A Room-by-Room Study of Trichloroethylene Exposure Point Concentration Variation: TO-15 Summa versus HAPSITE Data

Amy R. Quintin (amy.quintin@woodplc.com), Kathryn A. L. Sarsfield, and Michael J. Murphy (Wood, Chelmsford, MA, USA)
Lawrence Cain (US Army Corps of Engineers, Concord, MA, USA)

ABSTRACT: Indoor air at the Cold Regions Research and Engineering Laboratory (CRREL) Main Laboratory building in New Hampshire has been impacted by a documented sub-slab vapor source (vapor cloud) of trichloroethylene (TCE). Indoor air is currently monitored using two different sampling and analysis methods, 1) evacuated steel SUMMA® canisters in semi-annual sampling events as part of the regulatory process until the final remedy for the site is achieved, and 2) frequent two minute grab samples collected and analyzed with HAPSITE portable gas chromatograph with mass spectral detector (GC/MS) in a long-term monitoring program to ensure the building is safe for the workers. This paper describes and compares the results from nearly three years' worth of sampling the large multi-story commercial building. Chronic and shorter-term (21 day average or maximum) exposure point concentrations (EPCs) were calculated to compare results and conclusions with respect to various federal regulatory policies and/or guidance for responding to and managing TCE in indoor air.

The results show that SUMMA did not detect any concentrations above screening levels. The HAPSITE method reveals more variability in measured concentrations and did detect concentrations above chronic and short-term screening levels. The binomial probability distribution has been used to evaluate the data and estimated that between 140 and 200 random samples would be required to detect one result above 8.8 ug/m^3 at the same level of probability at this facility. The statistical analysis also showed that low probability and high probability rooms showed different relationships to meteorological covariates, with low probability rooms showing a significant relationship to mean sea level pressure, whereas the high probability rooms were likely most influenced by the Healthmate® air filtration units. The results of this study suggest that frequent or continuous sampling is essential for evaluating risks to health associated with short-term toxicants when the probability of detection is low.

INTRODUCTION

The Cold Regions Research and Engineering Laboratory (CRREL) Main Laboratory building is a large multi-story commercial building in New Hampshire with a documented sub-slab vapor source (vapor cloud) of trichloroethylene (TCE). This site is an active research facility with temporary mitigation measures in place, but source removal as part of a final remedy has not been completed. Consequently, indoor air is currently monitored using evacuated steel SUMMA® canisters in semi-annual sampling events as part of the regulatory process. Indoor air is also monitored daily during working hours with grab samples using a Hazardous Air Pollutants on Site (HAPSITE) (Inficon, Syracuse, NY, USA) as part of a long-term monitoring program to ensure the building is safe for the workers. Short-term concentration variation is particularly important at the facility because the main compound of concern is TCE, which may have short-term toxic developmental

effects. Significant amounts of work have gone into analyzing and communicating indoor air results and mitigating vapor intrusion impacts at the facility.

Indoor air results at CRREL are impacted by a wide variety of confounding variables including historical building contamination, sub-slab depressurization systems (SSDS) in place, porous concrete construction with a fairly open building envelope causing negligible differential pressure between indoor and outdoor air, exposed pipe chases with some historical piping left in place, and Healthmate® air filtration units in many rooms, although the use may be inconsistent. Yet we see that TCE indoor air data follow certain trends consistent with typical vapor intrusion sites, including a relationship to atmospheric pressure. We discuss some of the key reasons for indoor air variability in this room-by-room analysis, and evaluate the relationships of various covariates using linear regression. In order to evaluate the choice of sampling method, we also evaluate the probability of detecting certain results based on the dataset, and use this to calculate the number of random samples that would be required to detect the same result. An approach that has been used recently to illustrate the importance of using indicators, surrogates, and tracers (Lutes, 2017).

We then use our existing dataset to explore various methods of calculating chronic and shorter-term exposure point concentrations (EPCs), and discuss how the choice of characterization method can impact the risk management decisions. We discuss comparison to chronic USEPA Regional Screening Levels (RSLs) (USEPA, 2017) and three shorter-term regional USEPA guidance documents that specifically apply to TCE in indoor air (USEPA, 2012; 2014, and 2016a).

MATERIALS AND METHODS

This paper is subsequent to previously published indoor air characterization research at this facility (Quintin et. al., 2016). Therefore, the same sampling and analytical procedures and methods apply, and are summarized here. All samples were collected approximately 4 ft above floor level (breathing zone height) during the working day, by either 8-hour time weighted average (TWA) or grab sample. Each indoor air sample was collected and analyzed by one of two methods:

Method 1 – 8 h TWA TO-15: Evacuated steel SUMMA® canisters, with 8-hour flow controllers. The canisters were analyzed off-site by USEPA Method TO-15. All procedures followed USEPA protocol (USEPA, 1999), and project-specific QA/QC procedures. Sample collection is consistent with current guidance (USEPA, 2015). Data from six semi-annual events in February or March, and August have been considered.

