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TEMPORAL VARIABILITY OF CHLORINATED VOLATILE ORGANIC COMPOUND VAPOR CONCENTRATIONS IN A RESIDENTIAL SEWER AND LAND DRAIN SYSTEM OVERLYING A DILUTE GROUNDWATER PLUME

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Abstract

Some subsurface sewer and land drain networks will facilitate the migration of chlorinated volatile organic compounds (CVOCs) from dissolved contaminant groundwater plumes to indoor air. As this vapor intrusion (VI) pathway has only recently been documented, guidance for evaluating it, including recommendations for timing, frequency, duration and location for vapor sampling in subsurface piping networks is non-existent. To address this gap, a three-year investigation of CVOC concentrations from land drains, storm drains, and sanitary sewers was undertaken in a neighborhood overlying a large-scale dissolved chlorinated VOC (CVOC) groundwater plume. Vapor sampling included the collection of grab (time-discrete) samples from up to 277 manholes, hourly grab sampling from three manhole locations, and 24-h duration collection during week-long sampling from 13 land drain and sewer manholes. The spatial distribution of vapor and water concentrations and the temporal variations in the vapor values observed in this study suggest that week-long vapor sampling conducted at different times of the year and with samples collected at manhole locations overlying and outside a dissolved plume might be needed to ensure robust VI pathway assessment at other sites. These findings are expected to be of relevance to regulatory agencies involved in the development of current or future VI pathway assessment guidance.

***Keywords*:**

Vapor intrusion, indoor air, chlorinated volatile organic chemicals, groundwater, sewers, land drains

1.0 Introduction

Vapor intrusion (VI) field studies have shown that indoor air in buildings connected to sewer and land drain systems (sub-surface drainage systems that prevent water accumulation beneath building foundations) can be impacted by volatile organic chemical (VOC) vapors present in the sewers and land drains (Guo *et al.*, 2015; McHugh *et al.*, 2017; McHugh and Beckley, 2018; Pennell *et al.*, 2013; Riis *et al.*, 2010; Roghani *et al.*, 2018). This often occurs when contaminated groundwater enters the sewer or land drain system, as shown in Figure 1. In these cases, VOC contaminants volatilize and migrate along the piping headspace and finally enter buildings either via a direct connection to indoor air (sewer in Figure 1); or through the sub-foundation region and foundation cracks (land drain system in Figure 1). When such VI pathways exist, VI impacts can occur to buildings that are connected to the contaminated groundwater entry point, but do not overlie dilute VOC groundwater plumes (Riis *et al.*, 2010). As a result, VI risk assessments need to consider this “pipe-flow” VI pathway in addition to the conventional “soil VI” pathway where chemical vapors migrate upward from groundwater plumes through soil and then into a building (Guo *et al.*, 2015).

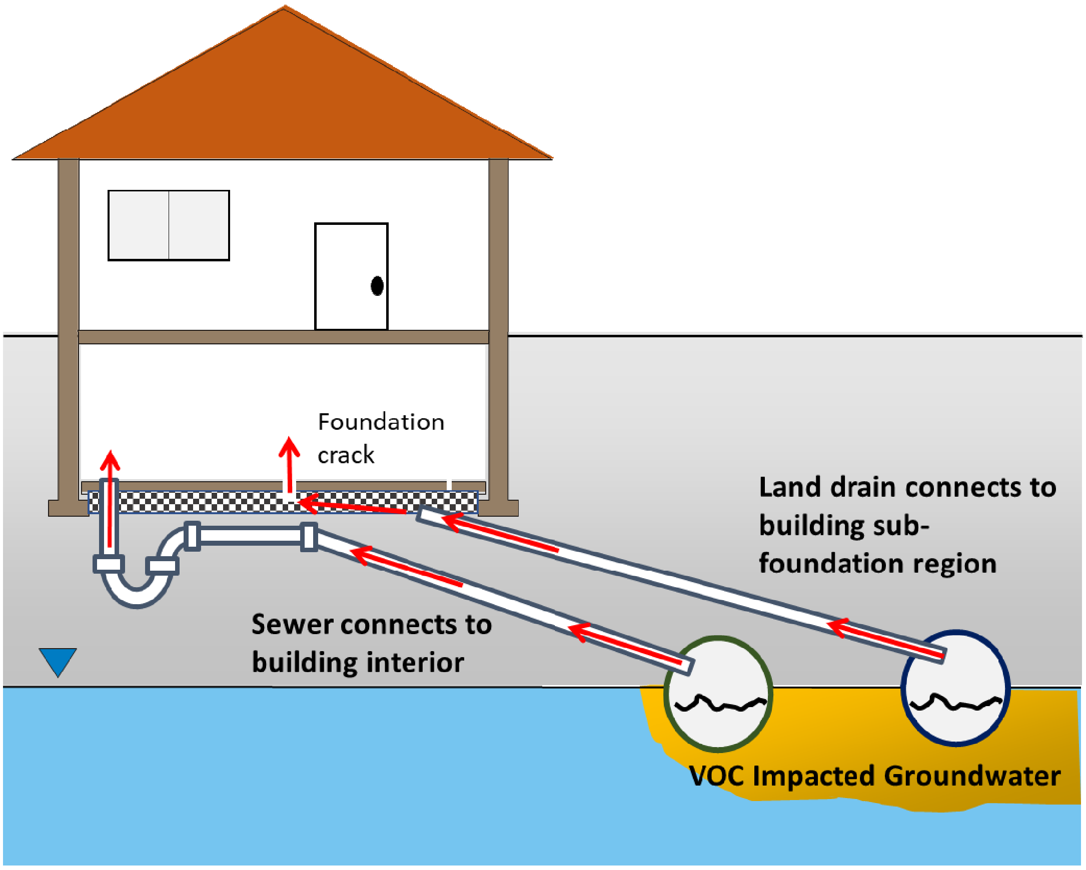


Figure 1. Conceptual illustration of sewer and land drain vapor intrusion pathways.

Although the evaluation of alternative and preferential VI pathways is mentioned in federal and state regulatory guidance (ITRC, 2007; NJDEP, 2013; USEPA, 2015), there is little guidance on how to specifically identify or assess their VI risks. The lack of available guidance is, in part, because these VI pathways have only recently been recognized and documented (Riis *et al.*, 2010; Pennell *et al.*; 2013; Guo *et al.*, 2015; McHugh *et al.*, 2017; McHugh and Beckley, 2018). While approaches for assessing potential indoor air impacts from VOCs in sewers and drains have yet to be developed or validated, guidance is likely to include requirements for source vapor concentration characterization and extrapolation of inhalation exposure using empirical relations or mathematical models. Thus, guidance for the characterization of VOC vapor concentrations in sewers, land drains, and other subsurface piping will be needed, including specification of sample collection and analysis methods and the time, duration, and frequency of sampling.

The presence of VOC vapors in subsurface piping networks has been reported in studies that discuss odor management in sewer networks, and most of these studies have focused on specific analytical constituents and their concentration levels (Corsi *et al.*, 1995; Quigley and Corsi, 1995; Corsi and Quigley, 1996; Yeh *et al.*, 2011; Huang *et al.*, 2012; Wang *et al.*, 2012a, 2012b, 2015). However, the temporal variability of VOC vapor concentrations in subsurface piping networks is not well-understood. Only a limited number of studies have investigated this topic, and their observations and conclusions were based on VOC vapor monitoring either from limited sampling locations or for short time period. Quigley and Corsi (1995) found weekday/weekend trends for three aromatic compounds in 17 sewer manholes during four 24-h sampling events, Sivret. *et al.* (2017) observed up to 10x diurnal VOC vapor concentration changes in a pump station wet well, and Roghani *et al.* (2018) reported over 100x changes in trichloroethylene (TCE) concentrations in two sewer manholes adjacent to a groundwater plume over a two-year period.

