

**USE OF COMPOUND-SPECIFIC  
ISOTOPE ANALYSIS TO  
DISTINGUISH BETWEEN VAPOR  
INTRUSION AND INDOOR SOURCE  
OF VOCs**



# INTRODUCTION

While the collection and analysis of sub-slab soil gas samples and indoor air samples often presents a convincing case for the risks that may be attributed to vapor intrusion,





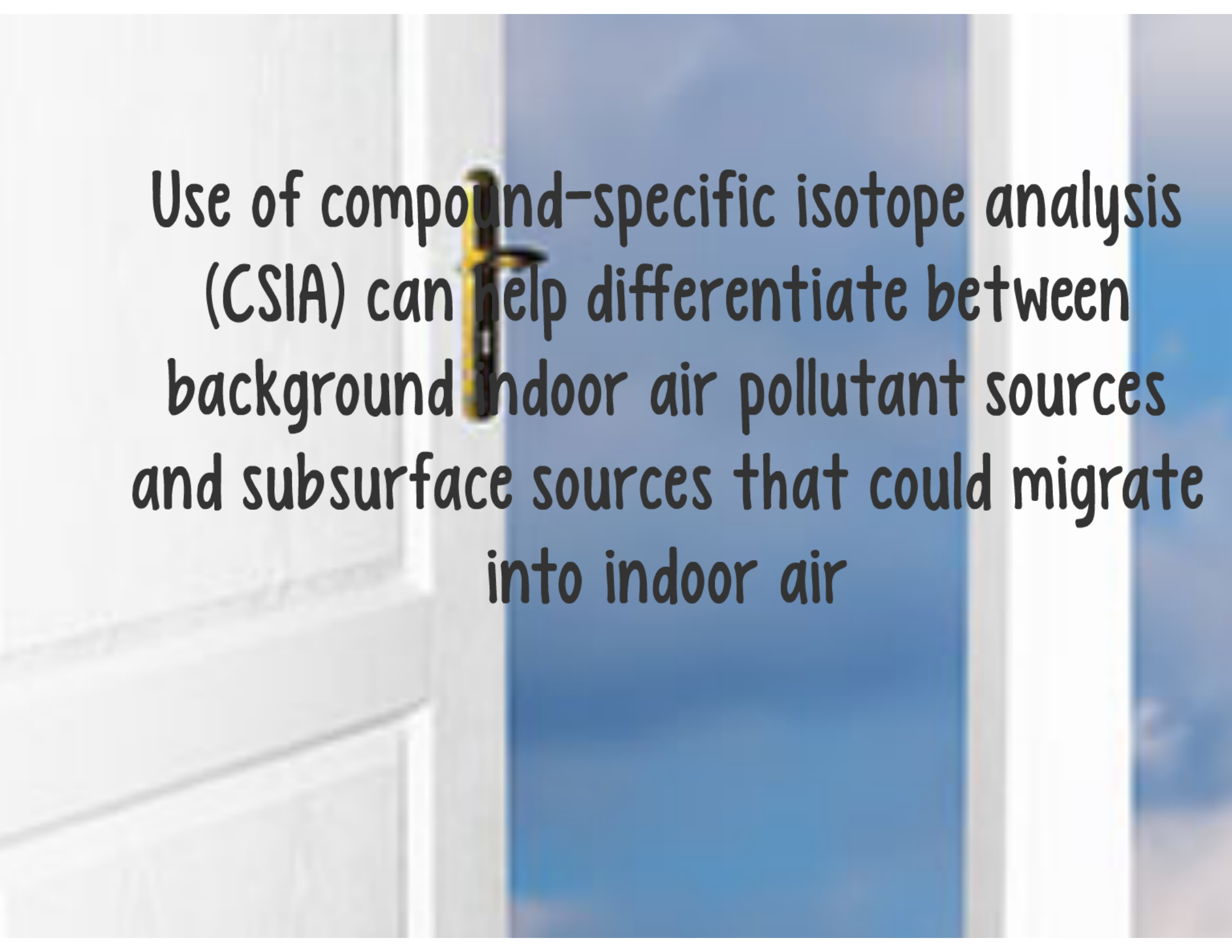
Vapor intrusion assessments are often complicated by the presence of "background" sources of indoor air pollutants

- Chemical product used for industrial processes
- Use of cleaning products
- Storage of household chemicals
- ...



