NOT present at sample point ■ One "False Positive" in the sample pair due to sample contamination introduced during collection or analysis

WHAT IS THE IMPACT OF "SAMPLE CONTAMINATION?"

ESTIMATION OF SAMPLE CONTAMINATION RATE:

$$\text{Contamination Rate} = \frac{\text{Number of "False Positive" Results}}{\text{Number of Pairs where Chemical Not Present in Sample Point}} \times 100\%$$

$$\text{i.e., Contamination Rate} = \frac{\text{No. of One-Detect Pairs} \times 0.5}{(\text{No. of Zero-Detect Pairs} + \text{No. of One-Detect Pairs})} \times 100\%$$

KEY POINT: **Equation estimates percentage of "false positive" detections for individual analytes.**

PERCENT "CLEAN" SAMPLES AFFECTED BY SAMPLE CONTAMINATION

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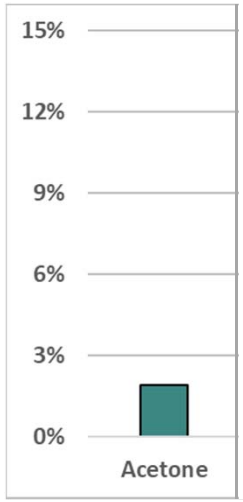
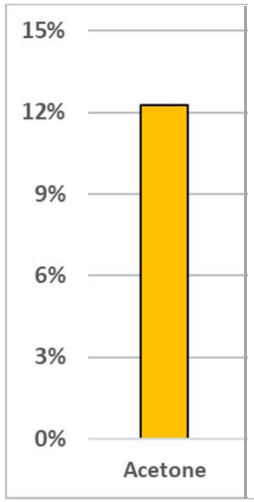
Groundwater



Acetone
(common lab contaminant)

Vapor

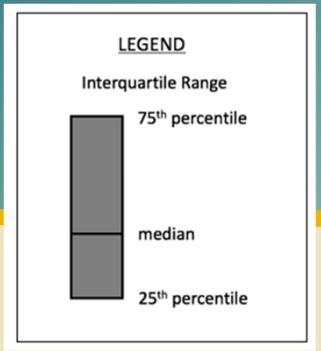


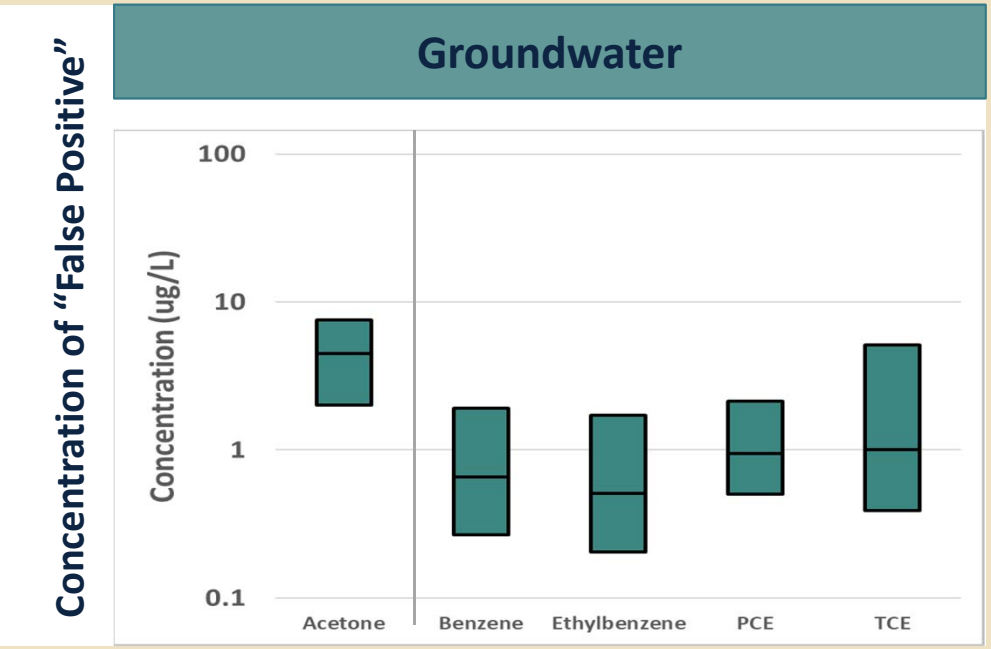
Acetone
(common lab contaminant)

KEY POINT: **For GW, contamination rate < 2% for all individual analytes.**
For vapor, acetone 12%; common site contaminants 4-6%.

Note: Evaluation of zero- and one-detect pairs.