The observations from past studies are informative but not sufficient to create broadly applicable guidance for characterizing VOC vapor concentrations in subsurface piping networks for use in VI pathway risk assessment. Thus, this study was undertaken to address this gap through high- and low-frequency sampling of chlorinated VOC (CVOC) vapors in land drains, storm drains, and sanitary sewers located in a neighborhood overlying a large-scale dissolved CVOC groundwater plume. Sampling was conducted over a period of about three years with the sampling efforts changing as more was learned about the levels and dynamics of vapor concentrations in the system. The sampling included multi-season synoptic collection of instantaneous grab samples from up to 277 manholes, hourly grab samples from two land drain locations and a sanitary sewer manhole, and multi-season week-long collection of 24-h duration samples from 13 land drain manholes.

2.0 Methods

2.1 Study Site

Air and water sampling were conducted over an approximately 1 km^2 residential area adjacent to Hill Air Force Base, UT. This area overlies a shallow dilute CVOC groundwater plume and throughout the study area there are land drain and storm water and sanitary sewer networks. TCE is the primary VI contaminant of concern within the study area where TCE dissolved groundwater concentrations range from approximately 5 ug/L to 100 ug/L (Hill Air Force Base, 2005). The land drain system has been previously confirmed as the source of CVOC indoor air impacts for one intensely studied residence (Guo *et al.*, 2015). The dissolved plume boundaries and 277 sampled manhole locations are presented in Figure 2.

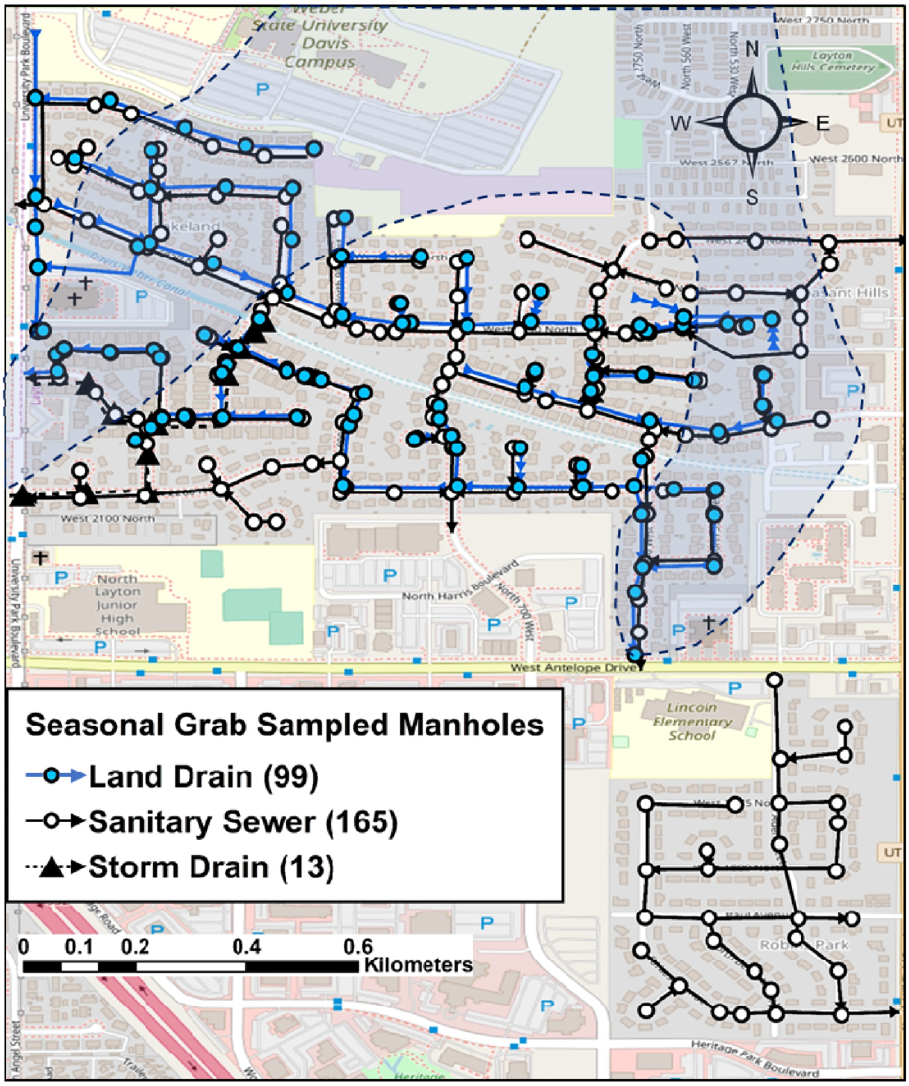


Figure 2. Study area and locations of sampled manholes. The shaded area bounded by the dashed line delineates the dissolved TCE groundwater plume. Arrows indicate direction of water flow in the subsurface piping networks.

2.2 Sample Collection Summary

Samples collections were performed from January 2016 to January 2019, through the following activities:

1) Multi-season grab sampling (January 2016 to April 2017): five synoptic grab sampling events were performed to characterize the spatial distribution of CVOC vapors in the subsurface piping networks and to assess seasonal variability. Each event included vapor sampling from up to 277 of the manholes shown in Figure 2 (165 sewer manholes, 99 land drain manholes, and 13 storm drain manholes). Since vapor phase VOCs in subsurface piping networks are often the result of contaminated groundwater infiltration, grab sampling of water from land drain manholes was also performed along with the vapor sampling when water was present. These data are useful for assessing the value of water sampling as another line of evidence for VOC characterization in subsurface piping networks.
2) Hourly high-frequency grab sampling (September 2017 to March 2018): hourly sampling was conducted over five months in the two land drain manholes and one sanitary sewer manhole shown in Figure 3 to provide initial insight into shorter-term temporal variability in CVOC vapor concentrations. All three were adjacent to the residence having a confirmed pipe-flow VI alternative pathway from the land drain network.
3) Daily high-frequency sampling (March 2018 to January 2019): A total of six week-long sampling events covering multiple seasons and involving the collection of daily 24-h samples were performed using the 13 manholes (9 land drain, 5 sanitary sewer, and 1 sanitary sewer/storm drain combination) shown in Figure 3. These locations were selected based on multi-season grab sampling results, with the intent of including locations with a range of concentrations and temporal variabilities.