It can be challenging to review chemical concentration and determine whether detected concentrations of benzene in indoor air are caused by indoor painting operations or by vapor intrusion from a known groundwater plume of gasoline





Use of compound-specific isotope analysis (CSIA) can help differentiate between background indoor air pollutant sources and subsurface sources that could migrate into indoor air



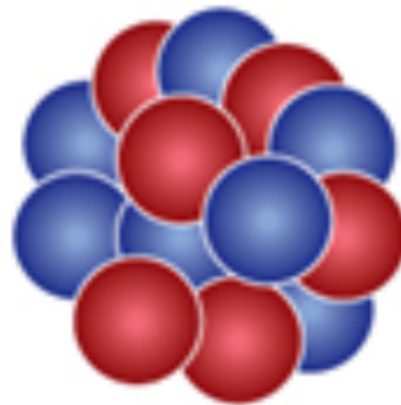
## IMPLEMENTATION

Many elements occurs as different isotopes species, differing in their number of neutrons present in the nucleus





carbon-12  
98.9%  
6 protons  
6 neutrons



carbon-13  
1.1%  
6 protons  
7 neutrons



carbon-14  
<0.1%  
6 protons  
8 neutrons



The change in the ratio of stable isotopes is called fractionation

These differences can be used to:

- Distinguish between different sources of contaminant
- Understand biodegradation and other transformation processes occurring in the environment



CSIA measures the carbon, chlorine and/or hydrogen isotope ratio for individual chemicals. The results are not reported as direct ratios of the isotopes but expressed relative to an international standard.

Measures are compared to the standard (PDB) and results are reported in parts per thousand.





$$\delta^{13}\text{C} (\text{‰}) = [((^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}) / (^{13}\text{C}/^{12}\text{C})_{\text{standard}}] \times 1000$$



Various processes can change the isotopic ratios of a compound. Molecular bonds containing the lighter isotopes are broken at faster rates than those containing the heavier isotopes

The parent compound becomes enriched in heavy isotopes (less negative values) while transformation products end with less of the heavy isotopes (more negative values)



Now let's turn our  
attention to the CSIA  
approach



# CSIA approach

- 1) Determination of stable isotope ratios of the targets VOCs present in the air ( $^{13}\text{C}/^{12}\text{C}$ ,  $^{37}\text{Cl}/^{35}\text{Cl}$  for PCE and TCE;  $^{13}\text{C}/^{12}\text{C}$  and  $2\text{H}/^1\text{H}$  in the case of benzene)
- 2) Use of those ratios to differentiate between VOCs sourced from the subsurface (true vapor intrusion) and those sourced from miscellaneous household products.

## Hint 1

Isotope ratios for VOCs originating from different manufactured sources are within a defined range

This range is small compared to the range of isotope ratios created by isotope fractionation effects that occur in the subsurface

## Hint 2

VOCs originating from subsurface sources commonly undergo biodegradation in groundwater and later in the unsaturated soil prior to entering indoor air

## Hint 3

The consequence of isotope fractionation is that isotope composition of VOCs originating from the subsurface is often clearly different than that of undegraded manufactured products acting as indoor sources of the same VOC

## Hint 4

This difference allows the successful differentiation between VOCs from indoor sources and those from true vapor intrusion sources



