

## Forensic Tools for Identifying the Source of VOCs During Vapour Intrusion Assessments

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### Introduction

Subsurface vapour intrusion to indoor air [1] is often the pathway of greatest potential risk to human health at sites contaminated with volatile organic compounds (VOCs) like chlorinated solvents and petroleum hydrocarbons. This is because humans inhale about 20,000 L of air each day, which is 10,000 times larger than the volume of water consumed. As a result, the concentrations in air that pose no significant risk are about 10,000 times lower than drinking water standards for the same compounds. Consumer products and building materials contribute VOCs to indoor air, so any time an indoor air sample is collected and analyzed as part of a vapour intrusion investigation, VOCs will almost certainly be detected, which is challenging to communicate to most building occupants. Furthermore, several compounds (benzene, chloroform, carbon tetrachloride, 1,2-dichloroethene, tetrachloroethene [PCE], naphthalene and ethylbenzene and potentially others) are frequently present at concentrations above risk-based screening levels [2]. As a result, there is a very high rate of false-positive outcomes (falsely concluding that vapour intrusion poses an unacceptable health risk) that are actually attributable to background VOC sources. In urban environments, even outdoor air can pose an unacceptable risk. This abstract and accompanying presentation describe several methods developed by the authors to resolve the relative contributions of background and subsurface sources on indoor air quality.

### Materials and methods

Several lines of evidence are available, and often two or more provide a more convincing argument. The selection of the most convincing and cost-effective line(s) of evidence is site-specific and requires professional judgement. Options include:

1. **Compound ratio analysis:** If there are two or more compounds present in the subsurface, their relative proportions are compared for soil gas and indoor air samples. If a certain chemical is contributed by a source inside the building, the relative proportion in indoor air will be higher than in soil gas.
2. **Attenuation Factor Calculations:** the ratio of the indoor air concentration of a certain VOC divided by the subsurface concentration is referred to as the “attenuation factor”. In most cases, the indoor air concentration is lower than the subsurface concentration by a factor of 100 to 10,000 or more, and commercial/industrial buildings generally have more dilution than residential buildings. Compounds attributable to background sources seldom have subsurface concentrations more than 10 times higher than the indoor air concentrations.
3. **Comparison to literature ranges for background VOC concentrations:** measured indoor air concentrations are compared to ranges published in surveys of indoor air quality in buildings not associated with contaminated land [1,2]. If the concentrations are within background ranges, the compound(s) are more likely to be attributable to a background source.
4. **Comparison to outdoor air samples:** outdoor air samples should be collected coincidentally with indoor air samples for quality assurance and control. If the concentrations measured in indoor air are similar to

or lower than the concentrations in outdoor air, the source of VOCs is likely outdoor air.

5. **Building pressure cycling:** A fan is used to: a) withdraw air from the building, which creates a negative pressure inside and promotes vapour intrusion, then b) blow air into the building, which creates a positive pressure and inhibits vapour intrusion. Indoor air samples are collected after each phase has been conducted for a period sufficient to approach a steady condition. VOCs originating in the subsurface will have higher concentrations under negative pressure and lower concentrations under positive pressure, but VOCs from background sources may have similar concentrations under both conditions.
6. **Compound-specific stable isotope analysis:** Atoms of carbon, hydrogen and chlorine have stable isotopes, and the atoms are the building blocks for most of the VOCs of concern in vapour intrusion. Several processes occurring in the subsurface (degradation, volatilization, diffusion) cause changes in the proportions of the stable isotopes in ways that do not happen for VOC sources inside the building. Samples of soil gas and indoor air are analysed for the isotope ratios. If the results are comparable, the source is likely vapour intrusion, but if the indoor air results are similar to published results for consumer products and not similar to the soil gas samples, a background source is implicated.
7. **Real-time analysis with a portable mass spectrometer (MS):** Portable MS instruments can provide real-time VOC concentration data that can be used to locate and identify interior background sources of VOCs. Several different instruments are available, with differing levels of sensitivity, speed and cost, and the selection depends on the site-specific chemicals of concern.

## Results and discussion

Some examples of how these tools are employed are presented here.

Figure 1 shows an example of the compound ratio analysis. Three hydrocarbons are plotted on the three axes, and distinct symbols are used to represent soil gas, indoor air and outdoor air. The indoor air and outdoor air data are clustered near each other and the soil gas data show notably more benzene and toluene, but less ethylbenzene. This supports a conclusion that outdoor air is the dominant contribution to VOCs in indoor air.

