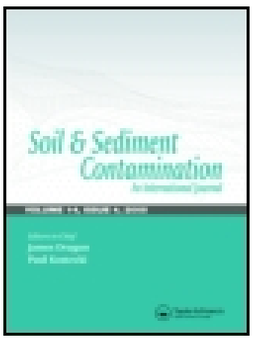

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Evidence of canister contamination causing false positive detections in vapor intrusion investigation results

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ABSTRACT

We have utilized the California GeoTracker database to evaluate field duplicate variability and the significance of sample contamination for groundwater and vapor samples collected from contaminated sites in California. Vapor duplicates are more variable than water duplicates with median percent difference in concentration of 25% compared to 7% for water samples. In addition, large differences in concentration were more common in vapor duplicates. For vapor analyte pairs, 20% of pairs had a percent difference in concentration of >300% while, for groundwater analyte pairs, only 3% had a percent difference of >300%. Contamination of samples during collection or analysis is also more significant for vapor samples. For water samples, sample contamination appears unlikely to result in false positive exceedances of drinking water standards; however, for vapor samples, sample contamination may result in false positive exceedances of indoor air screening values. For vapor samples, the use of reusable canisters and flow controllers is likely an important source of sample contamination.

KEYWORDS

Vapor intrusion; SUMMA canister; GeoTracker; data mining; duplicate

Introduction

Field duplicate sample pairs are two samples collected at the same point in time and space so as to be considered identical (USEPA, 2002). As part of environmental sampling programs, the collection of field duplicate sample pairs is typically a required component of the quality assurance/quality control program (e.g., NJDEP, 2005). Field duplicate sample pairs are usually collected at a frequency of 5–10% of total field samples. Field duplicate sample pairs are intended to provide an evaluation of the precision associated with all steps in the sample collection, handling, and analysis process. However, most field sampling programs involve the collection of only one or two field duplicate pairs. As a result, regardless of whether the agreement in analytical results between the duplicate samples is good or poor, it is difficult to use these results to evaluate the overall quality of the field investigation results.

In our experience, field duplicate vapor sample pairs collected and analyzed in accordance with USEPA Method TO-15 (USEPA, 1999) seem to exhibit higher variability than field duplicate groundwater sample pairs collected and analyzed in accordance with USEPA Method 8260 (USEPA, 1996). However, when evaluating analytical results from individual projects, it is difficult to determine whether there is a true difference in data quality between

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water and vapor samples, and, if so, the significance of this difference. Both TO-15 and 8260 are USEPA-specified methods for analysis of volatile organic compounds (VOCs) by gas chromatography/mass spectrometry and the laboratory procedures are fairly similar. However, vapor samples for analysis by Method TO-15 are collected using passivated metal canisters (i.e., metal canisters that have been treated to minimize sorption of VOCs to the canister surfaces) such as SUMMA, SilcoCan, or TO-Cans and flow controllers that are cleaned and reused. Water samples for analysis by Method 8260 are collected using 40 mL disposable glass vials (commonly called VOA vials).

In order to obtain a better understanding of variability within field duplicate sample pairs, we have utilized the California GeoTracker database to obtain a large dataset of analytical results for these sample pairs. This large dataset has allowed us to quantify the difference in field duplicate sample pair variability between vapor samples and groundwater samples. In addition, we have been able to identify sample contamination as an important factor associated with high duplicate pair variability in vapor samples.

Methods

Data source

GeoTracker is a database of corrective action sites maintained by the California State Water Resources Control Board. Parties conducting environmental assessments and corrective actions in California are required to provide reports, monitoring data, and other site information using the web-based interface (GeoTracker, 2017). As a result, the GeoTracker database serves as the Water Board's data management system for sites with environmental impacts. The database is also accessible by the general public through the web interface. Users may obtain information about individual sites or they may download electronic data available for all sites.

For this analysis, the GeoTracker database was downloaded on 19 January 2017. This downloaded database contained environmental monitoring data from corrective action sites covering the time period of September 2001 to November 2016. A query was used to extract analytical results for vapor and air samples collected into passivated metal canisters and analyzed by Method TO-15. As a control measure, only results reported in concentration units of $\mu g/m^3$, mg/m^3, ppbV, or ppmV were included. Since GeoTracker does not have a specific field that identifies original and field duplicate samples, we identified a set of potential duplicate samples as samples that included the characters "dup" or "fd" as part of the Sample ID. For each of these potential duplicate samples, we identified a matching primary sample by searching for a separate sample that had identical entries in all of the following fields: Site ID, Location ID, Sample Date, Laboratory, Analytical Method, and Units. Each matched pair (i.e., a sample with "dup" or "fd" in the Sample ID and a second sample with the same identifying information in the Site ID through Units fields) was retained as a field duplicate sample pair.

