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Research Article

Evaluating Duplicate Results Demonstrates Differences Between Direct and Canister Sampling Methods

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Abstract

Field duplicates of environmental samples are collected to evaluate field and laboratory precision. This study used field duplicate results to assess whether samples analyzed for volatile organic compounds collected using reusable summa canisters exhibit carryover contamination when compared to results for samples collected using direct sampling methods (e.g., soil gas collected by mobile laboratories via dedicated tubing and syringes or groundwater collected using disposable vials). This study utilized data sets of groundwater, soil gas, and indoor air from samples collected between 2000 and 2024 from multiple project sites and analyzed by different analytical laboratories. Volatile organic compound data were evaluated by sampling method (direct or reusable canister), analytical method, and medium following a similar approach to the one described in a prior study by McHugh et al. (2018). This evaluation included assessing the magnitude of the differences between primary and duplicate sample results by calculating percent differences and comparing the number of single-detect pairs versus non-detect pairs, which could be an indication of carryover contamination. Results showed that water samples collected using disposable vials and soil gas samples collected using direct sampling methods had greater precision (i.e., lower percent differences) and lower occurrences of single-detect pairs compared to soil gas or indoor air samples collected using evacuated canisters; confirming that reusable canisters may contain carryover contamination. Other factors contributing to uncertainty (i.e., low detected concentrations, sampling equipment certification process, quality control procedures, and laboratory best practices) were also considered to explain the discrepancies identified in this study.

Introduction

A high level of confidence in environmental data is crucial to making decisions throughout the site investigation and remediation process. To support data confidence, it is standard practice to collect duplicate samples during field data collection according to project data quality objectives and compare their results to evaluate the cumulative effects of both field and laboratory procedures on precision.

A previous study by McHugh et al. (2018) evaluated volatile organic compound (VOC) data for primary and duplicate samples collected from contaminated sites in California from September 2001 to November 2016. The McHugh study identified differences in the precision of field duplicate results based on sampling medium. Specifically, it showed that vapor samples (soil gas and indoor air) had a higher variability than aqueous (groundwater) samples. The authors hypothesized that differences in sample collection procedures might contribute to this higher variability in vapor samples, as soil gas and indoor air samples are typically collected using reusable canisters and flow controllers that may be subject to carryover contamination, whereas groundwater samples are typically collected using single-use glass VOA vials. The hypothesized explanation for variability in primary and duplicate sample results outlined in this prior study may account for differences observed in this current study's data set. To explore this hypothesis further, a comprehensive analysis of our duplicate data set was performed to test whether VOC samples collected using canisters show a higher frequency of carryover contamination compared to samples collected using direct sampling methods (including groundwater collected using VOA vials).

This study expands on the findings of McHugh et al. in the following ways:

1. The McHugh et al. study used data from 2001 to 2016, while the study presented in this paper evaluates data from 2000 to 2024, with most data collected between 2018 and 2024, reflecting the most current field and laboratory practices.
2. Unlike the McHugh et al. study, which utilized a publicly available data set assessed in aggregate, the data evaluated herein are from only three sites where we have direct knowledge and some control over the sampling techniques and laboratory procedures, reducing sources of uncertainty.
3. One data set in this study includes soil gas sampling conducted using multiple methods: sampling with dedicated

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tubing and syringes and evacuated canister sampling. This has created a unique natural experiment that allows for comparison of duplicate sample results from the same vapor medium sampled using different methods, providing a direct means to evaluate the hypothesis of canister contamination. In this paper, soil gas collected using small reusable glass syringes and immediately injected into the analytical system of the on-site mobile laboratory is termed "direct syringe" injection to distinguish it from soil gas samples obtained with reusable canisters.

Methods

Data Sets

The data in this study were extracted from databases containing validated analytical results for three vapor intrusion sites, two on the west coast (Site 1 and Site 2) and one on the east coast (Site 3). The extracted data were limited to results for primary and duplicate sample pairs and consisted of available analytical VOC results for groundwater, exterior soil gas, sub-slab soil gas, and indoor air samples.

Groundwater data were collected from 2000 to 2024, and data for the other media were collected from 2018 to 2024. Exterior soil gas refers to soil gas collected from probes outside of a building footprint, installed in either hardscape (e.g., pavement, asphalt) or landscape (e.g., grass, dirt), generally at depths of 5 and 15 feet. Exterior soil gas samples were collected using SUMMA canisters and analyzed by fixed laboratories, except for Site 1 from 2018 to 2022, where they were collected by on-site mobile laboratories using direct syringe injection. No exterior soil gas data were collected at Site 3. Sub-slab soil gas samples were collected from sub-slab sampling points installed through the building slab. Data for sub-slab soil gas at Site 2 were excluded from this evaluation due to the limited number of available duplicate pairs. The data sets used in this study are summarized below in Table 1, which includes the number of sample pairs (*N*) and timeframe during which the samples were collected. Data not used in this study (see Data Validation and Data Evaluation sections) are not included in Table 1.

Sample Collection Procedures

Groundwater

For groundwater sample collection, monitoring wells were first purged and then sampled. In general, all groundwater samples were collected using low-flow sampling methods. Water quality parameters were measured and monitored until three consecutive readings stabilized within specified criteria; samples were collected by cutting the tubing leading into the flow cell and filling the VOA vial sample containers directly from the tubing after at least two system volumes (including the total volume of the pump, tubing, and flow cell) had been purged from the well (Figure S1).

Exterior Soil Gas

Exterior and sub-slab soil gas samples at Sites 1 and 2 were collected and analyzed in accordance with the Advisory—Active Soil Gas Investigations (CalEPA 2015). For all exterior soil gas probes, a shut-in and leak test were successfully performed on each probe at each depth before sample collection to ensure the proper setup of the aboveground soil gas probe sampling system. The shut-in test involved assembling the aboveground valves, lines, and fittings (collectively referred to as the sample train) downstream from the most upstream valve, which remained closed throughout the test. The leak test was conducted to prevent sample dilution with ambient air. Both direct syringe injection and canister sampling procedures are described below.