Method 2 – Grab Portable GC/MS: HAPSITE, run in selected ion monitoring (SIM) mode for TCE. Two minute interval grab samples. All procedures followed USEPA protocol (USEPA, 2004), and project-specific QA/QC procedures.

The dataset selected for this study is limited to data collected following mitigation activities previously discussed. The sampling program was conducted using industry best practice for each sampling and analysis method. Sufficient data were available for comparison at 16 locations within the Main Laboratory Building. The sampling period covers 3 years, between October 2, 2014 and August 30, 2017. Rooms of varying sizes were included, plus two sample locations within hallways. The sample locations are illustrated in Figure 1.

FIGURE 1. Main lab: relative size and location of rooms assessed per floor.

Meteorological data recorded at Lebanon Airport (The Weather Company© LLC, 2017) were used to assess meteorological covariates, and included temperature, wind speed, pressure, and precipitation.

Samples were screened for possible bias during collection, and any samples not collected in the breathing zone, or impacted by a current background source of TCE in the building, were removed from the dataset. Samples not meeting QA/QC protocols were also removed. To resolve field duplicate samples collected as part of the quality assurance plan, the results were averaged if both the field sample and duplicate were TCE detections. If only one was a detection, the detection was selected. If neither was a detection, then the lower of the reported detection limits was selected. In several cases results with the portable GC/MS were collected at one location multiple times per day. These results were averaged following the same processing rules, resulting in one sample per sample location per day.

Statistical Analysis and Probabilities. The data were evaluated using regression modelling and analysis of variance (ANOVA) in R (R Core Team, 2018). Statistics were run per room for the two sampling and analysis methods, and evaluated with respect to relationships to meteorological conditions. Calculations and graphs produced in R used detection limits for non-detects. Regression diagnostics identified an improvement when the TCE data were log-transformed. Therefore, TCE concentrations were log-transformed prior to performing the statistical evaluation of meteorological covariates.

Binomial probability calculations were performed using the actual sample numbers and results. The data ware divided into “elevated” and “un-elevated” results in order to calculate the proportion. “Elevated” results were considered any result above 8.8 ug/m^3. The proportion of “elevated” results is also the probability of detecting one “elevated” result. The proportions per room were then used to calculate a hypothetical random sample number that would be necessary to attain one “elevated” result with 95% confidence (a 5% probability of not detecting an “elevated” sample). The formula for calculating probabilities in the Binomial distribution has been reduced to the following equation and solved for n:

$$n = Log(0.05)/(Log(1-p))$$

where n is the hypothetical random sample number, p is the calculated probability of a successful result based on real data, and 0.05 is the confidence interval, or probability of underestimating p (5%).

Exposure Point Concentrations. Data collected using the two different sampling and analysis methods (8 h TWA TO-15 vs grab portable GC/MS), have been used to estimate EPCs. An EPC is the average medium-specific chemical concentration a receptor may contact at an exposure point over the exposure period (USEPA, 1989). In chronic exposure assessments the EPC calculation process is intended to provide a conservative estimate of average exposure over a chronic exposure period. For short-term assessments a shorter exposure period is considered. In practice this may mean chemical sampling occurs over a shorter period, or even a single sampling event. The most conservative EPC estimates use a maximum detected concentration. Comparing EPCs to screening criteria in a screening assessment allows for a rapid assessment of potential occupational inhalation exposure.

EPCs were calculated for each of the 16 rooms included in this study for both sample collection/analysis methods. The standard process of identifying chronic EPCs is to select the lower of the calculated UCL generated using ProUCL software (ProUCL 5.1) (USEPA, 2016b) and the maximum detected concentration. (USEPA, 2002). This process has been completed independently for each room and for each method of data collection.

In addition to the chronic EPCs, “short-term” EPCs have also been generated. These short-term EPCs have been calculated for 21-day periods that coincide with the collection of the semi-annual 8 h TWA samples. For each month of 8 h TWA sample collection, a 21-day period (the seventh through twenty seventh day of the month) has been selected as the basis for short-term EPC calculation. These short-term periods were typically in February and August. In 2015, the first quarter sampling was conducted in March instead of February and the short-term EPCs were based on data from that month.

