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Discerning Background Sources of VOCs from Vapor Intrusion Sources Using Multiple Lines of Evidence

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ABSTRACT: Quantification of background concentrations for many chlorinated volatile organic compounds (VOCs) in indoor air is a critical issue at many RCRA and CERCLA sites with the potential for vapor intrusion. Because of the complexities of the vapor intrusion pathway, one line of evidence indicating background sources is often insufficient to convince regulatory agencies that the source is not vapor intrusion. An approach for more clearly discriminating background indoor sources of VOCs from vapor intrusion sources using multiple lines of evidence has been developed at two large sites in Denver.

The approach relies on use of the following lines of evidence:

1) population distribution statistics from site-specific background data,
2) indoor air VOC spatial relationships to groundwater VOC concentrations, concentration reductions over time, and JE model estimates of indoor air concentrations,
3) "indicator" VOCs without common background indoor air sources (e.g. 1,1-DCE),
4) COC ratios in multiple media when more than one chlorinated VOC is present in groundwater,
5) time series plots for indoor air VOCs and relationships to changes in resident and resident activities, and
6) time series plots showing pre- and post-mitigation results for VOCs to demonstrate differential behavior of VOCs with large background contributions.

Population distribution statistics for site-specific background data can be used to indicate the probable percentage of samples that will exceed a specific regulatory goal purely due to background contributions.

While several state regulatory agencies will not allow JE modeling (using site-specific parameters) as a justification to avoid indoor air sampling, the basic concept may be used in combination with groundwater concentrations and indoor air concentrations to support non-groundwater source arguments over low concentration portions of a groundwater plume.

The VOC ratio approach for sites with multiple chlorinated VOCs has been evaluated at a site where an indicator VOC is also present. Henry's Law corrected median groundwater VOC ratios to 1,1-DCE were compared to measured indoor air VOC ratios over and near a large groundwater plume in Denver, Colorado. The results indicate that the TCE/DCE ratio provides an excellent marker of vapor intrusion versus background-dominated VOCs in indoor air. Prediction of the maximum probable vapor intrusion produced concentration of VOCs in indoor air is also possible using the VOC ratio approach. Such predictions can provide evidence of a *de minimus* vapor intrusion contribution for a VOC in indoor air.

Time series plots of indoor air VOCs at a residence can provide strong supporting evidence for indoor source arguments. The argument can be especially clear when one or more VOC shows dramatic changes in concentration related to a change in ownership or tenancy. For homes with mitigation systems installed, a comparison of pre-mitigation versus post-mitigation indoor air VOC concentrations can demonstrate the dominance of indoor sources for a VOC which does not show concentration reductions concomitant with other vapor intrusion derived VOCs.

INTRODUCTION

There are a number of possible approaches to defining "background" indoor air concentrations:

- Literature data
- Site-specific background sampling
- Paired sub-slab, indoor and outdoor air sampling
- Use of an "indicator" VOC as a measure of vapor intrusion
- Use of VOC ratios to fingerprint vapor intrusion

Literature data on "background" indoor air concentrations of VOCs has proliferated in the past few years. There a now a number of recent background studies in several states and countries, using comparable sampling methods (generally 24-hour SUMMA canister collection and TO-15 analysis) (Foster et. al., 2002; Kurtz and Folkes, 2002; Sexton et al, 2004; NYSDOH, 2004). There is still concern that such studies are location specific and may not apply in areas with different climates or industries.

While a number of states rely on literature data for an assessment of background concentrations, many states do not allow this approach and require site-specific background data. Costs can be very high to conduct a statistically valid background study and this approach generally cannot be justified at smaller sites.

The paired sub-slab, indoor and outdoor air approach selected by some states is a costly and more intrusive method that still does not necessarily resolve whether an indoor concentration is caused by background sources. Obtaining representative sub-slab concentrations may require several samples, raising the cost even more. Variations in sub-slab to indoor air attenuation can make this approach somewhat subjective when deciding whether indoor sources are significant contributors. Also, it is uncertain how this method can be applied in situations where crawl spaces rather than slabs are present.