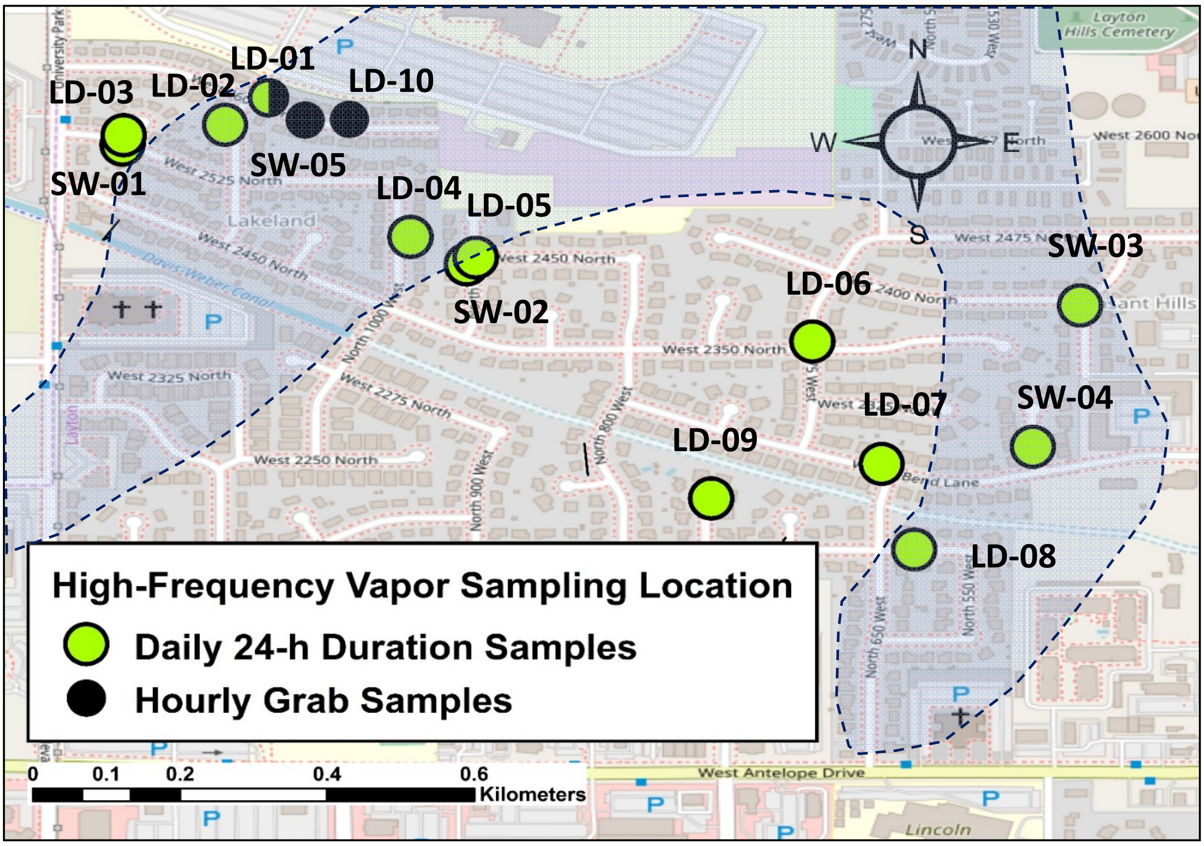


Figure 3. Locations where hourly (black) and daily 24-h duration (green) vapor samples were collected for extended sampling periods. LD = land drain manhole; SW =sanitary sewer manhole. SW03 is a sanitary sewer/storm drain combination manhole.

2.3 Vapor Sample Collection and Analysis Methods

Multi-season grab samples. Manhole vapor samples were collected using a method similar to that described in McHugh *et al.* (2017). A vacuum box sampler was used to draw vapor samples (minimum 500 mL) into a Tedlar bag via weighted nylon tubing inserted through vent holes in the manhole covers. If vent holes were not present, the cover was opened just enough to allow passage of the sampling tubing. The distal end of the weighted tubing was inserted to a depth approximately 0.3 m above the base of the manhole or manhole water level. The vapor samples were analyzed on-site using an SRI gas chromatograph equipped with a dry electron capture detector (GC/DELCD) (SRI instrument, CA) , and the minimum detection level (MDL) for TCE analysis by this method was 1.5 ppb_v. The GC/DELCD was calibrated daily prior to sample collection and calibration checks and duplicate vapor samples were analyzed every 10 sample injections for QA/QC purposes. The average relative percentage differences between duplicate samples was 26.9%.

Hourly high-frequency grab sampling. Hourly vapor grab samples were collected directly onto the GC using an external pump, autosampler, and permanent nylon and stainless-steel sampling lines extending to each manhole. Permanent sampling lines were installed to a depth 0.3 m above the manhole base or water level. Samples were analyzed real-time using an SRI GC equipped with an electron capture detector (ECD). The minimum detection limit for TCE was 1.5 ppb_v. The GC/ECD was calibrated approximately every 4 weeks during the sample collection period.

Daily 24-h duration samples. 24-h duration samples were collected daily on multi-bed sorbent tubes comprised of Tenax-GR and Carboxen-569 sorbents. The vapor samples were collected using a customized sampler which was suspended in the manhole approximately 0.3 to 0.5-m above the base of the manhole or water level. The sampler pulled vapor through each sorbent tube at a controlled flowrate (about 50 mL/min) using a Gilian LFS-113 air pump (Sensidyne, FL). The flowrate for each pump was calibrated before and after each 24-h tube sample collection using a Sensidyne Gilibrator-2 bubble flowmeter (Sensidyne, FL). Flowrate variation over a 24-h period was typically less than 5% and never exceeded 10%. Sorbent tubes were analyzed using a Markes Ultra auto-sampler and Markes Unity thermal desorber (Markes International, UK) connected to an HP5890 gas chromatograph equipped with a Restek 60 m Rxi-5 capillary column and an HP5972 mass spectrometer. Samples were analyzed using selective ion mode (SIM). The 24-h average CVOC concentration was calculated based on the CVOC mass loading for sorbent tube and the vapor sample volume. The minimum TCE detection level was 0.07 ppb_v. Duplicate samples were collected in manhole LD-02 and SW-03 and the variations in concentrations for duplicate samples and duplicate analyses were less than 30%.

2.4 Water Sample Collection and Analysis

Water samples were collected from land drain manholes and selected storm drain manholes where possible during the area-wide seasonal grab sampling events. Samples were collected from each manhole in 40 mL volatile organic analysis (VOA) vials, which contained 0.5 mL 2% hydrochloric acid for preservation. All samples were stored at 4 °C and shipped to Arizona State University for headspace analysis within two weeks of sample collection. An SRI GC/DELCD was used for sample analysis with the minimum detection level of 0.7 µg/L for TCE. Calibration checks and duplicate vapor samples were analyzed every 10 sample injections for QA/QC purposes. The average relative percentage differences between duplicate samples was 21.6 %.

3.0 Results and Discussion

3.1 TCE vapor and water concentrations spatial distributions

Five area-wide synoptic sample collection events were conducted from early 2016 to mid-2017. The first event (January 2016) included 82 manhole locations. As knowledge of the manhole system and the ability to differentiate types of manholes improved, all accessible manholes within the area were being sampled by August 2016.

TCE vapors were detected throughout the land drain, storm drain, and sanitary sewer network. The results of all synoptic sampling events can be found in Supplemental Information Figure S1-S4. Figure 4 provides an overview of the range of TCE vapor concentrations detected and how that changed over the five multi-season synoptic sampling events. In this figure, TCE vapor concentration distributions are presented in four concentration categories which ranges from less than 4 ppb_v to over 400 ppb_v. To provide some context for these concentrations, published indoor air screening levels for TCE range from about 0.09 – 0.4 ppb_v (e,g., MADPH 2017, USEPA 2019), with the lower level based on a 10^{-6} risk level and the upper based on 10^{-5} risk level, with both also considering non-cancer risks. Manhole vapor concentrations were found to be 100x and 10x greater than the indoor air screening level of 0.4 ppb_v (USEPA, 2019) in approximately10 % and 40% of manhole sampling locations, respectively. For context, indoor air TCE concentrations in a study house located in this area were about 1% - 2% of the nearby land drain vapor concentrations when the house was under-pressurized (Guo *et al.*, 2015; Holton *et al.,* 2015) . Thus, residences near the higher-level manhole TCE vapor concentrations measured in this study could be at risk of VI impact above the 0.4 ppb_v indoor air screening level, but only if there are piping conduits connecting their homes to the land drain system.

One important observation from these synoptic sampling results is that the presence or concentrations of TCE in the piping networks cannot be anticipated by groundwater plume data. The poor correlation can be seen in Figures 5 and 6, which present the maximum TCE vapor and water sample concentrations from the five synoptic sampling events superimposed on a map showing the extent of the groundwater plume. About half of the locations where vapor concentrations were >40 ppb_v were located outside of the groundwater plume boundary, indicating that the piping networks were a conduit for dissolved and vapor-phase CVOC transport to areas outside the groundwater plume. Although it was difficult to identify the exact locations where groundwater entered the subsurface piping networks, TCE liquid samples were all above 0.7 µg/L in the high-TCE-vapor-concentration-level manholes that were located outside TCE groundwater plume boundary. This suggests that the migration of infiltrated groundwater along the subsurface conduit's flow pathway is the primary mechanism for VOC migration outside of the groundwater plume boundary. Thus, it is important that any future VI pathway assessment guidance recommend sampling in subsurface piping networks beyond the boundaries of dissolved groundwater plumes, particularly, when the depth of subsurface piping networks is close to or deeper than groundwater table.