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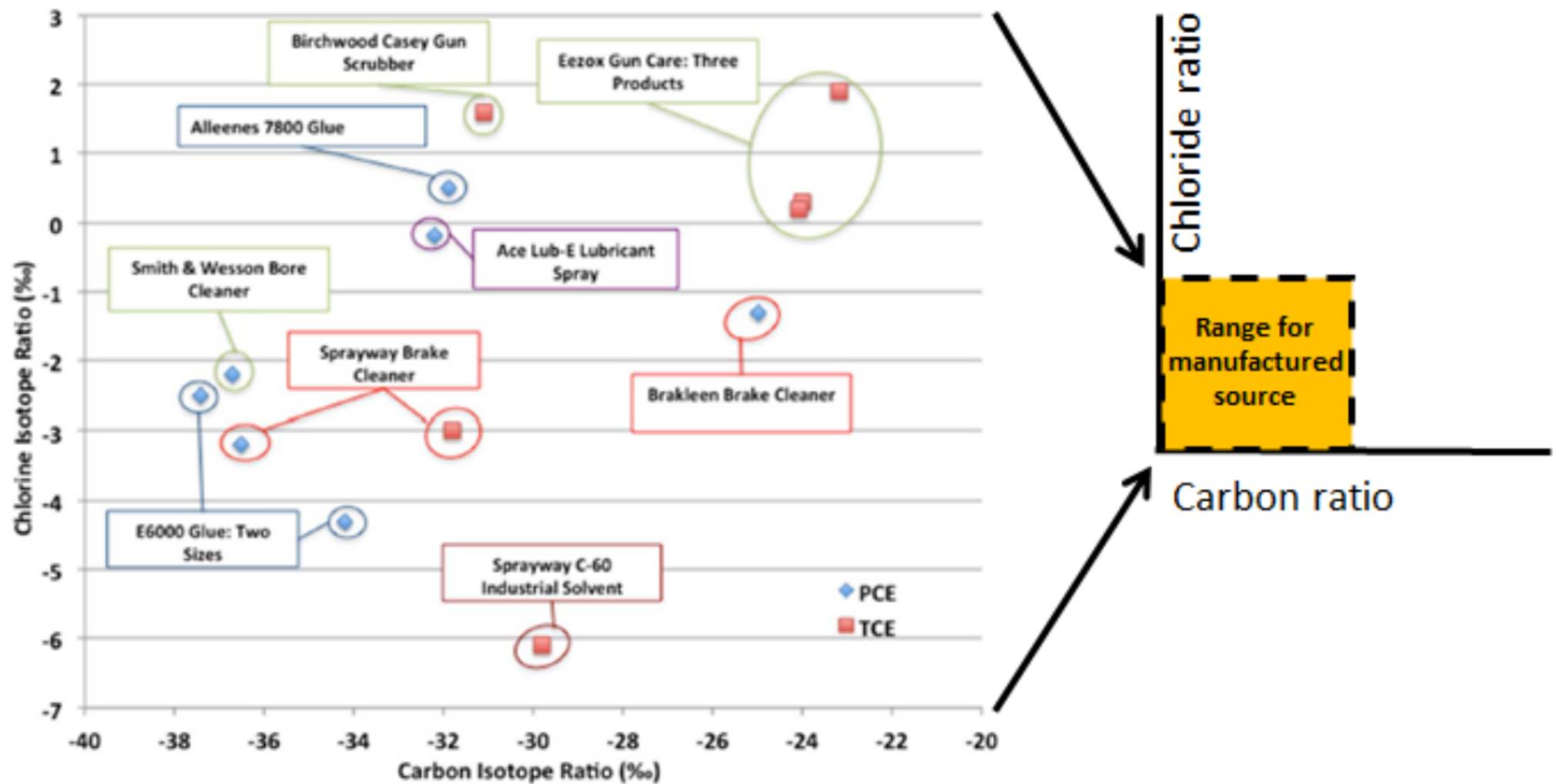


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From Thomas E. McHugh – GSI Environmental