Where an 'indicator" VOC is present (one with negligible background), the indoor air concentration of the indicator VOC can be used directly to evaluate risk as long as the other chemicals of concern (COC) at the site occur in predictable relative abundances.

The VOC ratio approach does not require an indicator chemical, but does require at least two poorly biodegradable COCs with one that generally has very low background indoor air concentrations. The subsurface source can be "fingerprinted" according to distinctive VOC ratios when the VOC with the lowest background is used in the denominator.

The present study has data available from two large sites in Colorado where site-specific background data are available, an indicator chemical is present, and several chlorinated VOCs have been measured in multiple media over long time frames. Thus, multiple approaches to determining the background contribution to indoor air concentrations can be evaluated. The focus of this study is on trichloroethylene (TCE), since the Colorado Department of Public Health and Environment (CDPHE) has recently instituted a lower indoor air action level of 0.8 μg/m^3 and a screening level of 0.016 μg/m^3 for this compound.

METHODS

There are a number of lines of evidence that can be used to demonstrate a non-groundwater source for TCE in indoor air. It is widely recognized that TCE is available in a number of consumer products as both an intentional and an unintentional ingredient. In many cases its presence is not noted on product labels.

One widely recognized approach to documenting sub-surface versus indoor sources for volatile organic compounds is the use of chemical ratios in the potential source (groundwater) and comparing those to the same chemical ratios in indoor air (CDPHE, 2004, Kurtz et. al., 2004 a and b). This approach is based on purely physical chemical rationale. For chlorinated organic compounds, which do not readily break down in groundwater or soil, the chemical ratios measured in the source are preserved during the volatilization process (subject to slight adjustments for relative volatility of the compounds). Therefore, a map of chemical ratios in the indoor air should reflect that in the underlying groundwater, if groundwater is the source of the indoor air chemicals.

High quality, direct measurements of soil vapor can provide supporting evidence for the predicted soil vapor and indoor air chemical ratios based on the more widespread groundwater data.

In addition, one would expect that the potential for vapor intrusion is generally greater in areas overlying higher concentration portions of the shallow groundwater and practically non-existent beyond the groundwater plume boundary.

There are several methods for demonstrating different sources for 1,1-DCE (dominantly groundwater derived) and TCE. These can include a comparison of the pre- and post-mitigation behavior of the two compounds in indoor air and the impact of changes in resident on the TCE concentration independent of the 1,1-DCE concentration. The relationship of indoor TCE concentrations to home remodeling/refinishing/solvent use can also be demonstrated.

Statistics for background indoor air in the Redfield and nearby areas indicate that a significant percentage of indoor air tests are expected to exceed 0.8 μg/m^3 TCE due to background, indoor sources.

Air samples discussed were collected over a 24-hour time frame in SUMMA canisters and were analyzed for eight VOCs by method TO-15 in selective ion monitoring mode.

RESULTS AND DISCUSSION

Spatial and Temporal Variation of Groundwater TCE/DCE Ratios. Historic groundwater data from individual shallow wells over the time period 1998 to 2001 were averaged in order to determine appropriate pre-mitigation groundwater ratios. The variability of TCE/DCE ratios in shallow groundwater in the test area is fairly low. Groundwater ratios were adjusted for the relative volatility of the two compounds by multiplying the groundwater concentrations by the ratio of their respective Henry's Law constants (at 10 degrees C). In this way, the resulting ratio represents the ratio predicted in the vapor phase that could directly impact indoor air via the vapor intrusion pathway. The majority of the volatility adjusted groundwater data has very low TCE to 1,1-DCE ratios (less than 0.11). The main exception to this occurs in the southeastern-most portion of the test area. In the latter area, TCE/DCE ratios rise to values greater than 0.5.