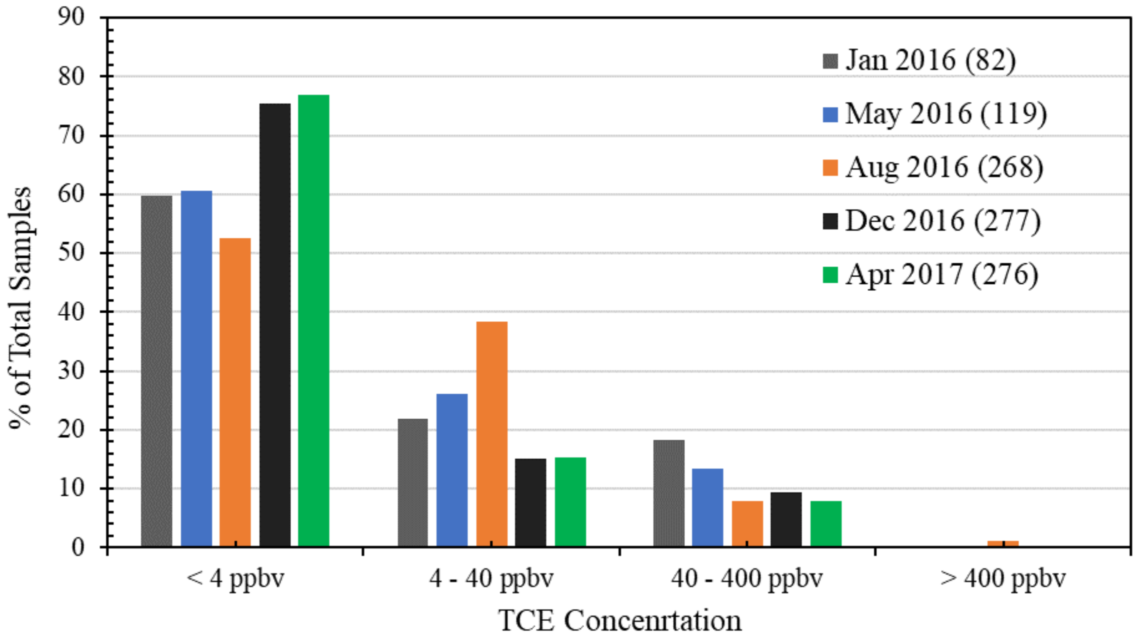


Figure 4. TCE manhole vapor concentration summary of five seasonal synoptic sampling events, categorized relative to a 0.4 ppb_v indoor air screening level. Numbers of sampled manholes for each event are shown in brackets.

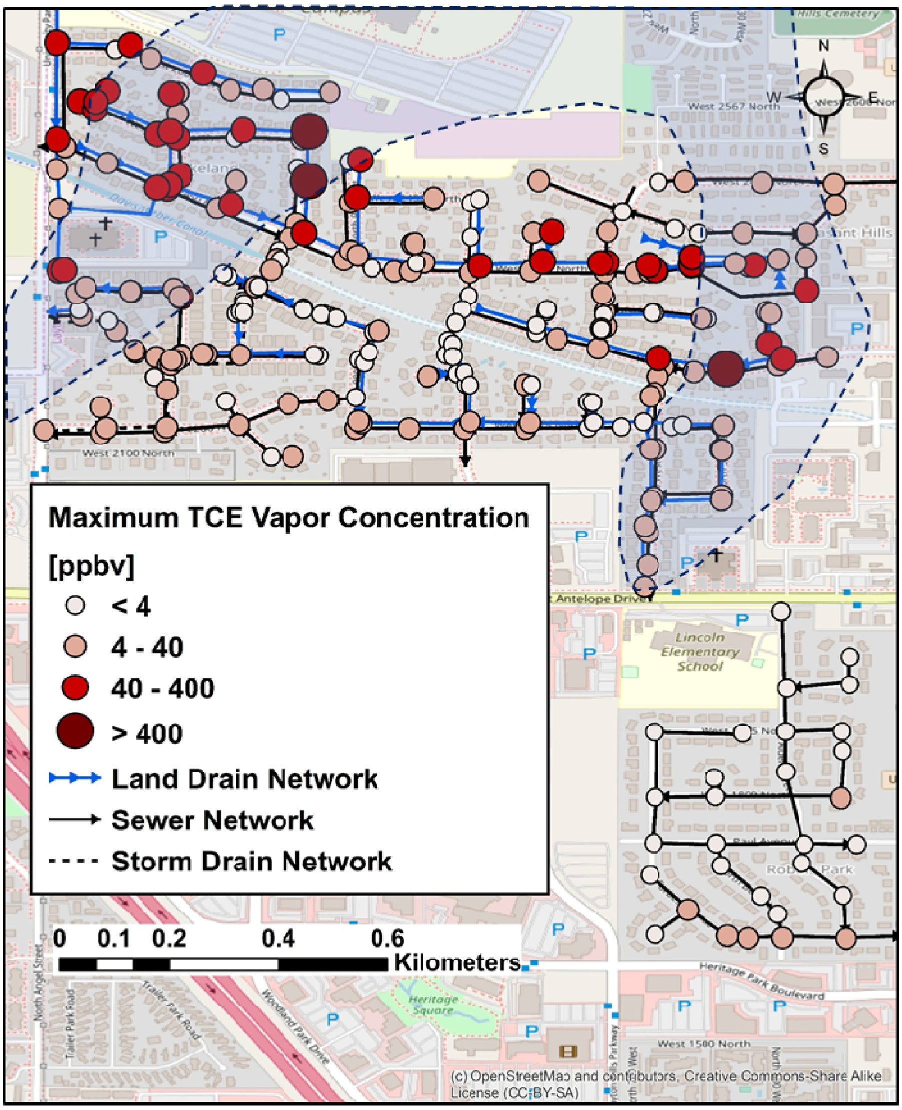


Figure 5. Maximum TCE concentrations in vapor samples collected from manhole headspace sampled during the five quarterly synoptic surveys, categorized relative to a 0.4 ppb_v indoor air screening level. The shaded area indicates the extent of the TCE groundwater plume.