The calculation of the average concentration includes only detected results (detection limits for non-detected results were not included in this 21-day average, which is a conservative approach). This approach provides a comparison at varying times of the year. Both 21-day averages and maximum detected concentrations were identified for each 21-day period evaluated. For each 21-day period within each room (quarter 1 and 3 for each year only), there may be multiple grab portable GC/MS samples, however there is only a single 8 h TWA sample.

Screening Level Risk Evaluation. The screening values for commercial/industrial workers were considered the most appropriate values for comparison. The implicit assumptions within each screening value is that workers are present breathing indoor air for 8 hours per day. Short-term assumptions vary. All screening values used within this evaluation are based on toxicity values from IRIS, which were most recently updated in 2011 (USEPA, 2011; USEPA, 2018). The TCE chronic inhalation noncancer Reference Concentration (RfC) is 2 µg/m^3. The TCE inhalation cancer Unit Risk Factor (URF) is 4.1 x10^{-6} (µg/m^3)$^{-1}$.

The chronic EPCs have been compared to the non-cancer based ambient air Regional Screening Level (RSL) for a worker, which is 8.8 µg/m^3 (HI of 1) (USEPA, 2017). The short-term 21-day average EPCs have been compared to USEPA Region 10 short-term noncancer ‘not to be exceeded’ 21-day average air level of 8.4 ug/m^3 (HI of 1) (USEPA, 2012). The short-term maximum concentration EPCs detected within the 21-day periods

have been compared to USEPA Region 9 Accelerated Response Action Level at of 8 µg/m^3 (HI of 1) and Urgent Response Action Level of 24 ug/m^3 (HI of 3) (USEPA, 2014). Short term maximum concentrations have also been compared to the USEPA Region 7 Action Level for an 8-hour worker of 6 µg/m^3 (HI of 1) (USEPA, 2016a).

The screening values identified above are all based on noncancer effects, although TCE is also a carcinogen. The cancer risk associated with TCE in indoor air is a function of lifetime average exposure, and current cancer risk calculation procedures do not include evaluations of short-term exposures, except in the context of early life stage susceptibility to carcinogens with a mutagenic mode of action. This is not a concern for the current evaluation, which is focused on an adult worker scenario. The final phase of the screening evaluation is to identify cases where the EPC is higher than either the chronic or short-term screening criteria.

RESULTS AND DISCUSSION

Samples collected in 16 locations in the CRREL Main Laboratory building were included. A total of 3,413 TCE indoor air results were collected by grab portable GC/MS, reduced to 2,998 samples after field duplicates and temporal duplicates were resolved. A total of 114 TCE results were collected by 8 h TWA TO-15, reduced to 108 samples after field duplicates were resolved. Per room the grab portable GC/MS sample number ranged from 11 to 564, and the 8 h TWA TO-15 sample number was 6 for 15 locations, and 18 for RM R05. As expected, the ratio of portable GC/MS samples to 8 h TWA samples collected at a given location is generally substantially higher than 1 (ranging from approximately 2 to as high as 94). Figure 2 shows that the range of concentrations is also much greater for the Portable GC/MS data than for the 8h TWA data. Despite the much wider range of results for the grab portable GC/MS methodology, the calculated chronic EPCs are generally similar to the 8 h TWA TO-15 EPCs. The results show no specific correlation between the number of samples collected per location and the chronic EPC.