The same process was used to identify groundwater field duplicate pairs. However, to obtain a groundwater dataset matched to the vapor dataset, we included only groundwater field duplicate pairs for sites where we were able to identify vapor field duplicate pairs.

The data reduction process yielded a dataset of 1252 vapor field duplicate sample pairs analyzed by Method TO-15 (from 365 sites) and 1535 groundwater field duplicate sample pairs analyzed by Method 8260 (from 78 sites). Because each sample was analyzed for several volatile compounds, the dataset included a total of 52,522 vapor analyte pairs and

78,043 groundwater analyte pairs. For each data record (i.e., each analyte pair), we extracted the following additional information for our analysis: sample collection date, laboratory, sample matrix (e.g., soil gas, indoor air), analyte, detect/non-detect status, detection limit, detected concentration (for detected compounds). This full dataset is provided as supplemental material (Table S-1).

Data analysis methods

Each analyte pair in the dataset was classified into one of three groups: (i) both results in the pair below detection limits (i.e., "zero-detects" group), (ii) one detected concentration result and one non-detect result (i.e., "one-detect" group), and (iii) both detected concentration results in the pair (i.e., "two-detect" group). For calculations using one-detect analyte pairs, the detection limit was used as a proxy for the non-detect result.

For each analyte pair in the one-detect and two-detect groups, the percent difference in analyte concentration between the two results was calculated as shown in Equation (1):

$$\text{Percent Difference} = \frac{\text{Higher Concentration} - \text{Lower Concentration}}{\text{Lower Concentration}} \times 100\% \qquad (1)$$

This calculation is different from the relative percent difference (RPD) calculation typically used for evaluation of laboratory quality control results where the difference in concentration is divided by the average of the two concentration results. When the difference in concentration is small, the two calculations yield similar results; for example, a pair with an RPD of 30% yields a percent difference value from Equation (1) of 35%. However, when the concentration difference is large, the RPD approaches a maximum value of 200% while the percent difference calculation is not bounded. For example, a pair with a 10× concentration difference yields an RPD of 164% and a percent difference of 900%. Thus, our percent difference calculation provides greater resolution for sample pairs showing large concentration differences.

Results and discussion

The dataset of vapor analyte pairs included 45,433 zero-detect pairs (87%), 1606 one-detect pairs (3%), and 5483 two-detect pairs (10%). The dataset of groundwater analyte pairs included 72,080 zero-detect pairs (92%), 599 one-detect pairs (1%), and 5364 two-detect pairs (7%).

For analyte pairs with at least one detection (i.e., the one-detect group and the two-detect group), the simple percent difference calculation confirmed our anecdotal observations that vapor duplicates show higher variability than groundwater duplicates (Figure 1). The median percent difference for the vapor analyte pairs (25%) was significantly higher than the median percent difference for groundwater pairs (7%) by the Mann–Whitney U test ($p < 0.001$). In addition, large differences in concentration were more common in vapor duplicates. For vapor analyte pairs, 20% of pairs had a percent difference of >300% while, for groundwater analyte pairs, only 3% had a percent difference of >300%. A percent difference of 300% corresponds to a concentration difference of 4× (e.g., 10 μg/m^3 in one sample vs. 40 μg/m^3 in the paired sample).

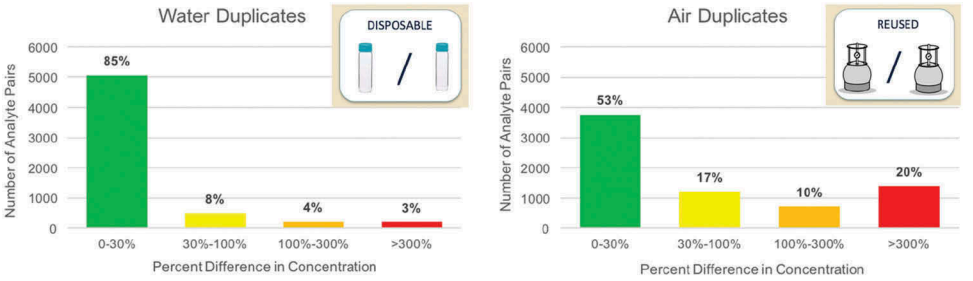

Figure 1. Duplicate variability for water duplicates and air duplicates.