The generally low groundwater TCE/DCE ratios imply that any TCE in indoor air derived from groundwater will essentially always be less than the amount of 1,1-DCE derived from groundwater.

Time series graphs for 1,1-DCE, TCE, 1,1,1-TCA and the TCE/DCE ratio in shallow groundwater monitoring wells in the test area provide supporting evidence for the general constancy over time of TCE/DCE ratios in individual groundwater wells. This suggests that interpretations made from TCE/DCE ratios in pre-mitigation indoor air results remain valid at the present time. The TCA/TCE ratio tends to decrease over time due to the preferential breakdown of 1,1,1-TCA in groundwater. Interpretations derived from TCA/TCE ratios would need to be updated periodically.

Spatial Variation of Pre-Remediation Indoor Air TCE/DCE Ratios. Pre-remediation (and unremediated) indoor air TCE/DCE ratios were computed from the sample at each location with the highest 1,1-DCE concentration. This sample was chosen because 1,1-DCE provides the best indicator of vapor intrusion due to its high volatility and generally non-existent indoor background. In the cases where 1,1-DCE was not detected, the sample with the highest TCE concentration was selected. Although no TCE/DCE ratio was computed for the latter samples, other chemical ratios can be calculated for these to provide additional information. The latter situation generally occurred outside the mapped groundwater plume.