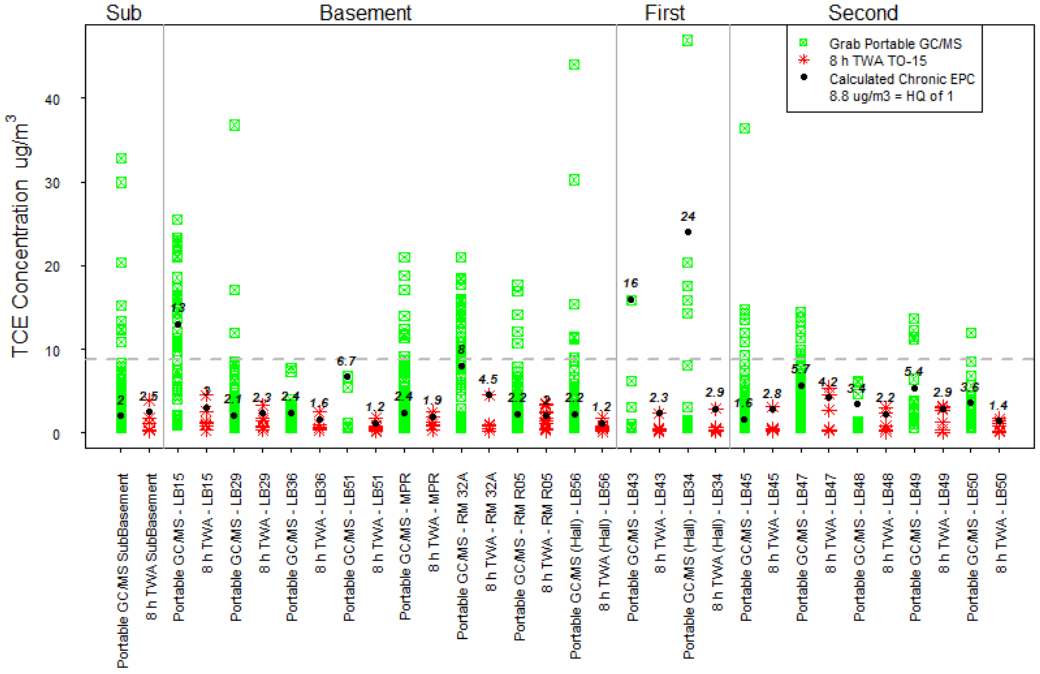

FIGURE 2. Comparison of processed data and chronic EPCs per room

Results of Statistical Analysis and Probabilities. Approximately 4% of detected TCE concentrations (120 out of 2,998 samples) were above 8.8 µg/m^3, which is a lower percentage than the 10% reported in Quintin et al. (2016). The outcome of the binomial probability calculations were proportions of these "elevated" events between 0% and 60% per room. Using the binomial probability calculations, the room-by-room probability was used to estimate the random sample number that would be required to attain the actual detected level of probability.

The rooms with a higher percentage of "elevated" results typically had fewer samples, suggesting that they were sampled during periods when there was a known vapor intrusion event, and not part of the standard sampling program. These samples likely show a high bias in the proportion of elevated results. The rooms with a higher sample number are more likely to provide an accurate representation of probability within the building. These low probability rooms generally had a similar probability of success (1.8% to 2.2%), and estimated sample numbers required for detecting one successful result between 140 and 200 samples.

The linear regression indicated a large difference between the predictive capacity of meteorological covariates in the high probability rooms and the low probability rooms. Sea level pressure was a very consistent predictor in the low probability rooms, but not in the higher probability rooms. The presence of Healthmate® air filtration units was noted in rooms where higher concentrations were known to correspond to the unit not running, and lower concentrations correspond to the unit running. Since Healthmate® air filtration units have the ability to directly remove TCE from the air they may be overriding the effects of meteorological conditions in the high probability rooms.

The room-by-room ANOVA showed that the low probability rooms had a significant relationship between TCE concentrations and mean sea level pressure. The probability that this is wrong (Type I error) was very small in each high probability room ($P < 0.001$). The probability of incorrectly rejecting the null hypothesis (Type II error) was very low: $< 2.2 \times 10^{-16}$. This relationship was generally reversed in the high probability rooms (i.e., rooms with lower relative sample numbers). Due to the limited numbers of samples per room, particularly for the 8 h TO-15 data, the room-by-room ANOVA data include both grab portable GC/MS data and 8 h TWA TO-15 data.

Short-term Assessment. The short-term EPCs for the six quarters between the two different methods showed a higher level of variation than the chronic EPCs, with the widest divergence of EPCs for the shortest sample durations (i.e., using maximum detected concentrations as the EPC). The EPCs have been compared to appropriate screening levels, based on the assumed critical exposure time specified by the individual guidance documents, as shown in Table 1. A portion of individual EPCs are above the selected screening level in the grab portable GC/MS for both chronic, and short-term (21-day average and 21-day maximum detected concentration) EPCs. All 8 h TWA TO-15 TCE concentrations are below 8.8 µg/m^3 (associated with HI = 1 for the worker).

TABLE 1. **Screening level risk evaluation results.**

Guideline	Screening Level µg/m3	EPC Type	Grab Portable GC/MS # EPC Above	8 h TWA TO-15 # EPC Above
Chronic RSL	8.8	Chronic	3	0
Region 10	8.4	21-Day Average	4	0
Region 7	6	21-Day Maximum	23	0
Region 9 Accelerated	8	21-Day Maximum	13	0
Region 9 Urgent	24	21-Day Maximum	1	0

CONCLUSIONS

Grab portable GC/MS methodology detected a wider range of TCE concentrations than 8 h TWA TO-15, including 4% of all results above 8.8 µg/m^3. Between 140 and 200 random samples would be required to detect "elevated" results (above 8.8 µg/m^3) at the same level of probability. Low probability rooms showed a significant relationship to mean sea level pressure, whereas the high probability rooms were likely most influenced by the Healthmate® air filtration units. These results suggest that when monitoring variable, low probability scenarios for potential short-term toxicants, high frequency sampling is an essential component of the sampling program.