- *Exterior Soil Gas (direct syringe injection)*: When collected by the mobile laboratories through direct syringe injection, after passing the shut-in test to check for leaks in the above-ground fittings, a tracer compound was placed at each soil gas sampling location near the sample train connection and the surface where ambient air could enter the sampling system. Each soil gas probe was then purged to remove stagnant air and ensure representative subsurface conditions. Purging was typically completed using a pump set at approximately 200 cc/min and a default of three purge volumes was used as recommended by the CalEPA Advisory (CalEPA 2015). Following purging, each sample was actively collected using a probe and tubing by connecting a 250 mL airtight glass syringe with a Teflon seal to the valve at the end of the probe tubing. The syringe was immediately injected into the mobile laboratory's analytical instrument purge-and-trap system for on-site analysis and stored in a cool, dark location prior to injection to prevent photo-degradation. Each sample was analyzed by gas chromatograph mass spectrometer within 10 min of collection. Before use, glass gastight syringes were decontaminated by disassembling and heating, except for components that cannot withstand heat, such as the barrel, which were cleaned by

Table 1

Data Set Summary

	Site 1		Site 2		Site 3	
Medium	***N***	**Timeframe**	***N***	**Timeframe**	***N***	**Timeframe**
Groundwater	945	2006–2024	11,135	2000–2024	2731	2015–2020
Exterior soil gas (direct syringe)	5165	2018–2022	—	—	—	—
Exterior soil gas (canister)	1431	2018–2024	236	2007–2024	—	—
Sub-slab soil gas	287	2018–2023	—	—	2326	2018–2024
Indoor air	3626	2018–2024	70	2020–2021	2614	2017–2024

Note: "—" medium not sampled at this site.

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rinsing with methanol or expunging with nitrogen or zero air.

- *Exterior Soil Gas (canister)*: When exterior soil gas was collected using canisters, after passing the shut-in test, a flexible bag shroud was installed over the probe and sampling train and filled with approximately 20% to 30% helium. Leak testing was conducted concurrently with purging. Following purging, a soil gas sample was collected, maintaining the helium in the shroud at approximately 20% to 30% during sample collection. When there was approximately 3 to 5 in Hg of vacuum remaining, the SUMMA canister valve was closed.

Examples of exterior soil gas sampling are shown in Figures S2a and S2b (direct) and Figures S3a and S3b (canister), respectively.

Sub-Slab Soil Gas

Initial sub-slab soil gas samples were collected by drilling a small diameter hole through the slab and advancing a stainless-steel vapor pin. Subsequent sampling events, if necessary, utilized the same vapor pins. At Site 1, a helium shroud was used, and sub-slab soil gas samples were analyzed for helium to confirm that there was no leak in the sampling train. At Site 3, leak testing was conducted using modeling clay and a short PVC pipe to create a water dam, which was then used to test for leaks. In addition, carbon dioxide and oxygen levels were measured, and comparisons between the probe and the atmospheric readings ensured no connection between the subsurface and the interior.

In each case, sub-slab soil gas sampling was conducted after indoor air sampling to avoid cross-contamination of indoor air from soil gas. Sub-slab soil gas samples were collected as 15-min grab samples; Site 1 used individually certified SUMMA canisters while Site 3 used batch-certified SUMMA canisters. An example of sub-slab soil gas sampling is shown in Figure S4.

Indoor Air

Indoor air samples were collected from the breathing zone (approximately 3 to 5 feet above the ground) using 6-L SUMMA canisters equipped with flow controllers to ensure a constant air intake rate. To verify the vacuum integrity in the canister and confirm the absence of leaks in the fittings, a "shut-in test" was performed and passed by briefly opening and then closing the valve on each canister, creating a vacuum within the flow controller. The indoor air samples used in this study were either 24- or 8-h time-weighted average samples, with duplicates collected for the same duration as their associated primary samples. Sites 1 and 2 used individually certified SUMMA canisters, and Site 3 used batch-certified SUMMA canisters. An example of indoor air sampling is shown in Figure S5.

All samples, including primary and duplicate samples, were properly labeled and packaged (groundwater samples were placed in ice-cooled chests) and transported to a National Environmental Laboratory Accreditation Program—certified analytical laboratory following chain-of-custody procedures.

Field Duplicate Sampling Procedures

Field duplicate samples are typically collected to assess the overall precision associated with sample collection, preservation, storage and analytical methods. Duplicate samples in this study were collected at a frequency of 10% of the total samples or at least once per laboratory or per field day, in accordance with appropriate agency guidelines (California Environmental Protection Agency [CalEPA] 2011) and were selected from areas with some level of predicted contamination to represent a variety of conditions throughout the project sites.

Duplicate samples were collected by the same sampling personnel, at the same time, from the same sampling location, using the same procedures, the same type of equipment and containers, following the same preservation, storage, and transport procedures as the primary samples, and were submitted for the same analyses to the laboratory, where they were analyzed independently. In some cases, they were submitted as blind duplicates, ensuring that the laboratory analyst could not identify their source; this factor is not expected to substantially affect the evaluation of the duplicate data.

For groundwater, primary and duplicate samples were collected sequentially in bottles designated for the same analyses before filling bottles for other analyses.

For exterior soil gas samples collected via direct syringe sampling with a mobile lab, duplicate samples were collected sequentially immediately after the primary sample using a second glass syringe.