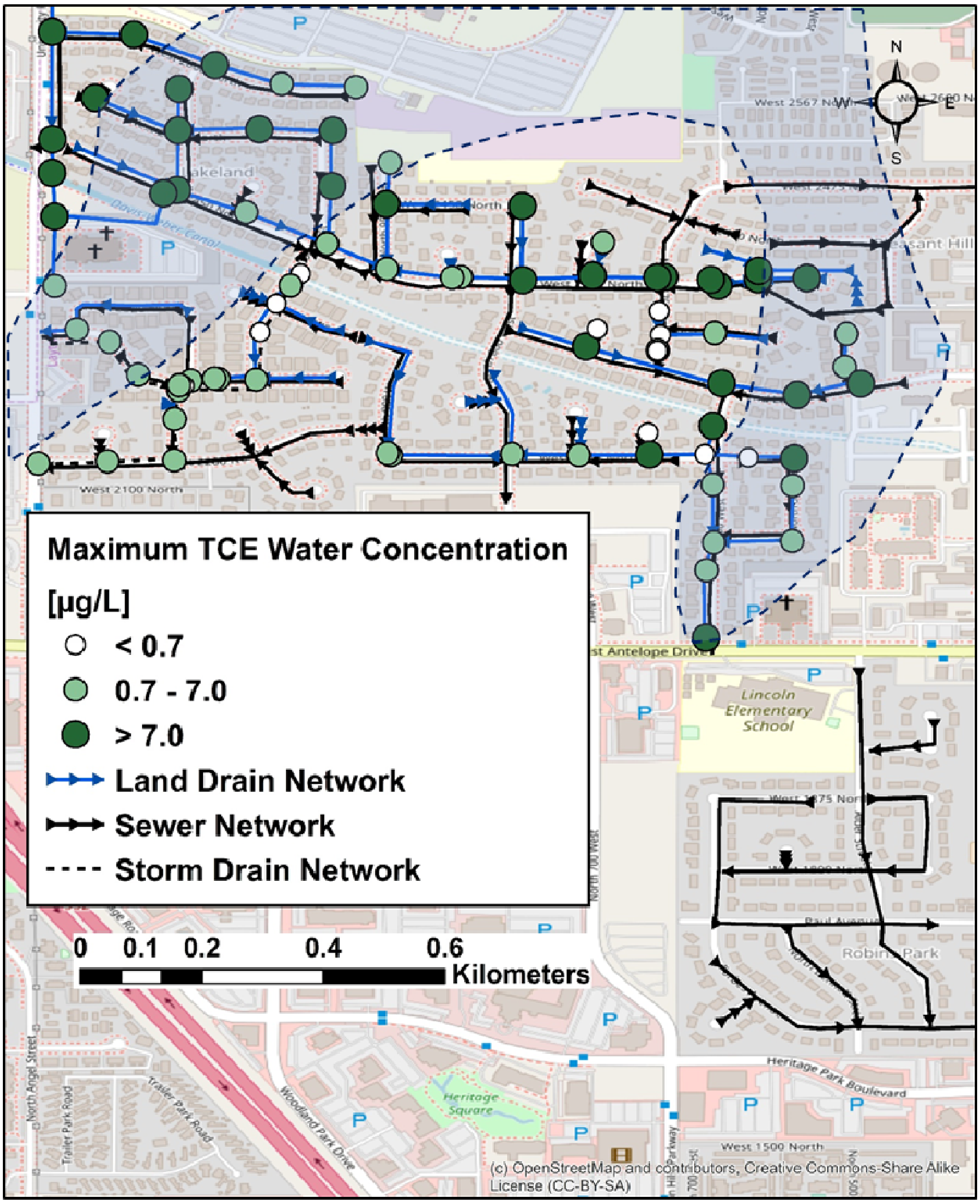


Figure 6. Maximum TCE concentrations in water samples collected from land drain manholes during the five quarterly synoptic surveys. The shaded area indicates the extent of the TCE groundwater plume.

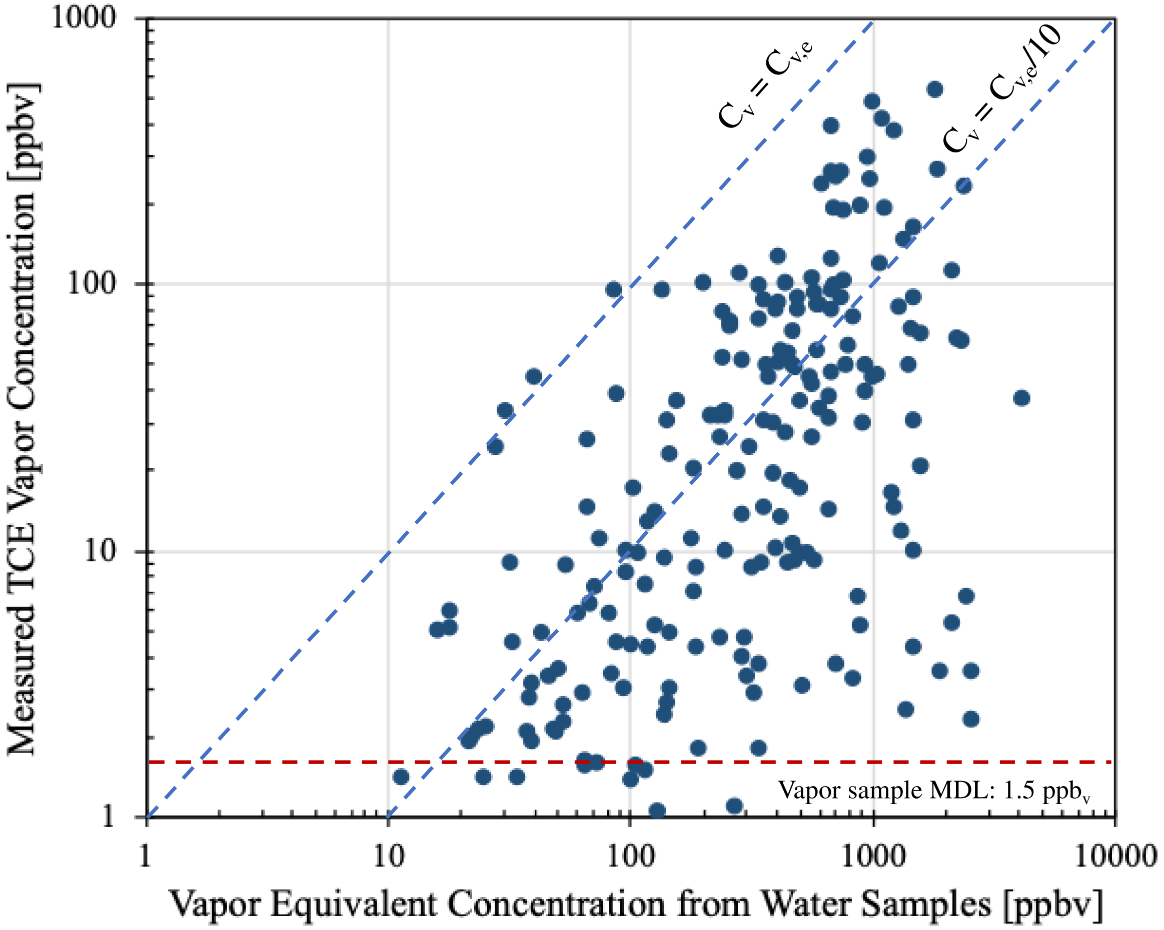


Figure 7. Vapor equivalent concentration ($C_{v,e}$) vs. measured vapor concentration (C_v) for water and vapor samples collected in the same manhole. The Dimensionless Henry's Law Constant used in these calculations was 0.4 L-H_2O/L-vapor (USEPA, 2019).

VI guidance documents, from federal to state, all recognize dissolved VOC concentration in groundwater as one important line of evidences for VI risk assessment, since dissolved water concentrations can be used to predict vapor and indoor air concentrations, using the assumption of local equilibrium. Thus, we examined the correlation between TCE concentrations in water and vapor samples collected from the same manholes to evaluate the value of water sample collection in VI pathway investigation. The results are presented in Figure 7 where the measured headspace TCE vapor concentration (C_v) is plotted vs. the vapor equivalent concertation ($C_{v.e}$) for the water samples, calculated by multiplying the measured dissolved TCE concentration in a water sample by the dimensionless Henry's Law Constant for TCE (0.4 L-H_2O/L-vapor; USEPA, 2019). A total of 256 paired water and vapor samples are plotted in Figure 7. As can be seen, the measured TCE vapor concentrations were less than 10% of $C_{v.e}$ for 70% of the samples, suggesting that use of VOC concentrations from water samples will lead to over-prediction of VOC vapor concentrations when a simple local equilibrium assumption is applied. Corsi and Quigley (1996) identified headspace ventilation rate, water flowrates and the water flow conditions in manholes (fully submerged, partially submerged pipeline or water drops) as criticle factors that affect VOC migration rate from liquid to vapor phase in piping networks. Therefore, these factors should be evaluated if VOC liquid sample concentrations were used for VI risk characterization. However, sewer ventilation rates and water flow rates in pipelines could not be easily quantified, and accurate measures of these often require intensive efforts, such as tracer releasing. As such, it is best to collect and analyze vapor samples from subsurface piping networks, rather than water samples, for VI pathway assessment.