The shorter the time-frame considered in EPC calculation, the more likely there is to be a difference between the EPCs and accordingly the risk management conclusions between the two different methods. The higher variation in grab portable GC/MS data implies that if short-term risks are the primary risk management concern, multiple short duration samples are preferable over 8 h TWA TO-15. Short duration sampling is also likely to be especially beneficial in situations where concentrations may show wide fluctuations, where mitigation is not yet complete but workers are present, or where the source is unknown or changeable and short term investigation is needed to identify the source of contaminants.

ACKNOWLEDGEMENTS

We would like to acknowledge the U.S. Army Corps of Engineers, New England Division, for graciously allowing us to use and publish these data. We would also like to acknowledge our Wood staff for the considerable effort that went into planning and collecting these data.

REFERENCES

Lutes, C., Holton, C. Kurtz, J., and Truesdale, R. 2017. "Indicators, Tracers and Surrogates, Why Use Them, Probability Analysis, Definitions and Examples." 02a. EPA/AEHS, 21 March 2017 AM - EPA Workshop: Finding Practical Solutions for the Chlorinated VI Pathway. [internet] [cited 2018 March 25] Available from: https://iavi.rti.org/workshopsandconferences.cfm?archive=3.

Quintin, A.R., M.J. Murphy, L. Cain and D. Moore. 2016. Trichloroethylene in Indoor Air: TO-*15 Summa Data vs HAPSITE Data.* Proceedings of the 2016 AEHS Foundation Annual International Conferences - Volume 22. ISBN: 978-0-9888932-5-2.

R Core Team. 2018. R: A language and environment for statistical computing. R Version 3.4.4 (2018-03-15) R Foundation for Statistical Computing, Vienna, Austria. : [internet] [cited 2018 March 18] Available from: https://www.R-project.org/.

The Weather Company© LLC. 2017. Weather History for KLEB. West Lebanon, NH, Lebanon Municipal. [internet] [cited 2017 Nov 15] Available from: https://www.wunderground.com/.

U.S. Environmental Protection Agency. 1989. *Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part A)*. Office of Emergency and Remedial Response; EPA 540/1-89/002 (interim final). Washington, D.C. December.

USEPA. 1999. *Compendium Method TO-15. Determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS)*. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Center for Environmental Research Information, Office of Research and Development, Cincinnati, Ohio. EPA/625/R-96/010b.

USEPA. 2002. *Calculating Upper Confidence Limits for Exposure Point Concentrations at Hazardous Waste Sites*. Office of Solid Waste and Emergency Response/Office of Solid Waste and Remedial Response; OSWER 9285.6-10. December 2002.

USEPA. 2004. *Region 9, Richmond California, Standard Operating Procedure 910, Volatile Organic Compound Analysis of Air and Soil Vapor by Field Portable GC/MS*, ICF Consulting for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA Contract No. 68-W-01-028). EAST Document Control Number 00902002-4703.

USEPA. 2011. *Toxicological Review of Trichloroethylene*. In Support of Summary Information on the Integrated Risk Information System (IRIS). EPA/635/R-09/011F.

USEPA. 2012. *OEA Recommendations Regarding Trichloroethylene Toxicity in Human Health Risk Assessments*. United States Environmental Protection Agency, Region 10. December 13, 2012.

USEPA. 2014. *EPA Region 9 Response Action Levels and Recommendations to Address Near-Term Inhalation Exposures to TCE in Air from Subsurface Vapor Intrusion*. United States Environmental Protection Agency, Region 9. July 9, 2014.

USEPA. 2015. *OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air*. OSWER Publication 9200.2-154, Office of Solid Waste and Emergency Response, June.

USEPA. 2016a. *EPA Region 7 Action Levels for Trichloroethylene in Air*. Memorandum from Mike Beringer. November 2, 2016.

USEPA. 2016b. ProUCL Version 5.1.00. Statistical Software for Environmental Applications for Data Sets with and without Nondetect Observations, May. [internet] [cited 2018 Feb 20] Available from: https://www.epa.gov/land-research/proucl-software.

USEPA. 2017. USEPA Regional Screening Levels (RSLs). Generic Tables: November 2017. [internet] [cited 2018 Feb 20] Available from: https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-november-2017

USEPA. 2018. Integrated Risk Information System (IRIS); on-line database search. National Center for Environmental Assessment, USEPA. [internet] [cited 2018 Feb 20] Available from: www.epa.gov/iris