For vapor and air samples (sub-slab soil gas, exterior soil gas samples collected using canisters and analyzed by a fixed lab, and indoor air), primary and duplicate samples were collected simultaneously into two SUMMA canisters. While the primary and duplicate samples were collected simultaneously for these media at all sites, the approach used to collect the duplicate samples varied by site. At Sites 1 and 2, laboratory-provided stainless-steel flow splitters were used to collect the primary and duplicate samples from the same inlet, splitting the medium into two canisters. An example of indoor air sampling using a duplicate-t flow splitter is shown in Figure S5. At Site 3, sub-slab soil gas primary and duplicate samples were collected using flow splitters. For indoor air at Site 3, the primary and duplicate sampling canisters were placed next to each other and deployed and collected simultaneously.

Laboratory Analytical Methods and Data Validation

Groundwater samples were analyzed for VOCs by United States Environmental Protection Agency (US EPA) Method 8260. Exterior soil gas samples were analyzed by US EPA Method 8260 using an Agilent 7890B GC/5977A MS instrument when collected via direct syringe sampling by the on-site mobile laboratory and by US EPA Method TO-15 when collected using canisters. Sub-slab soil gas and indoor air samples were analyzed by US EPA Method TO-15 SIM. Data for each site were analyzed by different environmental testing laboratories, which were certified for the analyses conducted.

For Site 1, the reported results for sub-slab soil gas and indoor air were limited to the main chemicals of

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concern for the project, specifically the following chlorinated VOCs (cVOCs): 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1-dichloroethene (1,1-DCE), cis-1,2-dichlorethene (cis-1,2-DCE), trans-1,2-dichloroethene (trans-1,2-DCE), tetrachloroethene (PCE), trichloroethene (TCE), and vinyl chloride. For Sites 2 and 3, the results for all analytes reported by the laboratory were used.

The data used in this study were validated according to the US EPA National Functional Guidelines for Organic Superfund Methods Data Review (US EPA 2020). Laboratory analytical data for Sites 1 and 2 were reviewed using either the US EPA Verification and Validation Stage 2 or Stage 4 approach, depending on the type of data, and data for Site 3 were validated using Stage 2. Instrument calibration checks, method blanks, and sampling blanks were performed at the frequency specified in the corresponding analytical methods standard operating procedures. Laboratory control samples and duplicates, as well as matrix spikes and duplicates, were analyzed for each sample batch, as appropriate and in accordance with standard operating procedure requirements. Data were considered usable unless qualified as rejected due to serious deficiencies in meeting quality control (QC) criteria. Rejected data were excluded from the analyses conducted herein.

Data Evaluation

The data were evaluated by medium, sampling method, and analytical method using a similar approach to the one described in McHugh et al. The analyses included two main elements. The first element was to assess the magnitude of differences between primary and duplicate sample results by calculating the percent difference. The second element was to evaluate the number of single-detect pairs versus zero-detect pairs, which could be an indication of carryover contamination.

For each medium, sample, and constituent, the percent difference between the numerical results of the two duplicate samples was calculated as follows:

$$\text{Percent difference} = \frac{\text{higher value} - \text{lower value}}{\text{lower value}} \times 100$$

Percent differences were calculated for one-detect or two-detect pairs, where a one-detect pair refers to a duplicate pair for which one result was reported as detected, and the other result was reported as not detected. The reporting limit (or method detection limit, if available) was used to represent the value of the non-detect result in the one-detect pairs. Estimated values were used as reported. Percentage differences were not calculated for one-detect pairs where the reporting limit for the non-detect result was higher than the detected concentration, or where there was no method detection limit available. This scenario applied to a limited number of sample pairs. Selected statistical analyses of the percent differences between the media and sampling type were also conducted to assess the statistical significance of the results. Analyses were performed using US EPA's ProUCL 5.2.00 software and selecting an appropriate non-parametric statistical method to avoid assuming data normality. Other statistical analyses were performed using Microsoft Excel (e.g., chi-square, odds ratio).

In addition, a single-detection rate for sample pairs ("contamination rate") was calculated for each constituent in each medium, using the number of zero-detect and one-detect pairs. This measurement provides a general indication of which chemicals are more likely to result from carryover contamination, as it indicates that a chemical is detected more frequently in only one of the primary/duplicate sample pairs. The contamination rate was calculated as follows:

$$\text{Contamination rate} = \frac{N_{\text{one-detect-pairs}} \times 0.5}{N_{\text{one-detect-pairs}} + N_{\text{zero-detect-pairs}}} \times 100$$

This calculation was not performed if the number of one-detect pairs or zero-detect pairs for a particular chemical in a medium was zero.

Results

Percent Difference

Percent differences were categorized into the following groups: less than 30% (<30%), 30–99% (referred to as <100%), 100–299% (referred to as <300%), and 300% or higher (≥300%). The total number of duplicate pairs, the number and percent of each type of pair (e.g., zero-detect, one-detect, or two-detect pairs), and the number and percentage of percent differences in each category are shown by medium in Table 2 (groundwater), Table 3 (exterior soil gas), Table 4 (sub-slab soil gas), and Table 5 (indoor air), along with the percentages in each of the categories reported by McHugh et al. Note that the percentages in the tables may not total exactly 100% for each group, due to rounding. Figure 1 provides a graphical summary of the percent differences by sampling medium for data sets combined across the three sites.

For groundwater and direct syringe soil gas sampling, respectively, 97% and 99% of the differences for the duplicate results fall into either the <30% or <100% categories (Tables 2 and 3), indicating good agreement between primary and duplicate samples for these media. The fraction of results in the <30% category is higher than reported by McHugh et al. for groundwater and direct syringe soil gas, indicating better precision. Less than 1% of the duplicates for either medium fall into the ≥300% category, which is also lower than reported by McHugh et al.