3.2 Temporal Variability in Multi-Season Grab Sample Concentrations

The temporal changes in the multi-season grab sample results were assessed by looking at the maximum/minimum concentration ratio at each of the 268 locations where at least three sampling events occurred. Any sample result that was non-detect was assigned a value of one-half the MDL (0.75 ppb_v) in these calculations. The results were then parsed into the three groups shown in Figure 8 and discussed below:

- Group I: Locations where TCE manhole headspace concentrations were consistently below the MDL (67 of 268 manholes). These are locations where the temporal variability could not be assessed with the data and the concentrations at these locations are unlikely to cause VI indoor air impacts above a 0.4 ppb_v TCE indoor air screening level.
- Group II: Locations where TCE vapor concentrations were measured above the MDL at least once, at relatively stable levels as their maximum/minimum TCE vapor concentration ratios were <10x. This group includes 120 of 268 manholes, and of those, there were 64 locations where the maximum concentration was between 10x and 100x of a 0.4 ppb_v indoor air screening level.
- Group III: Locations where significant changes in concentration occurred as the maximum/minimum TCE vapor concentration ratios were >10x. This set includes about 30% (81 of 268) of the sampled manholes. Most of these locations (61) had contrasting concentrations that might be judged to be both of concern (>10x a 0.4 ppb_v screening level) and not of concern (<10x a 0.4 ppb_v screening level). The largest maximum/minimum TCE vapor concentration ratio was >500x.

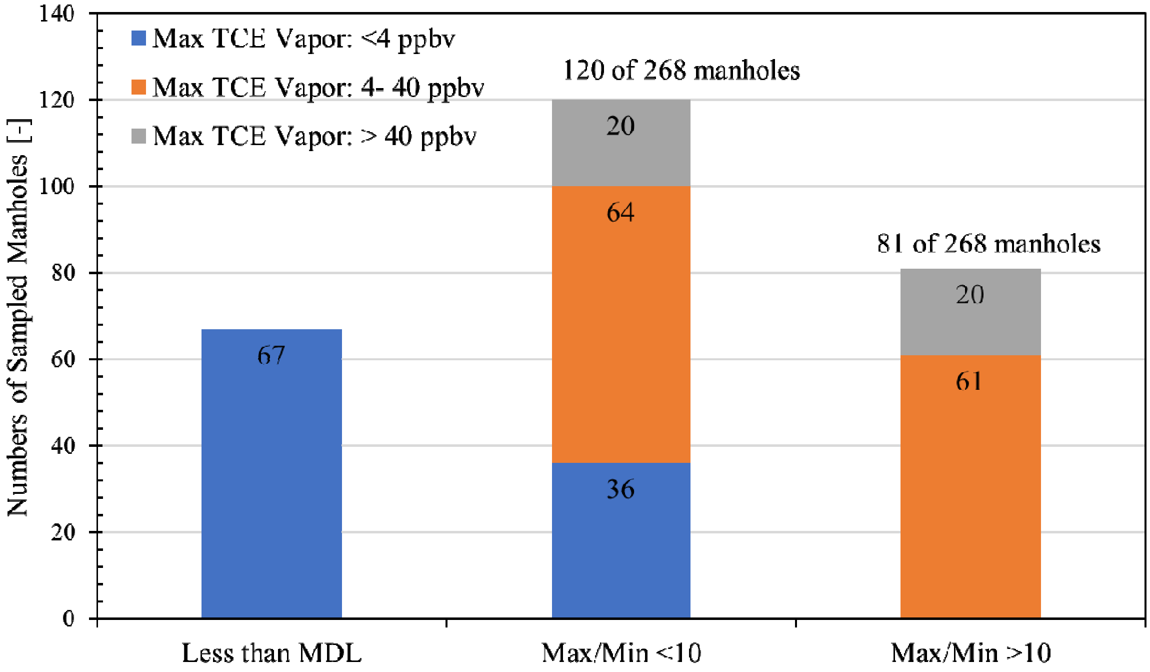


Figure 8. Summary of temporal TCE vapor concentration changes in multi-season grab sample results.

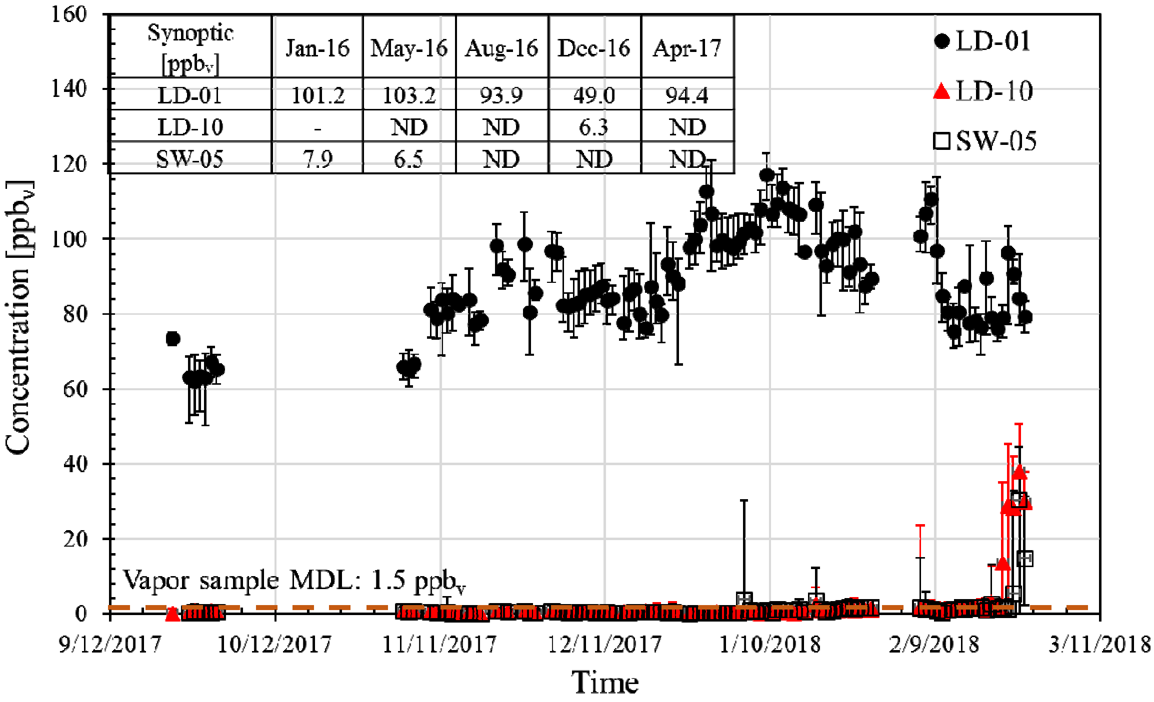
Overall, relatively stable vapor concentrations were observed at some locations and highly variable results were observed at others, without any way to anticipate the temporal variabilities or maximum concentration at any specific location. Of the Group III locations – those with the greatest changes between samples – the maximum concentration was measured during a winter sampling event at 21% of these manholes and the maximum concentration was measured in a summer sampling event at 72% of the manholes. This suggests that it would be prudent for future guidance to recommend multi-season sampling events when assessing potential VI impacts from subsurface piping networks.

3.3 Real-time Hourly Sampling Results

To assess if the changes observed in multi-season sampling results reflected long-term seasonal changes or shorter-term (hourly to daily) vapor concentration fluctuations, hourly grab sampling was conducted at selected manholes that had both consistent and highly variable multi-season results. Hourly samples collected from LD-01, LD-10 and SW-05 (Figure 3) for about five months (September 2017 to March 2018) were averaged for each day and plotted as presented in Figure 9, showing also the maximum and minimum result from each 24-h period.