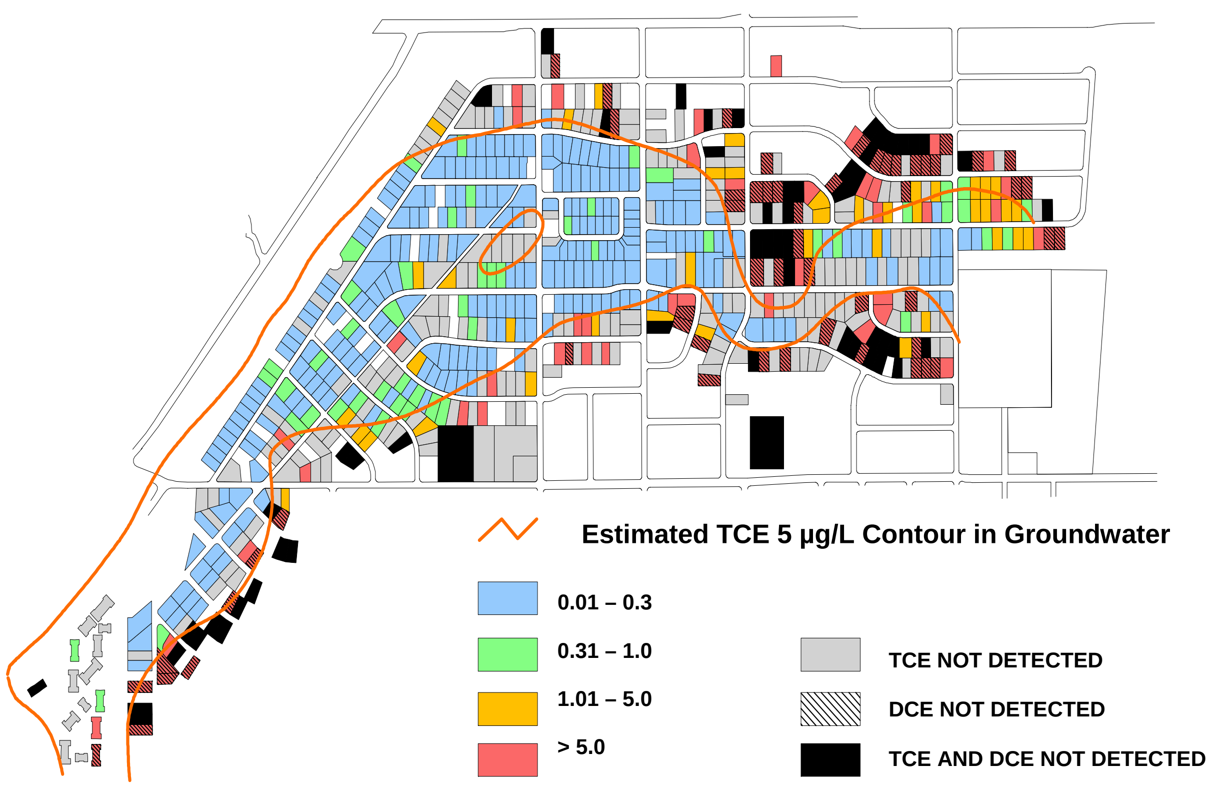

FIGURE 1. TCE/DCE ratios in pre-mitigation and unmitigated indoor air.

The variability of TCE/DCE ratios in pre-mitigation indoor air that overlies the groundwater plume is fairly low (Figure 1). The majority of the indoor air has very low TCE/1,1-DCE ratios (less than 0.3), similar to that in groundwater corrected for the relative volatility of the two compounds (their Henry's Law constants). The main exception to this occurs in the southeastern-most portion of the test area. In this southeastern area the TCE/DCE ratios in indoor air rise to greater than 1.0 over a small area that corresponds to that with higher groundwater ratios.

There are a number of locations within the plume that have anomalously high TCE/DCE ratios in indoor air compared to those in the underlying groundwater and surrounding vapor intrusion derived indoor air (locations shown in green, orange and pink on Figure 1). This is strongly suggestive of the dominance of indoor sources of TCE at these locations. Many of these locations correspond with those having maximum measured indoor air TCE concentrations greater than 0.8 $\mu g/m^3$.

The plume boundary and areas outside of the boundary are well marked by either non-detects for 1,1-DCE (and frequently TCE), or extreme TCE/DCE ratios that are not representative of those in nearby groundwater, suggesting indoor sources.

If desired, the measured indoor air 1,1-DCE at a location could be multiplied by the predicted TCE/DCE ratio to obtain a probable vapor intrusion derived concentration of TCE in indoor air.

Other Multimedia VOC Ratios. Groundwater and indoor air TCA/TCE ratios can provide supporting information for the interpretations made from the TCE/DCE ratios. A comparison of the TCA/TCE ratio between the two media can be used to identify locations with relative TCE abundances in indoor air that do not agree with those predicted based on underlying groundwater. In nearly all cases, locations with anomalous TCA/TCE ratios correspond with those where the TCE/DCE ratio also indicates a non-groundwater source for the TCE.

For example, unmitigated locations with TCE greater than 0.8 $\mu g/m^3$ and with TCE/DCE ratios indicative of a non-groundwater source generally correspond to locations with either non-detect 1,1,1-TCA (at a detection limit of 0.6 $\mu g/m^3$) or TCA/TCE ratios substantially below those than could be derived from groundwater. This strongly suggests a predominant indoor source for TCE in these situations.

Direct soil vapor measurements are available in the residential area. The measured ratios for TCE/DCE are all less than 0.5 and are in close agreement with those predicted from the Henry's Law corrected groundwater ratios in adjacent wells. The same correlation exists between the measured TCA/TCE ratios in soil vapor and the predicted ratios from adjacent groundwater wells. This strongly supports the use of volatility adjusted groundwater chemical ratios for prediction of indoor air chemical ratios derived from vapor intrusion.

The adjacent RCRA site (the CDOT MTL site) has single-family home mitigation system exhaust samples that have been collected on a quarterly basis over a 6-year time frame. The TCE/DCE ratios in these mitigation system exhaust samples show a high degree of consistency between locations as well as generally excellent reproducibility at individual locations. The measured soil vapor ratios closely correspond to those predicted from adjacent volatility corrected groundwater ratios. Because the spatial resolution of the mitigation system exhaust samples is greater than that generally obtainable from groundwater monitoring wells, mitigation system exhaust samples may be essential for supporting background arguments at sites with groundwater ratios showing large spatial variability.