For canister soil gas sampling, the combined total of the percent differences in the <30% and <100% categories is 94%, which is lower than the corresponding percent difference for both groundwater and direct syringe soil gas sampling. Notably, the fractions of duplicate results in the ≥300% category for canister sampling are about 3%, which is approximately three times the corresponding value for groundwater and 30 times the corresponding value for direct syringe soil gas sampling. The fraction of canister soil gas

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Table 2

Duplicate Evaluation of Groundwater Data

	Site 1		Site 2		Site 3		Combined Sites (1,2,3)		McHugh et al. (2018)
Data Summary	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	
Total duplicate pairs	945	—	11,135	—	2731	—	14,811	—	—
Zero-detect pairs	648	69%	9876	89%	2602	95%	13,126	89%	—
One-detect pairs	15	1.6%	80	0.7%	2	0.07%	97	0.65%	—
Two-detect pairs	282	30%	1179	11%	127	4.7%	1588	11%	—
Percent difference									
<30%	283	95%	1128	90%	125	97%	1536	91%	85%
30% to <100%	9	3.0%	95	7.5%	4	3.1%	108	6.4%	8%
100% to <300%	0	0%	27	2.1%	0	0%	27	1.6%	4%
≥300%	5	1.7%	9	0.7%	0	0%	14	0.83%	3%

Table 3

Duplicate Evaluation of Exterior Soil Gas Data

	Site 1: All		Site 1: Direct Syringe Sample		Site 1: Canister Sample		Site 2: Canister Sample		Combined Sites (1,2)		Combined Sites: Canister Sample (1,2)		McHugh et al. (2018)
Data Summary	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	
Total duplicate pairs	6596	—	5165	—	1431	—	236	—	6832	—	1667	—	—
Zero-detect pairs	4983	75%	3996	77%	987	68%	191	81%	5174	76%	1178	71%	—
One-detect pairs	80	1.2%	51	1.0%	29	2.0%	4	1.7%	84	1.2%	33	2.0%	—
Two-detect pairs	1533	23%	1118	21%	415	29%	41	17%	1574	23%	456	27%	—
Percent difference													
<30%	1450	90%	1057	90%	393	89%	38	84%	1488	90%	431	88%	53%
30% to <100%	132	8.2%	104	8.9%	28	6.3%	1	2.2%	133	8.0%	29	5.9%	17%
100% to <300%	19	1.2%	7	0.60%	12	2.7%	4	8.9%	23	1.4%	16	3.3%	10%
≥300%	12	0.74%	1	0.086%	11	2.5%	2	4.4%	14	0.84%	13	2.7%	20%

Table 4

Duplicate Evaluation of Sub-Slab Soil Gas Data

	Site 1		Site 3		Combined Sites (1,3)		McHugh et al. (2018)
Data Summary	***N***	**Percent**	***N***	**Percent**	***N***	**Percent**	
Total duplicate pairs	287	—	2039	—	2326	—	—
Zero-detect pairs	240	79%	1288	63%	1528	66%	—
One-detect pairs	11	3.6%	70	3.4%	81	3.5%	—
Two-detect pairs	36	12%	681	33%	717	31%	—
Percent difference							
<30%	25	53%	584	78%	609	76%	53%
30% to <100%	10	21%	103	14%	113	14%	17%
100% to <300%	6	13%	45	6.0%	51	6.4%	10%
≥300%	6	13%	19	2.5%	25	3.1%	20%

results in the <30% category is higher than reported by McHugh et al., and the fractions in the other categories are lower than those reported by McHugh et al.

In addition, the change from direct injection using an on-site mobile lab to canister sampling using fixed laboratory analysis for soil gas at Site 1 has also made a difference

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Table 5

Duplicate Evaluation of Indoor Air Data

Data Summary	Site 1		Site 2		Site 3		Combined Sites (1,2,3)		McHugh et al. (2018)
	N	Percent	*N*	Percent	*N*	Percent	*N*	Percent	
Total duplicate pairs	3626	—	70	—	2614	—	6310	—	—
Zero-detect pairs	2994	82%	50	71%	1712	65%	4756	75%	—
One-detect pairs	104	2.8%	5	7.1%	64	2.4%	173	2.7%	—
Two-detect pairs	528	14%	15	21%	838	32%	1381	22%	—
Percent difference									
<30%	512	81%	15	75%	798	88%	1325	85%	53%
30% to <100%	76	12%	2	10%	59	6.5%	137	8.8%	17%
100% to <300%	25	4.0%	0	0.0%	33	3.7%	58	3.7%	10%
≥300%	19	3.0%	3	15%	12	1.3%	34	2.2%	20%