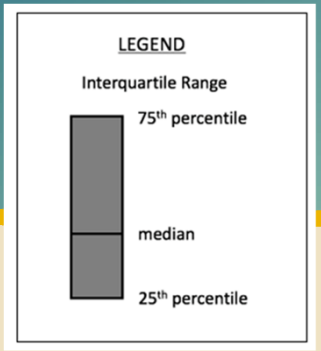
DOES SAMPLE CONTAMINATION MATTER?

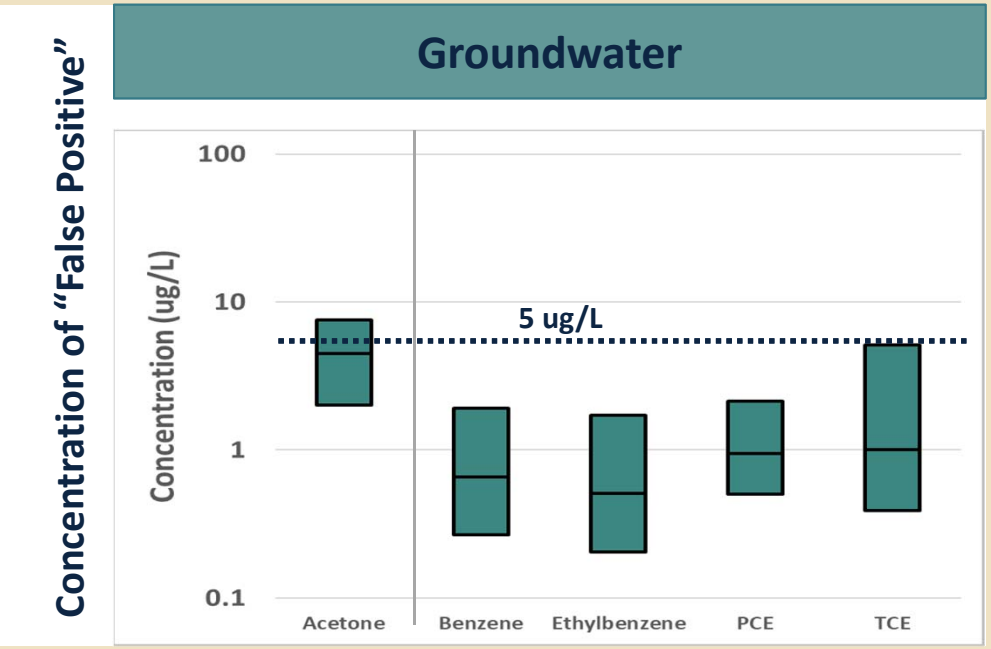




KEY POINT: **For site contaminants, median GW concentrations are about 1 µg/L.**

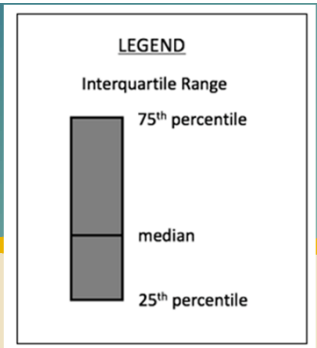
DOES SAMPLE CONTAMINATION MATTER?





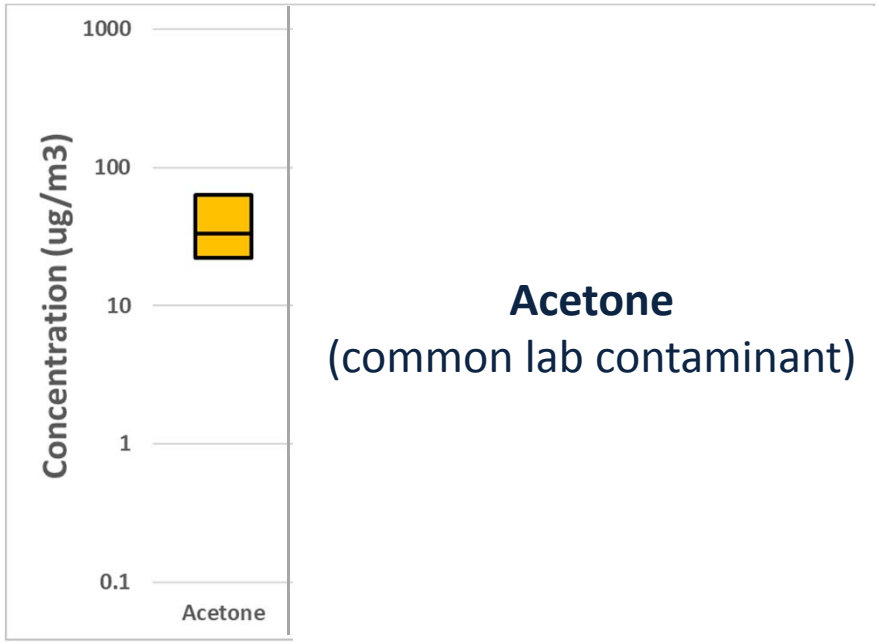
KEY POINT: **In most cases, the "False Positive" GW concentration is less than typical groundwater screening levels (e.g., MCLs).**

SOIL GAS VS. INDOOR/OUTDOOR?