Groundwater TCE Concentrations. TCE concentrations in shallow groundwater would be expected to have a relationship to areas with measurable TCE in indoor air based on Johnson-Ettinger modeling (using site-specific parameters). Areas beyond the mapped TCE plume boundary would not be expected to have significant vapor intrusion derived TCE in indoor air (Johnson et. al, 2002, CDPHE, 2004). This is contrary to the high indoor air TCE measurements in many locations beyond the plume boundary, suggesting a non-groundwater source for much of this TCE.

A number of locations with historically high concentrations of TCE in indoor air have shown decreasing indoor air TCE with time. This may be explained by their location over areas of the groundwater plume that have shown significant decreases in TCE concentration over time, most likely due to the action of the on-site groundwater remediation system over the past four years.

Time Series Graphs of Indoor Air Chemicals at Selected Locations. One way to demonstrate the presence of a non-groundwater source for indoor air TCE is to prepare time series plots of the concentrations of the four potential groundwater-derived chemicals in indoor air (1,1,1-TCA, 1,1-DCE, TCE, and PCE). If TCE is groundwater derived, changes in its indoor air concentration should closely mirror that of 1,1-DCE (a chemical considered to rarely have any background indoor air source). In addition, the relative abundance of groundwater derived TCE should be less than that of 1,1-DCE. One caution to note is that all VOCs in indoor air, regardless of source, will tend to vary together to some extent due to their common response to changes in air exchange rates caused by differences in the number of open windows in a home in different seasons.

Frequently TCE may show a relationship with either PCE or 1,1,1-TCA, but not 1,1-DCE. This is because TCE is commonly a contaminant in 1,1,1-TCA-rich consumer products (Henschler et. al., 1980) and is frequently formulated as a combination with PCE in other products (Sack et. al., 1992).

There are several other methods for demonstrating different sources for 1,1-DCE (dominantly groundwater-derived) and TCE. These can include a comparison of the pre- and post-mitigation behavior of the two compounds in indoor air and the impact of changes in resident on the TCE concentration. The relationship of indoor TCE concentrations to home remodeling/refinishing/solvent use can also be demonstrated.

A time series plot of the concentrations of the four potential groundwater-derived chemicals in indoor air (1,1,1-TCA, 1,1-DCE, TCE, and PCE) shown in Figure 2 illustrates where background sources are the apparent cause of TCE concentrations above 0.8 $\mu g/m^3$, as indicated by dramatic changes in the TCE concentration relative to 1,1-DCE when there is a change in resident in a particular home. This effect is likely due to changes in consumer product use/storage and furnishings between different residents as well as the impact of remodeling, recarpeting, or cleaning of a home prior to sale.

Statistics for Background TCE in Indoor Air. For the two sites investigated, 1,1-DCE is at least three times more abundant in groundwater than TCE or PCE. Because 1,1-DCE