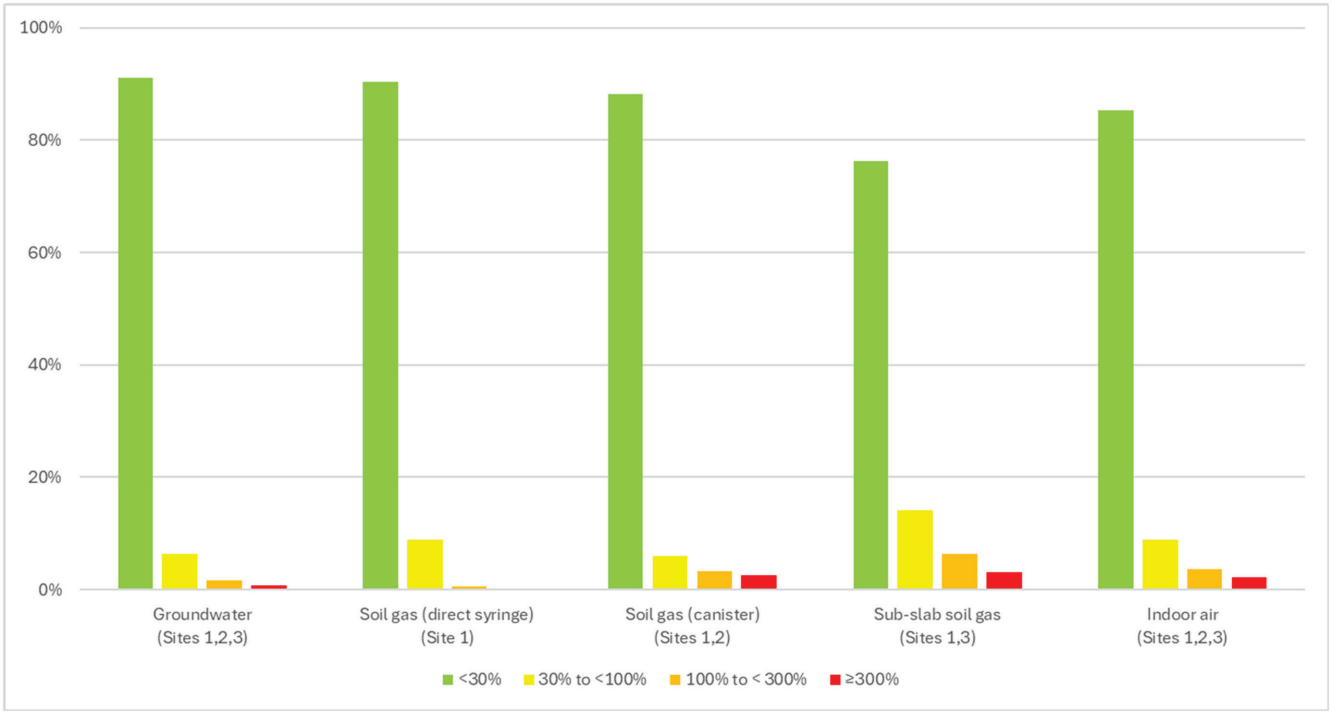

Figure 1. Duplicate percent differences by medium for combined data sets.

in the overall detections; the percent of two-detect pairs has increased from 21% for direct sampling to 29% for canister sampling (Table 3). This is due to some extent to the lower reporting limits achievable by the fixed laboratory.

For sub-slab soil gas and indoor air, the proportions of the duplicate data comparisons in the <100%, <300%, and ≥300% categories are similar to or slightly higher than those for exterior soil gas canister sampling. As with the exterior soil gas canister results, sub-slab soil gas and indoor air have noticeably higher portions of results in the two highest percentage categories as compared to groundwater and direct syringe soil gas sampling (Figure 1).

For sub-slab soil gas and indoor air, the proportions of results in the <100%, <300%, and ≥300% categories are overall much lower than observed by McHugh et al. Specifically, 24% and 15% of sub-slab soil gas and indoor air results, respectively, fall into the three highest categories, compared to 47% reported by McHugh et al.

Statistically, an analysis of variance (ANOVA) of multiple groups was performed using each medium/sample type as a separate group and the percent differences for each medium as the test variable. The *p*-value for the ANOVA is 5×10^{-12}, which is less than 0.05, indicating that there is a statistically significant difference between the median percent differences in the media-specific data sets. This finding was supported by a chi-square analysis by medium/sample type, which produced a *p*-value of 5×10^{-29}, confirming that the distribution of the percent difference categories differed significantly from the expected distribution.

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Because of the observed similarity among media collected using the same sampling approach, two-sample comparisons were also performed between percent differences for the combined groundwater and exterior soil gas ("direct" sampling) data sets and the combined soil gas, sub-slab soil gas, and indoor air (canister sampling) data sets. The Wilcoxon–Mann–Whitney test indicated statistically significant results, rejecting the null hypotheses that the medians of the two samples were equal (p-value of 0.045) and that the median of the direct data set was higher than the median of the canister data set (p-value of 0.023). These findings support that the median percent difference for the direct data set is significantly lower than the canister data set. This conclusion was further supported by a chi-square analysis comparing the "direct" versus canister sample types, which yielded a p-value of 1×10^{-16}, indicating that the distribution of the percent difference categories differed significantly from the expected distribution.

To assess the magnitude of this difference, an odds ratio was also calculated for canister versus direct sample types, with the <300% and ≥300% groups representing a "positive" result. The odds ratio for a canister sample pair being in the "positive" (higher percentage) groups was 8.5 (95% confidence interval of 4.7–15), indicating that a canister sample pair was about 8 times more likely to fall into the higher percent difference groups than a "direct" sample pair.

Single-Detection Rate for Sample Pairs (Contamination Rates)

The single-detection rates for the sample pairs (contamination rates) for TCE and PCE for each medium and site are presented in Table 6 (groundwater), Table 7 (exterior soil gas), Table 8 (sub-slab soil gas), and Table 9 (indoor air). Tables that include contamination rates for the complete list of chemicals analyzed for each medium are included as Tables S1 through S4. Contamination rates for groundwater at Site 3 and for exterior soil gas and indoor air at Site 2 are not shown due to the relatively small number of one-detect pairs in these data sets. Figure 2 summarizes the contamination rates for PCE and TCE by sampling medium for Site 1 to illustrate how the rates vary by medium.

Minimal contamination is observed in the groundwater duplicate samples for Sites 1 and 2 (Table 6). In addition, the contamination rates for soil gas for direct syringe sampling (Table 7) are similar to those for groundwater.

For exterior soil gas canister sampling and sub-slab soil gas, contamination rates are higher than those for groundwater or direct syringe soil gas sampling. Figure 2 shows the relative contamination rates among the media for TCE and PCE. As shown in Table S4, for indoor air, 1,2-DCA has a higher contamination rate than most other chemicals.

Discussion

Differences between duplicate samples indicate potential issues with data accuracy, making it challenging to determine the true level of the constituent(s). Robust field and analytical QC procedures are essential to reduce data variability and ensure reliable decisions. Data uncertainty can impact several key areas:

- Regulatory compliance: if one duplicate exceeds a regulatory threshold and the other does not, it may be unclear whether a site is in violation or compliant, influencing decisions about remediation, monitoring, or closure.
- Risk assessment: reliable data are essential for assessing risks to human health and the environment. Large differences between duplicates can lead to either overestimating or underestimating risks, which may result in unnecessary interventions or missed hazards. If a false positive is accepted due to inconsistent duplicates, unnecessary remediation may occur; conversely, if a false negative is missed, insufficient action may be taken.
- Resource allocation: decisions about allocating resources for further investigation, remediation, or monitoring depend on confidence in the data. Uncertainty caused by inconsistent duplicate results often means additional sampling or analysis, increasing costs and timelines.