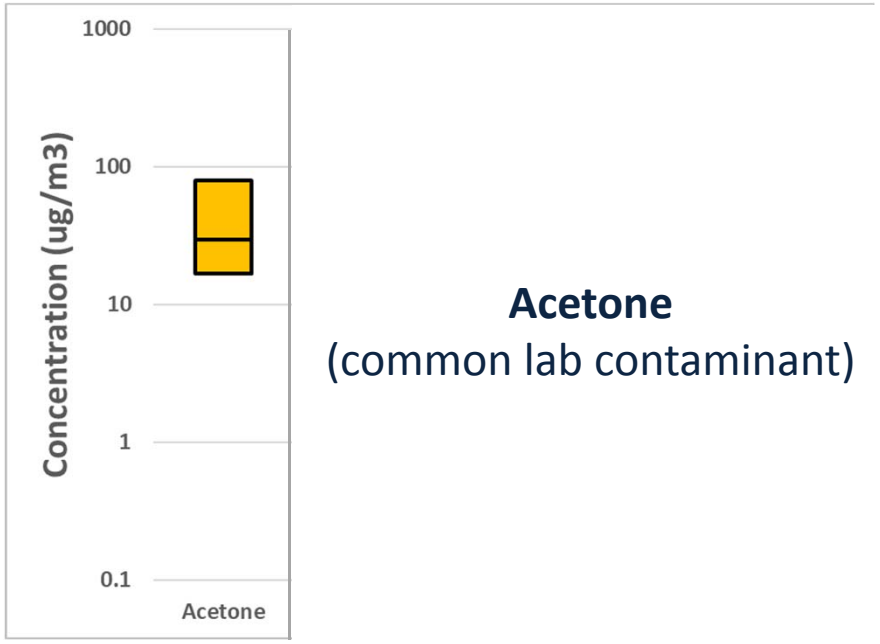
Concentration of "False Positive"

Soil Gas



Acetone
(common lab contaminant)