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# Hint 2

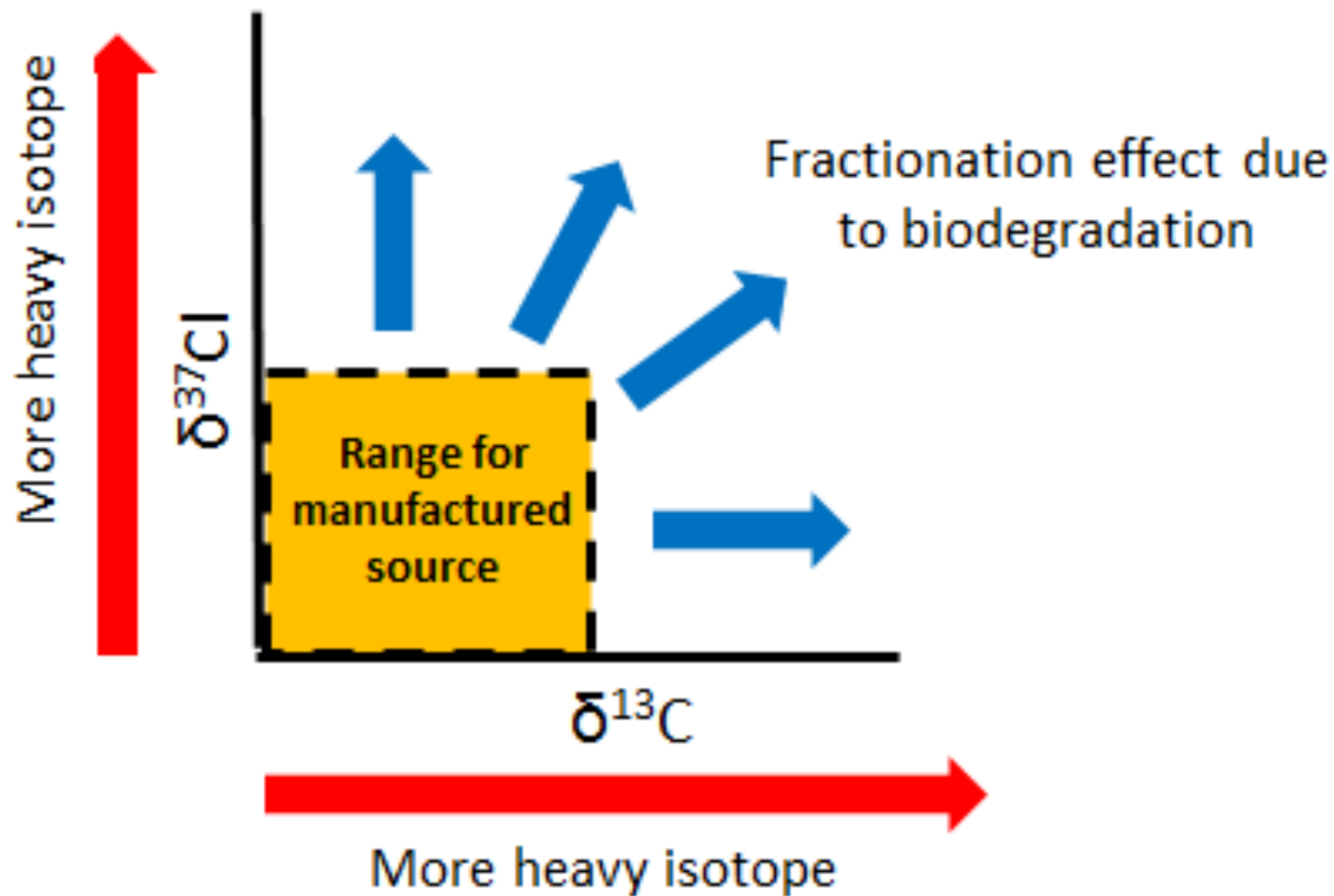
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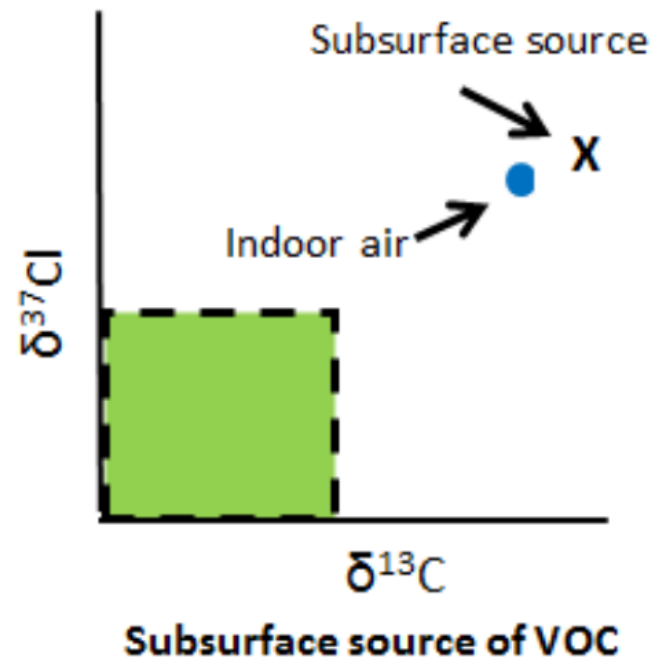
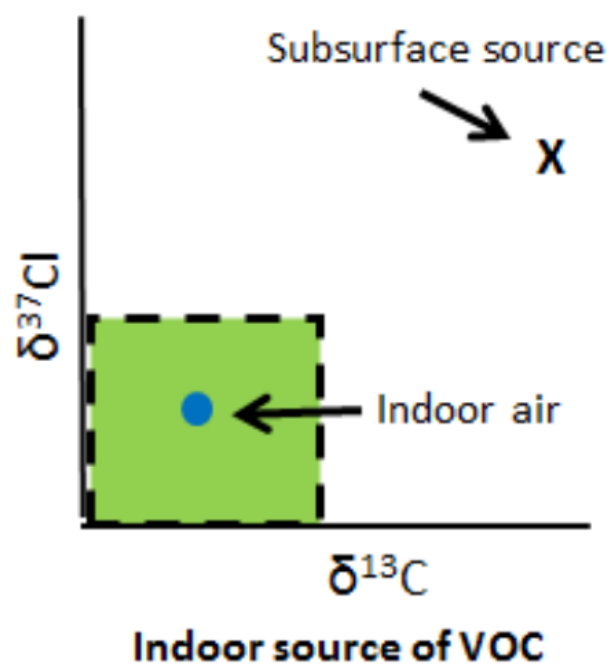
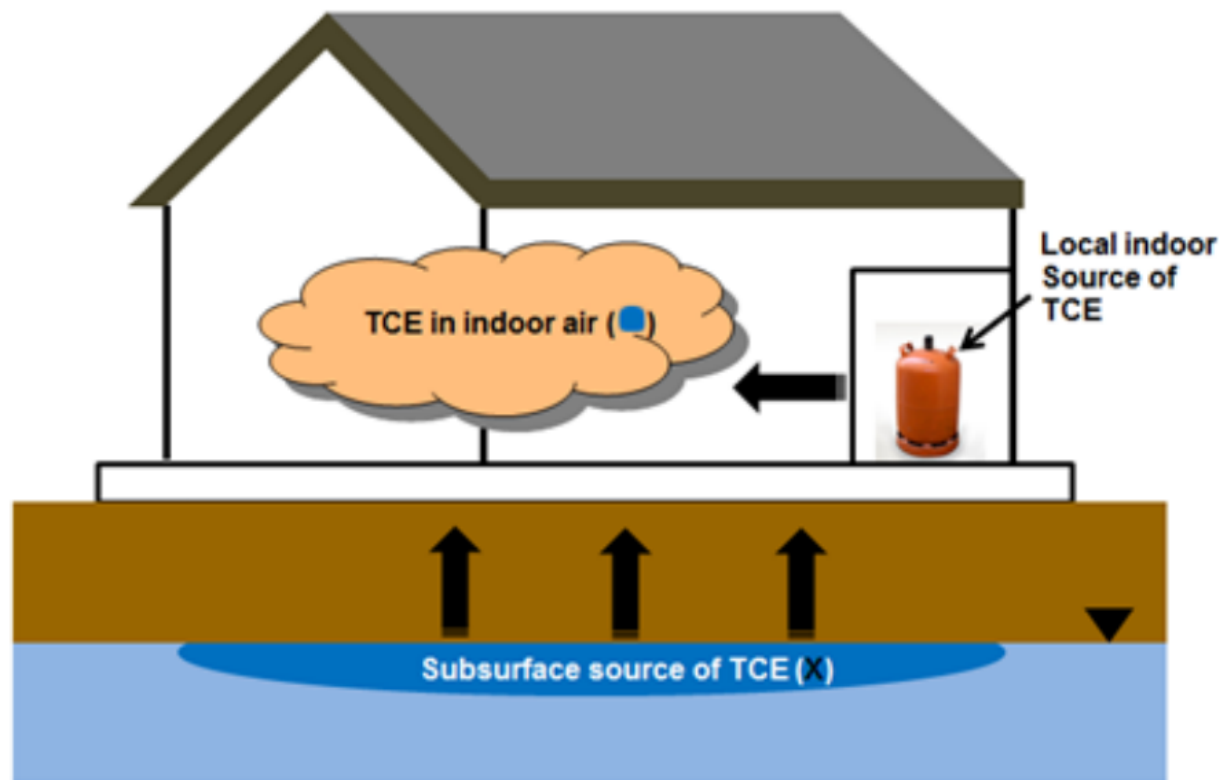