Table 6

Groundwater Contamination Rate

Site	Chemical Name	One-Detect Pairs	Zero-Detect Pairs	Contamination Rate
1	Tetrachloroethene	2	73	1%
	Trichloroethene	0	9	NC
2	Tetrachloroethene	3	106	1%
	Trichloroethene	2	34	3%

Abbreviation: NC = not calculated.

Table 7

Exterior Soil Gas Contamination Rate

		Direct Syringe Sample			Canister Sample		
Site	Chemical Name	One-Detect Pairs	Zero-Detect Pairs	Contamination Rate	One-Detect Pairs	Zero-Detect Pairs	Contamination Rate
1	Tetrachloroethene	10	190	3%	6	25	10%
	Trichloroethene	12	215	3%	12	35	13%

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Table 8

Sub-Slab Soil Gas Contamination Rate

Site	Chemical Name	One-Detect Pairs	Zero-Detect Pairs	Contamination Rate
1	Tetrachloroethene	4	12	13%
	Trichloroethene	6	12	17%
3	Tetrachloroethene	1	0	NC
	Trichloroethene	2	6	13%

Abbreviation: NC = not calculated.

Table 9

Indoor Air Contamination Rate

Site	Chemical Name	One-Detect Pairs	Zero-Detect Pairs	Contamination Rate
1	Tetrachloroethene	45	252	8%
	Trichloroethene	25	304	4%
3	Tetrachloroethene	2	8	10%
	Trichloroethene	5	13	14%

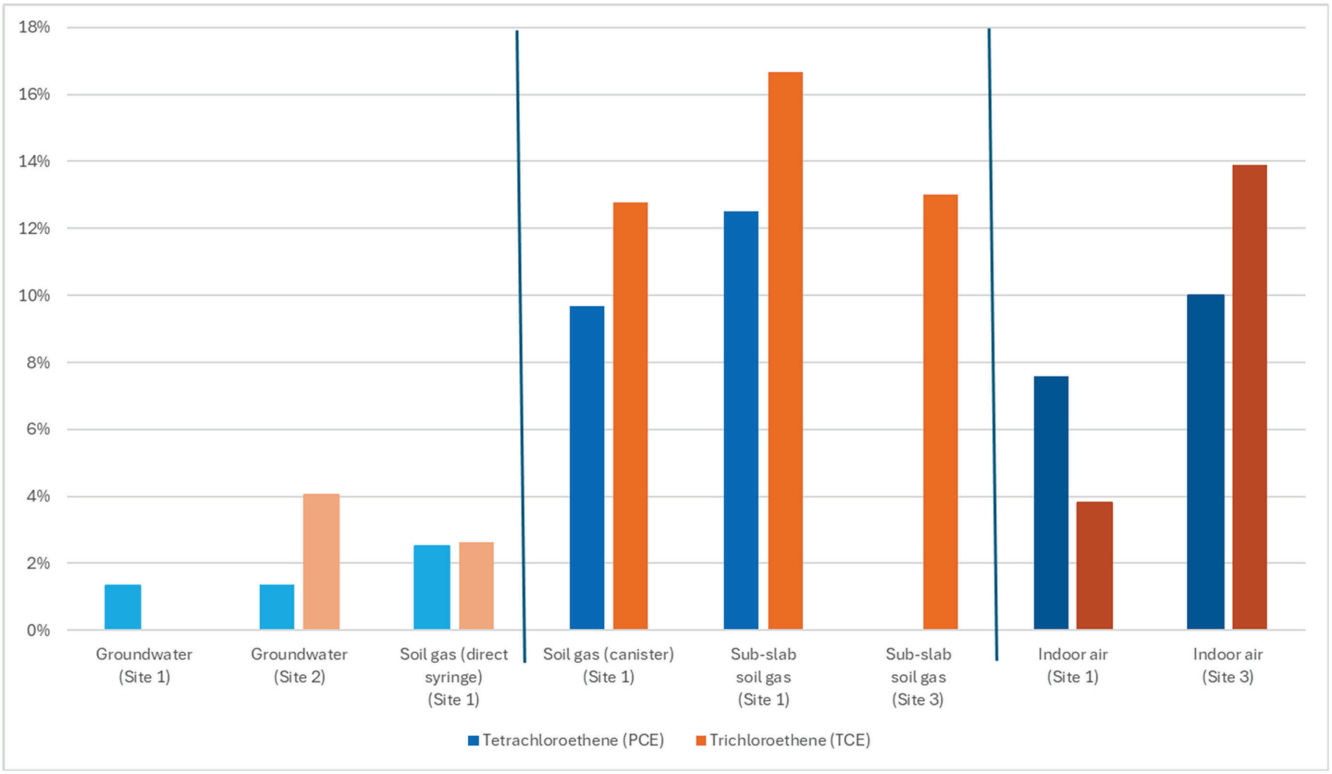

Figure 2. Contamination rate for PCE and TCE by medium.

- Scientific conclusions: discrepancies between duplicates can undermine confidence in study findings, leading to more conservative interpretations or the need for further research.

Recognizing differences between field duplicate samples helps identify results that may be inaccurate or unusable. Addressing these discrepancies through investigation, improved sampling and analytical protocols, and resampling when necessary, is essential for resolving critical uncertainties.

These considerations highlight the importance of data quality and managing uncertainty in environmental investigations. This study evaluates the effectiveness of current sampling techniques and analytical protocols and offers suggestions for improving data reliability in future investigations.