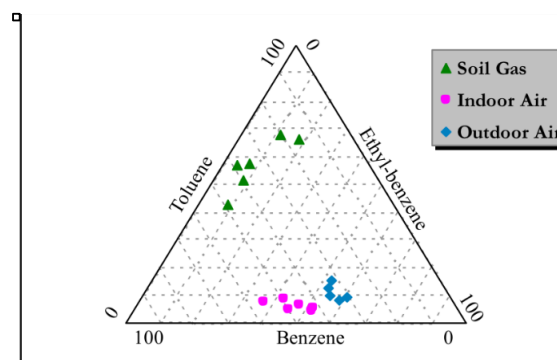


Figure 1: Compound ratio analysis plot

Figure 2 shows the attenuation factors calculated for paired sub-slab and indoor air samples, with benzene (the primary compound of concern) in blue and all other compounds in green. The range of attenuation factors expected from mathematical modeling was 0.01 to 0.001, which is consistent with experience at other similar buildings where vapour intrusion was confirmed. All of the data show attenuation factors that are higher than expected, many are greater than one (meaning the indoor air concentration is higher than the sub-slab concentration and there are almost as many values greater than one as less than one. The attenuation factors also show no clear trend as a function of the soil gas concentration

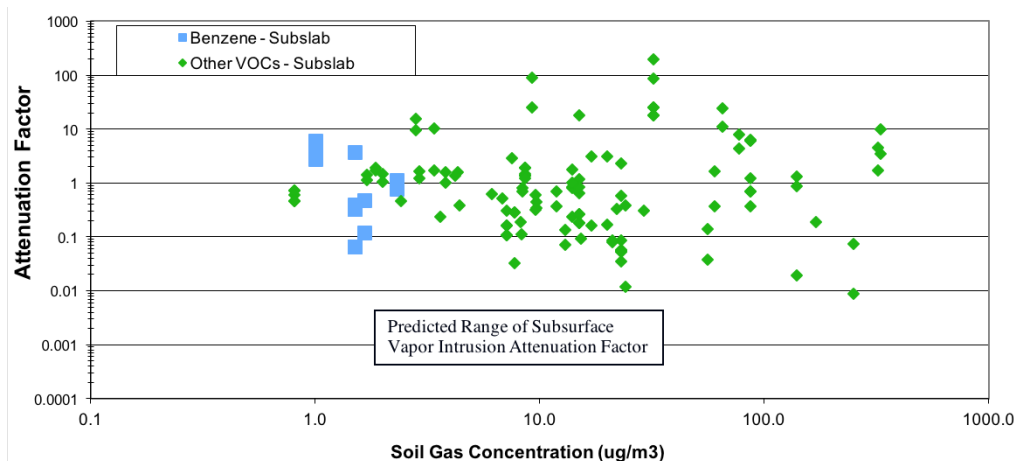


Figure 2: Attenuation factor analysis

Figure 3 shows an example of building pressure cycling. The concentration of trichloroethene (TCE) was low (<2  $\mu\text{g}/\text{m}^3$ ) under natural building pressure and ventilation conditions, but increased to 11  $\mu\text{g}/\text{m}^3$  under negative pressure and decreased again to <1  $\mu\text{g}/\text{m}^3$  under positive pressure. This trend is indicative of a sub-surface source.

Figure 4 shows an example of compound-specific stable isotope analysis. Both carbon ( $^{13}\text{C}$ ) and chlorine ( $^{37}\text{Cl}$ ) isotopes were analysed in a sample of soil gas and indoor air from two buildings. The results for one building match up closely with the soil gas sample indicating subsurface vapor intrusion as the source. The results of the other building do not match up with the soil gas and are within published ranges for manufactured products, indicating the source is a consumer product inside the building.