Manhole headspace TCE concentrations were consistently below the MDL for over 90% of the sampling period in both LD-10 and SW-05, followed by spikes to 51 ppb_v and 45 ppb_v, respectively, in early spring. This pattern is consistent with their multi-season sampling results: at LD-10 and SW-05 the TCE headspace concentrations were <MDL for three of four events and three of five events, respectively. In contrast the LD-01 concentrations were mostly in the 50 – 120 ppb_v range, with differences between daily maximum and minimum TCE vapor concentration being <35% of the 24-h averaged TCE concentration values each day. LD-01 hourly TCE concentrations ranged from 50.3 ppb_v to 122.7 ppb_v with an averaged value of 89.9 ± 13.4 ppb_v (average ± standard deviation), which was consistent with the multi-season results that ranged from 49 - 103 ppb_v from seasonal synoptic survey samples.

To provide additional insight to short-term concentration variations, Figure 10 presents hourly sample results vs. time for a five-day period at the LD-01 location. A diurnal pattern is evident in the data with the TCE vapor concentrations reaching their highest level in late afternoon and decreasing during the night. This short-term (24 h) variability in TCE vapor concentration was not significantly different from the long-term (multi-season) variation. The ratio of daily maximum/minimum concentrations was typically <1.2, while it was about 2 for the multi-season sampling data at LD-01.



Synoptic [ppb$_v$]	Jan-16	May-16	Aug-16	Dec-16	Apr-17
LD-01	101.2	103.2	93.9	49.0	94.4
LD-10	-	ND	ND	6.3	ND
SW-05	7.9	6.5	ND	ND	ND

Figure 9. 24-h averaged manhole headspace TCE concentrations at LD-01, LD-10 and SW-05 (see Figure 2). Error bars denote the daily maximum and minimum values.

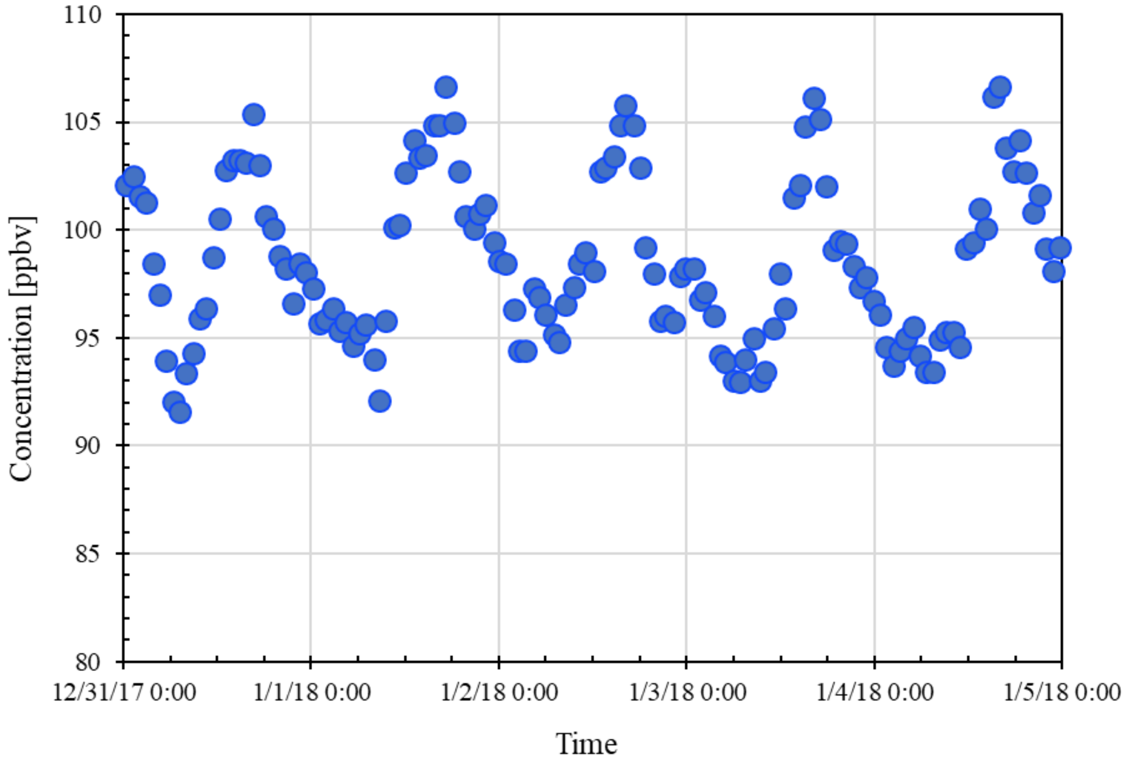


Figure 10. Diurnal behavior of TCE vapor concentrations in the LD01 manhole headspace.

3.4 24-hour Thermal Desorption Sampling Results

To further assess the temporal variability in manhole headspace vapor concentrations, six week-long sampling events were conducted from March 2018 to January 2019. During each, 24-h time-integrated samples were collected from 13 manholes. The 13 manholes were selected based on their multi-season grab sampling results, with the goal of including locations with different patterns of results: two manhole locations where concentrations were consistently below the MDL (Group I in Figure 8); five manhole locations where concentrations varied by <10x (Group II in Figure 8); and six manhole locations where concentrations varied by more than 10x (Group III in Figure 8).

Table 2. Statistical summary of the week-long period 24-h sampling results with corresponding seasonal grab sampling results at each location.

Seasonal Variation	Manhole ID	TCE Vapor Concentration [ppb$_v$]								
		Multi-Season Grab Sample Results					Weekly Averages of the 24-h Sample Results		Averages Across the Six Week-Long Sampling Events	
		Jan-16	May-16	Aug-16	Dec-16	Apr-17	Maximum	Minimum	Max 24-h Value/Weekly AVG Value	Min 24-h Value/Weekly AVG Value
Group I: All < MDL	LD-08	NA	NA	<MDL(s)	<MDL(s)	<MDL(s)	0.1	<MDL(w)	3.2	0.27
	LD-09	NA	NA	<MDL(s)	<MDL(s)	<MDL(s)	<MDL(w)	<MDL(w)	2.6	0.17
Group II: <10x Multi-season Max/Min	LD-05	49.0	37.3	13.6	31.9	19.5	37.9	11.2	1.3	0.71
	LD-01	101.2	103.2	93.9	49.0	94.4	65.6	29.9	1.4	0.65
	LD-07	NA	191.0	103.5	79.8	88.9	94.4	42.8	1.4	0.60
	SW-02	NA	3.0	2.1	5.0	<MDL(s)	0.6	<MDL(w)	3.0	0.29
	LD-06	NA	NA	31.2	98.2	83.2	59.8	1.1	2.4	0.48
Group III: >10x Multi-season Max/Min	SW-01	NA	23.9	136.7	<MDL(s)	36.7	78.4	0.4	2.3	0.54
	LD-04	NA	2.5	410.0	39.0	14.4	7.9	0.1	2.6	0.31
	SW-03	<MDL(s)	<MDL(s)	11.8	<MDL(s)	<MDL(s)	0.1	<MDL(w)	2.7	0.022
	SW-04	NA	NA	9.1	2.9	<MDL(s)	0.9	0.1	2.9	0.19
	LD-02	NA	<MDL(s)	1.9	385.7	55.3	198.8	1.9	2.4	0.24
	LD-03	37.0	62.3	4.3	49.7	45.5	127.5	4.5	1.6	0.45

NA – No sample available;
MDL(s) – TCE detection limit for the synoptic samples: 1.5 ppb$_v$.
MDL(w) – TCE detection limit for 24h samples: 0.07 ppb$_v$

The results of this study are presented in Table 2 and Figure 11. A summary of the week-long period daily-sample results along with their multi-season grab sampling results are provided in Table 2. Figure 11 presents the averaged week-long sampling results for locations with concentrations >MDL, with the error bars spanning the maximum and minimum 24-h TCE vapor concentrations that were measured during each week-long sampling period.