The results of this study indicate that water samples collected using disposable vials and exterior soil gas samples

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collected using direct syringe sampling methods demonstrated greater precision with smaller percent differences and lower rates of occurrence of single-detect pairs relative to zero-detect pairs (contamination rates) compared to media collected using canisters: exterior soil gas, sub-slab soil gas, and indoor air. Exterior soil gas collected with canisters, sub-slab soil gas, and indoor air samples exhibited a higher fraction of results within the higher percent difference categories (<30% and ≥300%).

These results confirm that direct syringe sampling or sampling using single-use containers yields greater precision than sampling with reusable canisters. This conclusion is also supported by a specific comparison of exterior soil gas sampling results at Site 1, where the sampling method was changed from direct injection sampling and analysis by mobile laboratory to sample collection using SUMMA canisters and fixed laboratory analysis. For direct sampling, approximately 99% of the duplicate results fall into the <30% or <100% difference categories, compared to 95% for canister sampling.

Overall, the portion of duplicate results in the ≥300% category for canister sampling is approximately three times that for groundwater and 30 times that for direct syringe soil gas sampling. This indicates that higher differences between duplicate results occur more frequently in samples collected using canisters, suggesting the potential for carryover contamination.

Several cases of carryover contamination were confirmed by laboratory investigations after being alerted to the potential issue, which provided an explanation for discrepancies between soil vapor canister sample and duplicate results. Chromatographic analysis and media history reviews revealed that anomalous results in many cases corresponded to the presence of residual contaminants in sampling equipment, even when standard cleaning and certification protocols were followed. In one soil vapor sampling event, a high concentration of PCE was detected in a single sample while the other two triplicates were reported as non-detects. An investigation by the laboratory traced the detected PCE to residual contamination in the flow controller, which had previously been used for a sample containing nearly 900,000 ppbv PCE. Despite passing cleaning and certification, adsorbed PCE persisted on the flow controller's internal surfaces and was released during subsequent sample collection, confirming the anomalous result was due to carryover contamination from prior use. Similar findings were observed for other VOCs, where elevated concentrations appeared only in samples collected with media previously exposed to high concentrations, while other replicates remained unaffected. These results highlight that media history and prior sample exposure are critical for data quality and that standard cleaning protocols may not fully eliminate contamination risks, especially after equipment exposure to high contaminant levels. Individual media tracking, rigorous cleaning validation, and comprehensive data review are essential for evaluating the reliability of environmental sample analyses and minimizing these potential interferences.

Unlike the previous study, which was essentially a data mining project, the current study used site-specific data and direct collaboration with laboratories to investigate the causes of observed discrepancies, allowing confirmation through laboratory investigations that carryover contamination is a plausible and frequently observed cause of variability in duplicate results.

One limitation of this study is that the calculation method used to evaluate the duplicate results relies on percent difference as an indicator of precision without considering their environmental context. For example, if two detected results were 2 and 8, this would represent a percent difference of 300% ($[8-2]\times100/2$). Depending on the medium and the context, results of 8 and 2 might be interpreted as either being similar (e.g., exterior soil gas) or substantially different (e.g., indoor air). The actual interpretation of these results would likely depend on applicable screening levels and potential human exposure to the medium. Percent differences may also be slightly exaggerated by the use of method detection limits (if available) to represent non-detect results rather than the higher reporting limits. Nevertheless, the size of the data sets used herein and the consistency of the findings suggest that this aspect is not a controlling factor in the analysis. In addition, this same limitation would apply to the data set used in the McHugh et al. study.

An analysis was conducted to assess whether reporting limits affect percent difference calculations and the interpretation of differences between paired samples. In general, percent differences for one-detect pairs are higher when reporting limits are lower relative to the same detected concentration because the difference between values is greater. Conversely, higher reporting limits for non-detects can shift results into lower percent difference categories. While higher reporting limits would typically reduce the number of results in the higher percent difference categories and diminish the apparent impact of our findings, this effect was not observed in the current data sets, given the numbers of pairs in those higher categories. Furthermore, a review of the pairs in the higher percent difference categories (<300% and ≥300%) showed that single-detect pairs where detections were close to the reporting limit and non-detects had an unusually high reporting limit (potentially "masking" a lower concentration) were very rare. For exterior soil gas results, only a few one-detect pairs fell into this scenario, representing approximately 0.1% of the data set, too small to affect the overall conclusion of this study. In summary, this analysis shows that the impact of reporting limits on this study is considered negligible.

The current results also compare favorably to the results reported by McHugh et al. Based on this current study, the precision of the groundwater data is similar with slightly lower fractions of results in the three higher categories. For exterior soil gas sampling, sub-slab soil gas, and indoor air, there are considerably lower portions of duplicate results in the three higher categories, where the total portion for the subject data ranges from 12% to 24% compared to 47% for the McHugh et al. study. These data suggest that field and laboratory precision for soil gas and indoor air may have improved over time since all soil gas and indoor air data included in this study were collected since 2018, which post-dates the data used by McHugh et al.

The higher contamination rates calculated for exterior soil gas canister sampling, sub-slab soil gas, and indoor

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air as compared to groundwater or direct syringe soil gas sampling support the hypothesis that carryover contamination may be present in some SUMMA canisters since these canisters are reused from various sites with varying levels of contamination. Most chemicals, including TCE and PCE in particular, have substantially higher contamination rates for exterior soil gas (canisters) and sub-slab soil gas than for groundwater. This indicates that there may be detections that could be related to carryover since there are more one-detect pairs for these chemicals. Figure 2 also illustrates the differences in contamination rate by medium for TCE and PCE, with higher percentages in exterior soil gas collected using canisters and in sub-slab soil gas. For indoor air, the contamination rates are slightly lower for Site 1 than for the exterior soil gas with canisters and sub-slab soil gas. However, the contamination rates for indoor air at Site 3 are similar to canister soil gas and sub-slab soil gas.