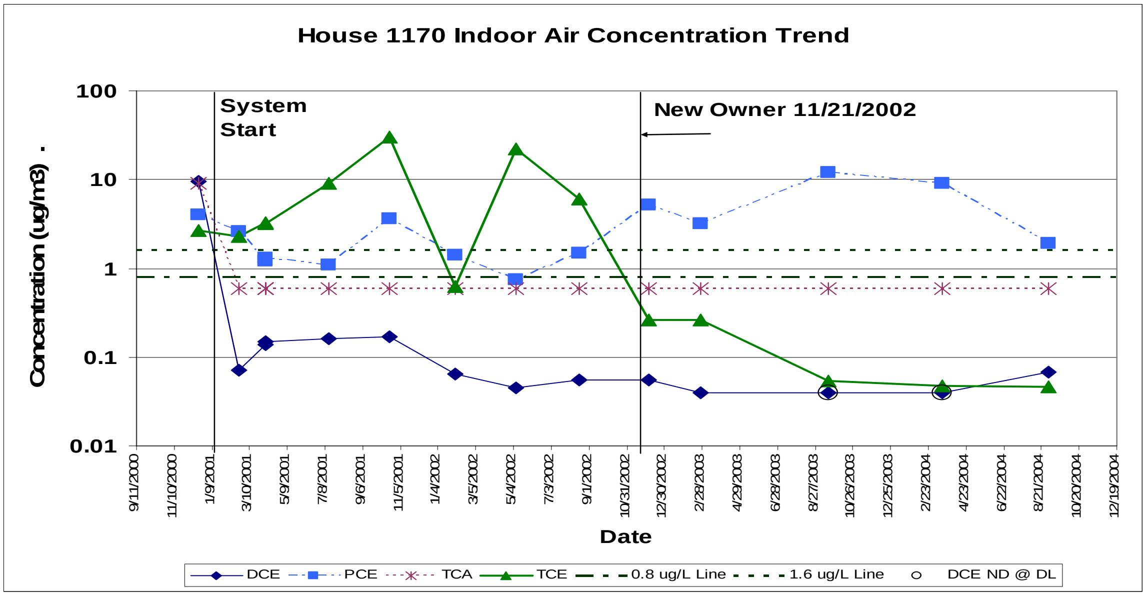

FIGURE 2. Impact of change of resident on indoor VOC concentrations

has the highest volatility of these three compounds, soil vapor derived from groundwater will be even more enriched in 1,1-DCE. The reporting limits for 1,1-DCE in indoor air are quite low (0.04 µg/m^3) and are comparable to those for TCE (0.02 to 0.26 µg/m^3).

In the above situation, post-mitigation indoor air with non-detectable 1,1-DCE will have no detectable groundwater derived TCE or PCE present because of the relative abundance and volatility of the three compounds in groundwater. The post-mitigation indoor air results from homes in the Redfield Site test area have been evaluated statistically. The results of this evaluation indicate that in approximately 6% of the samples, background (indoor source) TCE will exceed 1.6 µg/m^3 (Table 1). Likewise, background TCE is expected to exceed 0.8 µg/m^3 in approximately 15% of the samples. The median background TCE concentration is 0.14 µg/m^3. These results are similar to those recently found at other sites in Colorado, New York and Wisconsin (Foster and Kurtz, 2002; NYSDOH, 2004; Sexton et. al. 2004).

TABLE 1. Post-mitigation background indoor air with DCE <0.04 µg/m^3

Compound	Valid N	Percent Detects	Median	Minimum	Maximum	75th Percentile	85th Percentile	90th Percentile	95th Percentile
Methylene Chloride	1026	70.7	0.62	<0.42	230	1.9	3.8	6.4	13
1,1,1-TCA	1026	37.8	<0.6	<0.6	480	1.2	2.1	3.5	5.3
1,2-DCA	1026	20.7	<0.08	<0.08	1.10	<0.08	0.089	0.11	0.16
PCE	1026	64.4	0.92	<0.068	440	1.8	2.9	4.2	6.5
TCE	352	100	0.14	0.007	36	0.39	0.8	1.1	1.9
Vinyl Chloride	1026	16.7	<0.02	<0.02	3.6	<0.02	0.021	0.027	0.047

CONCLUSIONS

- Numerous lines of evidence may be available to separate background from vapor intrusion sources of indoor air VOCs
- Sites with multiple groundwater VOCs in fairly consistent proportions are most amenable to this approach
- In all cases a household survey and questionnaire are essential for identification of obvious sources
- Ratios allow prediction of the maximum probable vapor intrusion derived concentration of VOCs in indoor air
- Ratios allow definition of the outer extent of significant vapor intrusion
- Ratios identify locations with dominant indoor sources of VOCs.

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