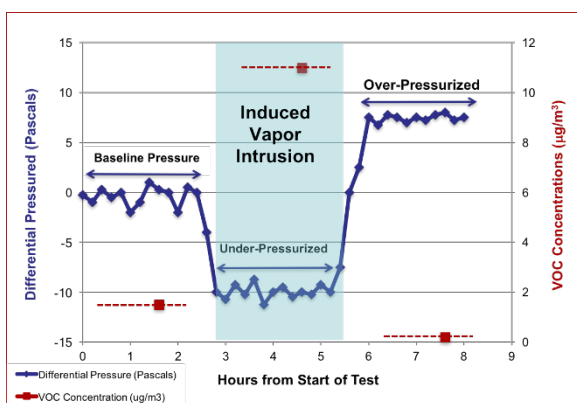


Figure 4: Building pressure cycling analysis

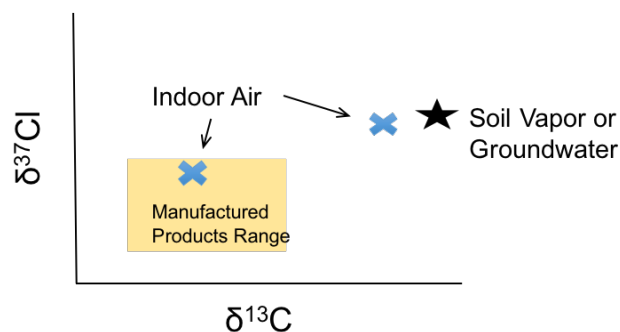


Figure 3: Compound-specific stable isotope analysis

Figure 5 shows an example of a real-time mass spectrometer (MS) analysis. A dual quadrupole MS capable of measuring TCE and PCE concentrations to as low as 1 part per billion every second was used to screen two buildings. At the locations of interior sources of TCE and PCE, the instrument clearly showed elevated concentrations. Removal of these background sources resulted in indoor air concentrations that posed no significant risk.

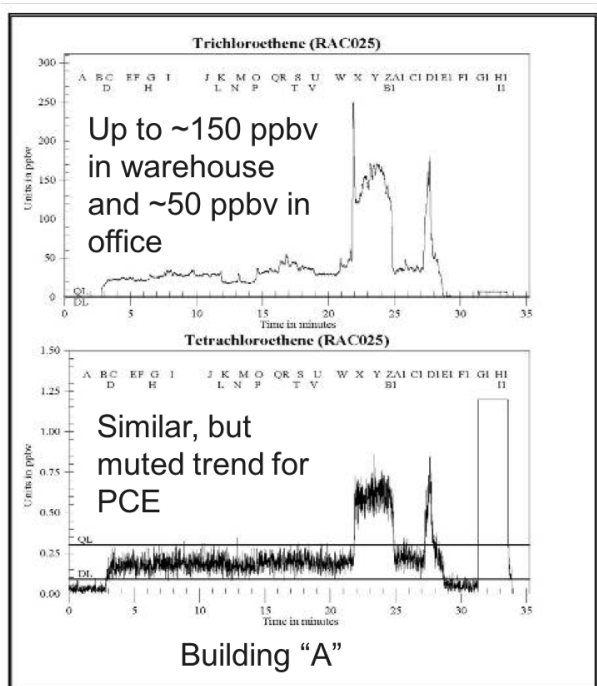


Figure 12c Unit 007 Survey Six for Trichloroethene and Tetrachloroethene

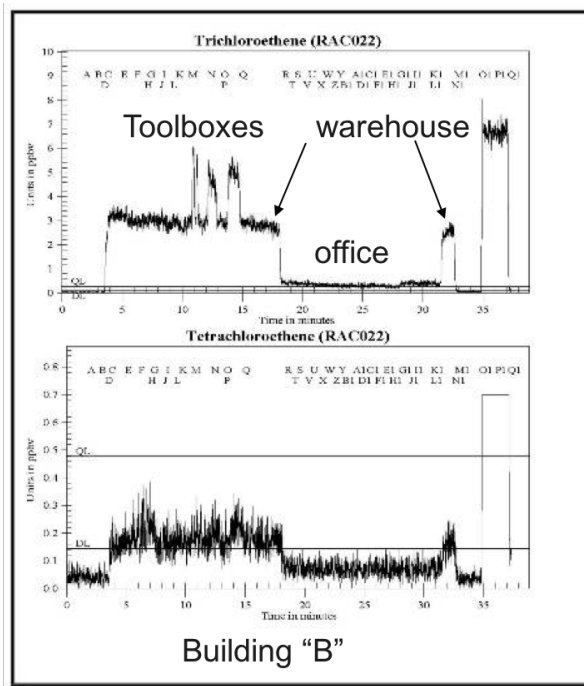


Figure 10c Unit 007 Survey Four for Trichloroethene and Tetrachloroethene

Figure 5: Real-time mass spectrometer analysis

### Acknowledgements

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### References

1. Health Canada, 2010. Federal Contaminated Site Risk Assessment in Canada, Part VII: Guidance for Soil Vapour Intrusion Assessment at Contaminated Sites, ISBN: 978-1-100-17674-1.
2. United States Environmental Protection Agency, 2011. Background Indoor Air Concentrations of Volatile Organic Compounds in North American Residences (1990–2005): A Compilation of Statistics for Assessing Vapor Intrusion, EPA 530-R-10-001, June 2011.