Note: The figure graphics are included in manuscript file to illustrate layout. Separate graphic files have also been provided.

In order to evaluate the relationship between concentration and duplicate variability, we sorted the analyte pairs by concentration using the lower of the two concentration results (Table 1). Although duplicate variability for both water and vapor samples was somewhat higher at low concentrations compared to high concentrations, the difference in precision was relatively small for all two-detect analyte pairs. This suggests good analytical precision across all concentration ranges. However, the duplicate variability is far higher for the one-detect analyte pairs. For the one-detect pairs, the median percent difference between the detection limit (for the non-detect result) and the detected concentration (for the detected result in the pair) was 113% for water analyte pairs and 665% for vapor analyte pairs (Table 1, "one-detect" rows). These concentration differences are far higher than the analytical precision exhibited for even the lowest concentration group where the analyte was detected in both samples (i.e., 7% for water pairs and 19% for vapor pairs; Table 1). These differences indicate that most of the one-detect cases are not attributable to poor analytical precision.

Variability in sample collection and handling is also unlikely to explain the large discrepancy between one-detect pairs and two-detect pairs. In cases where a VOC is actually present at a sample point, variability in sample collection or handling would typically result in dilution of the VOC in one of the two duplicate samples. For example, leakage of clean air into one of the two duplicate samples during sample collection would dilute the concentration of the

Table 1. Relationship Between Analyte Concentration and Duplicate Variability

Analyte pair group	Concentration range of lower concentration sample (1)	Number of analyte pairs	Median of percent differences (2)	90th percentile of percent differences
Vapor analyte pairs				
One detect	Non-detect	1606	665 ($p < 0.001$)	3831
Two detects	<1 µg/m^3	653	19 ($p < 0.001$)	171
Two detects	1–100 µg/m^3	3010	16 ($p < 0.001$)	130
Two detects	≥100 µg/m^3	1795	11	105
Water analyte pairs				
One detect	Non-detect	599	113 ($p < 0.001$)	1326
Two detects	<1 µg/L	859	7 ($p < 0.001$)	32
Two detects	1–100 µg/L	2983	6 ($p = 0.04$)	27
Two detects	≥100 µg/L	1522	6	25

Notes:

(1) Analyte concentration ranges are based on the lower of the two concentration results for each pair. The vapor dataset includes only one- and two-detect pairs from TO-15 analysis, with results reported in, or converted to, µg/m^3. This subset of data does not include 25 TPH-GRO analyte pairs only reported in ppbV in the original GeoTracker database that were not converted to µg/m^3 for this study.

(2) *p*-Value shown based on comparison with the highest concentration group using the Mann–Whitney *U* test.

target VOC. This would most likely result in detections in both of the duplicates at different concentrations. Sample leakage would be less likely to result in one detection well above the detection limit and one non-detect result (such a scenario would only result from one of the samples consisting almost entirely of leaked clean air). Similarly, leakage of the sample container during shipment would be more likely to result in sample dilution rather than removal of the target analyte below detectable concentrations. Instead, most of the cases where a target VOC is detected in one of two duplicate samples (i.e., one-detect pairs) are likely associated with non-site contamination being introduced into the sample during sample collection or laboratory analysis. Potential sources of this type of contamination include contamination of the sample container, contamination during sample processing, or carry-over contamination during sample analysis.

The comparison of vapor and water results indicates that sample contamination issues are much more significant for vapor samples than for water samples. For instance, there were 1606 one-detect vapor analyte pairs (i.e., 3.1% of all vapor analyte pairs) compared to 599 one-detect water analyte pairs (i.e., 0.77% of all water analyte pairs), and the median of percent differences between the detected concentration and the analytical detection limit was much larger for vapor one-detect pairs (665% vs. 113%, see Table 1).

One important difference between the collection of water samples vs. vapor samples is the use of disposable glass vials for water samples and reusable passivated containers for vapor samples. For vapor samples, incomplete cleaning of the reusable canisters and/or flow controllers is a possible source of contamination. Our analysis of field duplicates suggests that sample contamination can contribute to false positive detections of target analytes in water and vapor samples collected from contaminated sites. However, field duplicates are typically collected for only one in 10 to one in 20 site samples. For samples without field duplicates, it is difficult to quantify the impact of field or laboratory contamination on the analytical results. In order to estimate the overall impact of sample contamination on field investigation results, we used the results from the one-detect analyte pairs as an imperfect proxy for sample contamination. For this purpose, we assumed that all two-detect analyte pairs represented cases where a target analyte was truly present at the site, all one-detect pairs represented sample contamination in the sample with the detected result, and all zero-detect pairs represented an absence of both site contamination and sample contamination. These assumptions are imperfect because some one-detect pairs may be due to analytical precision and some two-detect pairs may be impacted by sample contamination. However, these alternative cases likely represent a small percentage of the overall dataset.