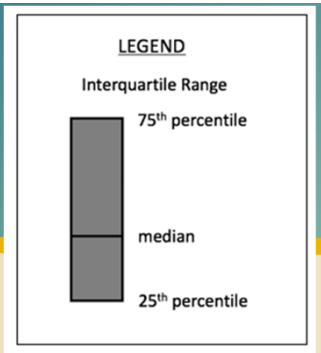
Indoor/Outdoor Air

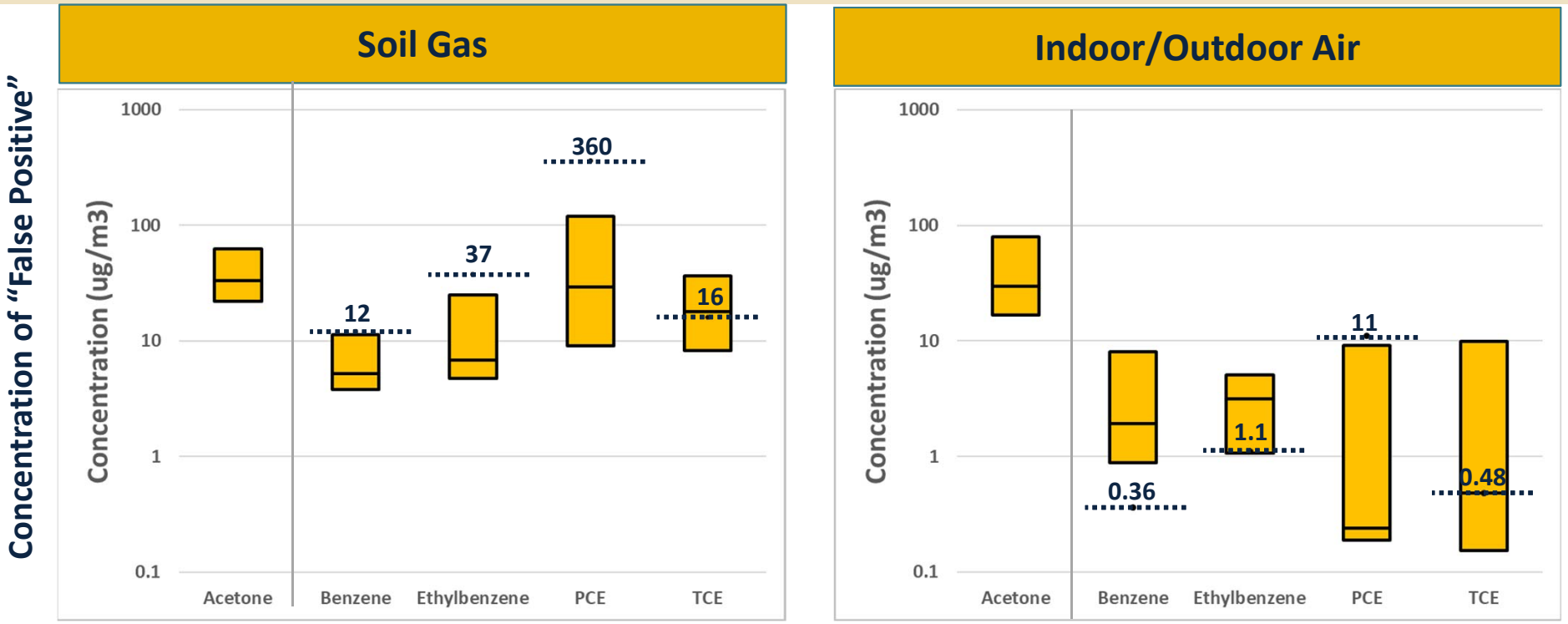


Acetone
(common lab contaminant)

KEY POINT: **For site contaminants, concentrations in affected soil gas samples about 10x higher than air samples.**

SOIL GAS VS. INDOOR/OUTDOOR?





KEY POINT: **"False Positive" concentrations generally less than screening levels for soil gas (except TCE). More problematic for indoor air.**

Note: Soil Gas SLs from USEPA VISL; residential Indoor Air Screening Levels per USEPA, Nov 2017 RSL table (TR=1e-6; THQ=1).

IMPLICATIONS: *SOIL GAS VS. AIR*

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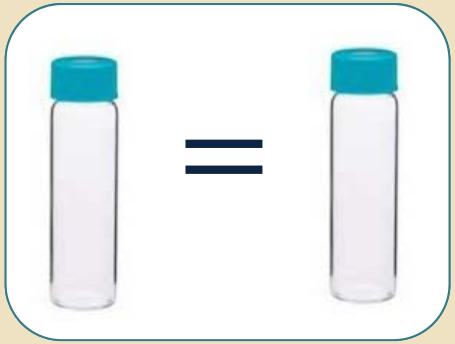
- Concentration of acetone similar between soil gas and air.
  → Non-site sources of sample contamination important.

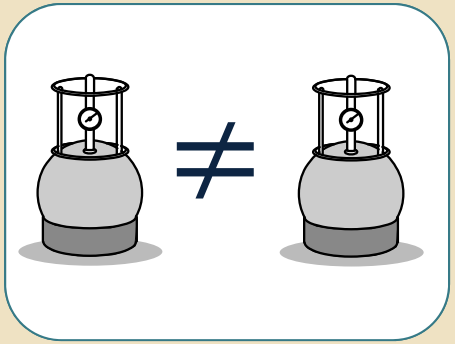
- Soil gas commonly contains higher VOC concentrations than air.
  → Sample contamination and carryover is a larger concern.

- "False Positive" conc. of common site contaminants approx. 10x higher for soil gas compared to air.
  → Source likely incomplete cleaning of reusable sample containers (Summa canisters).

KEY POINT: **Because indoor air screening values are so low, false positive detections of site chemicals will likely lead to additional investigation, response actions.**

CONTENTS OF PRESENTATION





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CONCLUSIONS

Vapor Duplicate Pairs

- Sample contamination causes detectable concentrations in 4-6% of "clean" samples (i.e., samples that would normally yield non-detect results).
- This "False Positive" rate is for *individual chemicals* (not for the false detection of any chemical in a *sample*. The sample false positive rate would be higher.)
- "False Positive" detections are likely to be above indoor air screening values.

KEY POINT: Majority (>90%) of results were not impacted by sample contamination. However, the possibility of sample contamination should be considered in cases of unexpected results.

RECOMMENDATIONS

Data Interpretation:

Consider Sample Contamination when:

- **Analyte is detected in small percentage of site samples. No clear pattern to detections.**
- **Detected analyte not otherwise expected to be a site contaminant (e.g., chlorinated solvent at petroleum release site).**

Project Planning**:

- **Does laboratory segregate soil gas from air canisters?**
- **Batch vs. individually certified-clean canisters**
- **Clean to detection limit, reporting limit, other limit?**

KEY POINT: **Don't make big decisions based on one or two detections in a sampling program.**

** Note: Our study did not evaluate whether any of these measures actually reduce the "false positive" rate.

THANK YOU!

STATE WATER RESOURCES CONTROL BOARD
GEOTRACKER

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