Collectively the results are mostly consistent with the synoptic and extended hourly sampling results. At some locations, the concentrations appear relatively temporally stable and were similar to grab sample, 24-h sample, and weekly-average results for those locations (e.g. LD-01,

-05, and -07). At those locations, grab samples collected at any time of the year would likely provide good insight to the concentrations, although increasing to weekly-average samples could decrease variability in sample results relative to grab or 24-h samples. At other locations (e.g., LD-02 and -03), the 24-h and weekly-average results span a wide range, but encompassing values similar to the multi-season grab samples. At those locations, multi-season sampling would be needed to characterize the range of vapor concentrations at those locations, and grab, 24-h, and weekly average samples would likely yield similar results. Then there are other locations (e.g., LD-06) where the multi-season grab samples suggested much less temporal variability than was revealed in the 24-h and weekly-average results or the maximum concentration detected in grab sampling was much greater than either 24-h sample or weekly-average results (e.g. 30x at LD-04).

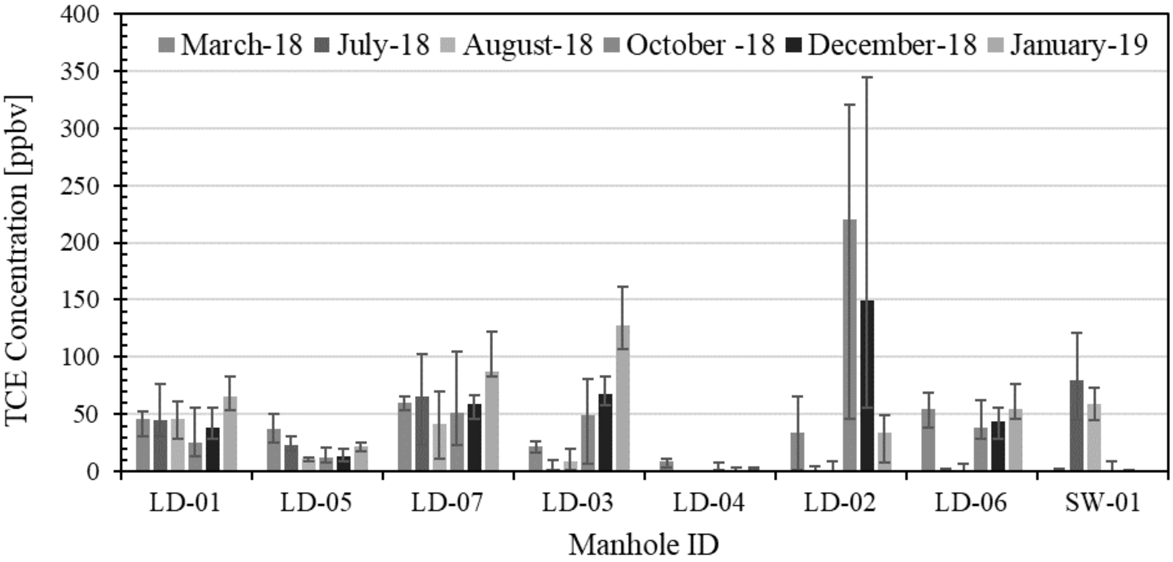


Figure 11. The weekly averaged TCE headspace concentrations of 24-h samples with error bars spanning the maximum and minimum 24-h concentrations of each week-long sampling period.

4.0 Implication for VI Alternative Pathway Sampling in Sewers and Other Subsurface Utility Conduits

Overall, the following observations are supported by the data collected in this study:

- Diurnal concentration changes in hourly TCE vapor samples were less than 50% at one intensely sampled location in this study. If concentration variations of this magnitude about an average are of concern, the uncertainty in concentration results can be minimized by collecting 24-h time-integrated samples.
- In our data set, individual 24-h average results ranged from 50% to 150% of the calculated weekly-average at some locations (e.g., LD-01 and -07), but also varied to a greater degree at other locations (e.g. LD-02 and -04). Thus, serious consideration should be given to week-long sample durations rather than grab samples or 24-h sample durations in designing alternate VI pathway assessment plans.
- Whether collecting grab, 24-h, or week-long samples, seasonal variability should be expected. This was greater than daily or weekly variability at many locations at our study site, so it is possible to measure concentrations of significance at some periods of the year while seeing insignificant concentrations at others. For example, over 10x seasonal variability was observed at 81 of 268 manholes in this study.
- Thus, multi-season synoptic events should be considered, as these are likely to provide more confidence in characterizing vapor distributions in subsurface utilities than one-time grab sampling events.
- Sampling location selection should not be overly constrained by dissolved plume delineation as concentrations of significance have been observed in this and other studies at locations outside of the dissolved plume footprint.

In brief, the results of this study suggest that robust alternate VI pathway sampling protocols would typically include week-long samples collected at different times of the year with samples collected at manhole locations overlying and outside the dissolved plume. Locations exterior to the plume might be chosen based on connectivity and how flow occurs in the sewer and drainage network, if that is known. It may be that week-long active vapor sampling at large numbers of locations might be impracticable at sites with large dissolved plumes like our study site, so we recommend that the utility and accuracy of passive sampling tools in sewer environments as alternatives to active sampling be evaluated in future studies.

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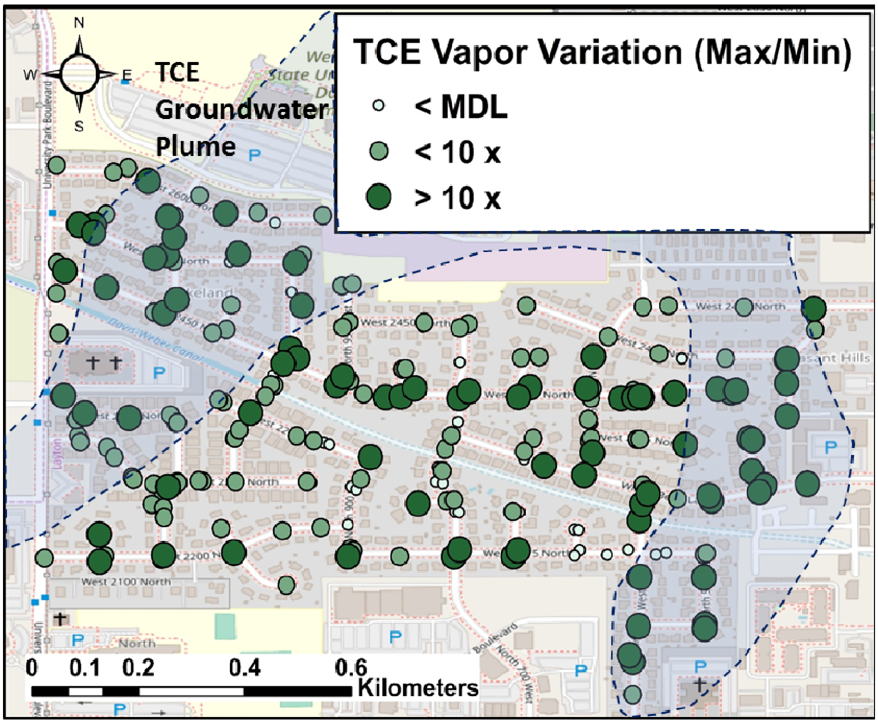
TCE Vapor Variation (Max/Min)
○ < MDL
● < 10 x
● > 10 x
TCE
Groundwater
Plume
N
E
S
W
0
0.1
0.2
0.4
0.6
Kilometers
West 2450 North
West 2100 North
Davis Weber Canal