Based on these assumptions, we calculated a "contamination rate" for common laboratory and site contaminants. The contamination rate was calculated using the zero-detect and one-detect pairs and provides an estimate of the percentage of samples where contamination was introduced into an otherwise clean sample:

$$\text{Contamination Rate} = \frac{\text{No. of One}-\text{detect pairs x } 0.5}{(\text{No. of Zero}-\text{detect pairs} + \text{No. of One}-\text{detect pairs})} \times 100\% \qquad (2)$$

This equation provides an estimation of the percentage of "false positive" *detections for individual analytes* given the assumptions described above. The factor of 0.5 was used because, in a one-detect pair, contamination was introduced into only one of the two samples in the pair. This analysis was completed for acetone (a common laboratory

contaminant), benzene and ethylbenzene (two common petroleum site contaminants), and tetrachloroethene (PCE) and trichloroethene (TCE, two common chlorinated solvent site contaminants). For water samples, the "false positive" contamination rate was less than 2% for all individual analytes evaluated. For vapor samples, the "false positive" contamination rate for acetone was 12% while the rate for the common site contaminants ranged from 4% to 6% (Figure 2).

To further evaluate the significance of "false positive" sample contamination, we looked at the range of measured concentrations for the detected results from one-detect pairs (Figure 3). Assuming that most of these detections are attributable to sample contamination, these detected concentrations provide a proxy for the magnitude of contamination introduced into the sample. For the vapor samples, we separately evaluated soil gas samples and indoor/outdoor air samples because some laboratories use different sets of canisters and flow controllers for the collection of soil gas vs. air samples. Soil gas samples commonly contain much higher concentrations of VOCs compared to air samples (USEPA, 2012; Yao *et al.*, 2013); therefore, canister and flow controller contamination and instrument carry-over contamination are likely to be more significant for soil gas samples compared to air samples. This would result in higher "false positive" detected concentrations for soil gas samples. For the water samples, the 75th percentile concentration for the common site contaminants was less than the federal drinking water standard of 5 µg/L for benzene, PCE, and TCE, and 700 µg/L for ethylbenzene (USEPA, 2017). Combined with the low sample contamination rate, this suggests that sample contamination is rarely the cause of a drinking water standard exceedance. For vapor samples, there was little difference in acetone concentration for the soil gas and air "false positive" detection samples. In contrast, the concentration of the common site contaminants was approximately 10× higher in the "false positive" soil gas samples compared to the "false positive" air samples. This implies that incomplete cleaning of reused passivated canisters and/or flow controllers is an important source of sample contamination for the common site contaminants while other sources of sample contamination appear to be more important for acetone. For benzene, ethylbenzene, and TCE, the median detected concentration attributable to sample contamination in the air samples was greater than the USEPA screening values for indoor air (USEPA, 2017). As a result, a false positive detection of these constituents as a result of sample contamination is likely to lead to additional site investigation or response actions.

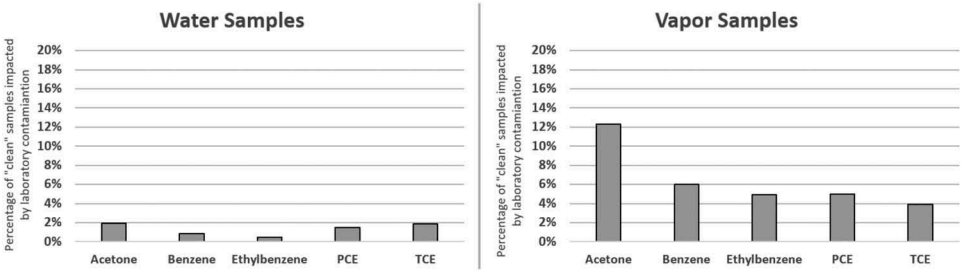

Figure 2. Contamination rate implied by the frequency of one-detect pairs in field duplicate samples.
Note: The figure graphics are included in manuscript file to illustrate layout. Separate graphic files have also been provided.