One consideration is that the indoor air samples for Site 1 are collected using individually certified SUMMA canisters, while the exterior soil gas canister samples and Site 3 sub-slab soil gas and indoor air samples are collected using batch-certified SUMMA canisters. Both batch and individually certified canisters are cleaned the same way. For batch certification, only one canister per batch is tested to confirm cleanliness, assuming all are clean if one is. For individual certification, each canister is tested to ensure all are contamination-free. Therefore, reliance on batch certification may increase the potential for carryover in the untested canisters. It is noted that the sub-slab soil gas samples for Site 1 are also collected using individually certified canisters, so there is not a consistent demarcation between batch and individually certified canister results.

Another limitation of this study is that the calculation method for contamination rate may overstate actual potential contamination, since some of the one-detect pairs are pairs where the detected concentration is close to the reporting limit. Based on the US EPA National Functional Guidelines (US EPA 2020), the difference between these two duplicate results would be considered acceptable if lower than the reporting limit; therefore, some of the one-detect pairs may reflect sampling differences rather than contamination.

This study used data from two locations in California and one in New England. While these data sets do represent some geographical diversity, it is uncertain whether these results would be repeatable in all climates. Nevertheless, with respect to canister contamination, climate is not expected to be a significant influencing factor. In addition, the results of this study did not suggest any noticeable differences in results across the climatic zones considered herein.

For the soil gas and indoor air samples used in this study, the sample volumes were 100 cc (soil gas collected using a syringe), 1 L (exterior soil gas and sub-slab gas collected with SUMMA canisters), and 6 L (indoor air collected using a SUMMA canister). Based on the results of the study, the varying sample collection volumes represented by the data do not appear to affect the sampling results in any way that is noticeable.

This study builds on the work of McHugh et al., independently confirming that canister sampling tends to show greater discrepancies between primary and duplicate sample results. This further supports the hypothesis that carryover contamination may be occurring in the reusable SUMMA canisters.

The advantages of the current study include: (1) This study uses more recent data from 2000 to 2024 (with most of the data being collected between 2018 and 2024) and better reflects the current state of field and laboratory practice. (2) The data used in this study were from three specific sites where sampling practices, quality assurance (QA)/QC measures, and laboratory procedures are relatively consistent and well documented, providing greater certainty in the analysis. (3) At one site, soil gas sampling was conducted using two different methods at separate times, creating a natural experiment. This allowed for a direct comparison of the precision of duplicate sampling results for the two methods. This comparison clearly shows that soil gas sampling via direct syringe has higher precision and lower contamination rates than sampling the same medium and locations using canisters.

Conclusion

Collecting field duplicate samples is a standard practice in environmental sampling and is generally required for QA/QC. This study indicates that duplicate sampling using canisters may produce data points that lead to varying interpretations. For example, if one data point is above a regulatory threshold while another is not, it creates uncertainty about the "true" level of contamination, potentially impacting subsequent steps in site assessment and remediation.

Given this knowledge, reducing uncertainty is crucial when collecting duplicate data. Using single-use sampling equipment during sample preparation and field activities can help minimize uncertainty. For canister sampling, requesting individual certification for canisters, flow controllers, and flow splitters can further reduce uncertainty. For indoor air samples, a flow splitter may or may not be used to collect duplicates; both options introduce some degree of uncertainty into the sample collection approach. If there is a substantial difference between primary and duplicate results and the data are crucial for interpretation of site conditions, resampling may be advisable.

There is likely also inherent uncertainty in the process of laboratory analysis. Some of this uncertainty is managed by requiring laboratories to be certified for specific analyses. Laboratories should maintain these certifications and robust QC procedures. While certifications set minimum standards, some laboratories only meet these requirements, while others have developed additional best practices to improve their QC performance beyond what is strictly required. For example, most laboratories currently do not individually certify flow controllers or t-connectors; therefore, requesting individual certification for these components of the sample train may encourage more laboratories to offer this service on a regular basis. Alternatively, laboratories that offer individual certification of each of the sampling train elements can be selected.

In some specific instances where substantial differences were observed between sample and duplicate results, close collaboration with the laboratory was essential to investigate potential field or laboratory factors that might have affected the results. For example, high VOC concentrations in soil vapor samples were traced to persistent contamination in canisters or flow controllers previously exposed to extreme analyte levels,

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despite passing rigorous cleaning and certification. Laboratory investigations confirmed that media history and prior sample use are critical for data quality, and that standard cleaning protocols, even individual certification, may not fully eliminate contamination risks after high contaminant exposures. Since these incidents, the laboratory for Site 1 has proactively started investigating media history, communicated potential high bias due to artifacts from canisters or flow controllers, and explored enhanced cleaning methods, such as humidification and alternative equipment designs, though these require further validation under field conditions. While an explanation may not always be discoverable, these experiences underscore the importance of robust equipment cleaning protocols, thorough cleaning verification, individual media tracking, rigorous data validation, and ongoing partnership between consultants and laboratories to achieve reliable and representative environmental data.

Conflict of Interest

The authors declare no competing financial or personal interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supporting Information

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally not peer reviewed.

Figure S1. Example of Groundwater Sampling.

Figure S2a. Exterior soil gas sampling via tubing and syringes for direct injection.

Figure S2b. Interior set up of a mobile laboratory for soil gas sampling using direct injection.

Figure S3a. Example of exterior soil gas sampling tubing used with canisters.

Figure S3b. Example of exterior soil gas sampling using a canister.

Figure S4. Example of sub-slab soil gas sampling.

Figure S5. Example of indoor air sampling with duplicate sample.

Table S1. Groundwater Contamination Rate.

Table S2. Exterior Soil Gas Contamination Rate.

Table S3. Sub-Slab Soil Gas Contamination Rate.

Table S4. Indoor Air Contamination Rate.

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