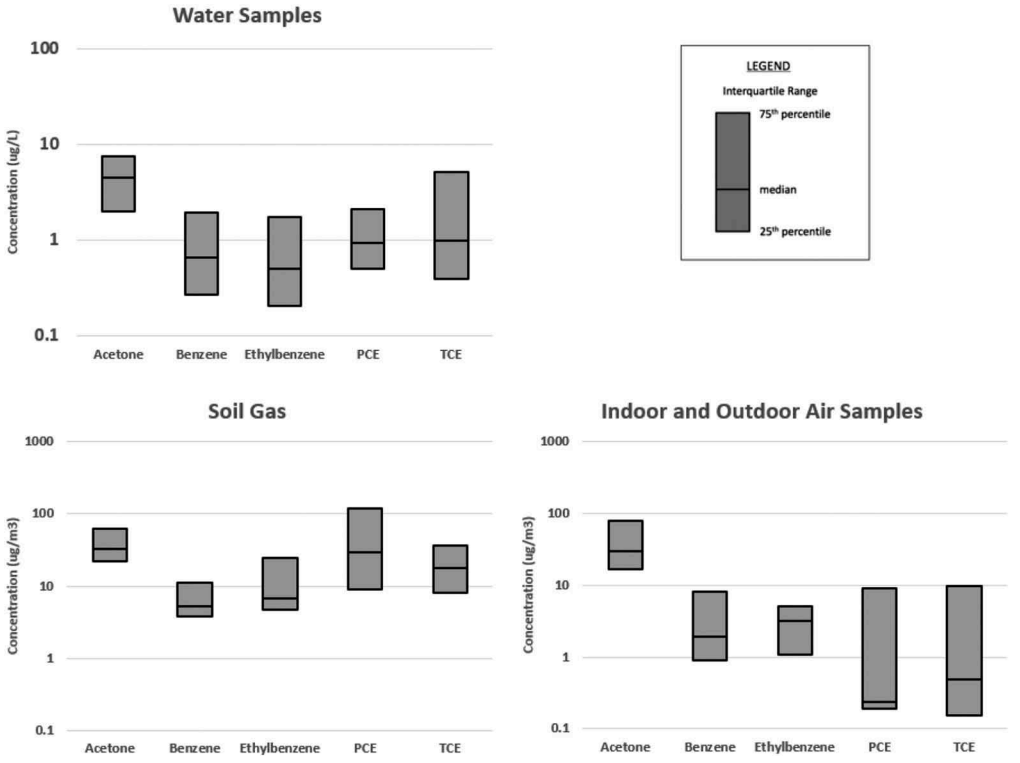

Figure 3. Magnitude of sample contamination implied by analyte concentrations in one-detect pairs from field duplicate samples.

Note: The figure graphics are included in manuscript file to illustrate layout. Separate graphic files have also been provided.

Our analysis of paired field duplicate samples from the GeoTracker database indicates that sample contamination is an important source of duplicate variability in both water samples and vapor samples. While this type of data mining study cannot identify the specific source(s) of this contamination, the frequency and magnitude of sample contamination is significantly higher in vapor samples suggesting possible carry-over contamination in the reusable passivated canisters and/or flow controllers used for the collection of vapor samples. Although the passivated canisters are cleaned by several rounds of flushing between each use, it may be possible for some VOCs to remain attached to slow desorption sites within the canister. The authors are aware of an anecdotal example where duplicate indoor air samples collected using passivated canisters resulted in a detection of 6 μg/m^3 of PCE in one sample and a non-detect result (<0.1 μg/m^3) in the other sample. Based on follow-up inquiries with the analytical laboratory, it was determined that the immediately prior samples collected in these canisters had PCE concentrations of 420,000 μg/m^3 (in the canister with the 6 μg/m^3 result) and <0.1 μg/m^3 (in the canister with the <0.1 μg/m^3 result). Although both canisters were individually certified clean prior to reuse, this certification testing was conducted immediately after canister cleaning. Slow desorption of PCE after the clean certification is a likely explanation for the detection of 6 μg/m^3 of PCE.

Our analysis suggests that, for common site contaminants, sample contamination causes detectable concentrations of the compound in approximately 4–6% of "clean" site vapor samples (i.e., samples that would otherwise yield non-detect results). Although the majority (i.e., >90%) of analytical results are not impacted by sample contamination, the possibility of this occurring should be considered when an analyte is detected in only a small percentage of samples collected from a site or when a detected analyte is otherwise not expected to be a site contaminant (e.g., detection of a chlorinated solvent at a petroleum release site). Failure to account for possible sample contamination could result in unnecessary site investigation or response actions.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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