# Hint 4

This difference allows the successful differentiation between VOCs from indoor sources and those from true vapor intrusion sources







A white door with a glass panel and a yellow handle. The text is overlaid on the door.

Let's take a look at  
investigations  
protocol



## 1) SAMPLING

### Subsurface sampling locations

Groundwater samples are recommended for characterization of isotope ratios in the subsurface source.

Isotope ratios in soil gas are more variable and, in some cases, less representative of vapors potentially entering the building





## Indoor air sampling locations

For most buildings, indoor air can be characterized through the collection and analysis of a single indoor air sample from the area of the building most likely to be impacted by vapor intrusion. For larger buildings one sample from each area may be justified.



## Sampling of water samples

Water samples for CSIA can be collected using the same sampling procedures used to collect samples to measure VOC concentrations

Samples for the analysis of carbon or hydrogen isotopes should be preserved using hydrochloric acid

Samples for the analysis of chlorine isotopes should be preserved using sulfuric acid



## Sampling of vapor samples

Vapor samples for CSA can be collected using canisters or sorbent tubes



The appropriate sample method is determined based on the sample volume required.



## Sample volume

1. Accurate measurement of carbon and chlorine isotope ratios requires 100 ng of the target VOC.
2. For a target petroleum VOC, the accurate measurement of carbon isotope ratios requires approximately 50 ng; accurate measurement of the hydrogen isotope ratio requires approximately 1000 ng.
3. The required sample volume is equal to the required mass divided by the concentration in the source medium.  
For sample volumes greater than 3 liters, use of an adsorbent tube



## 2) DATA INTERPRETATION

The measured isotope ratios for the subsurface samples and for indoor air can be used to determine the likely source of the target VOC in indoor air, based on:

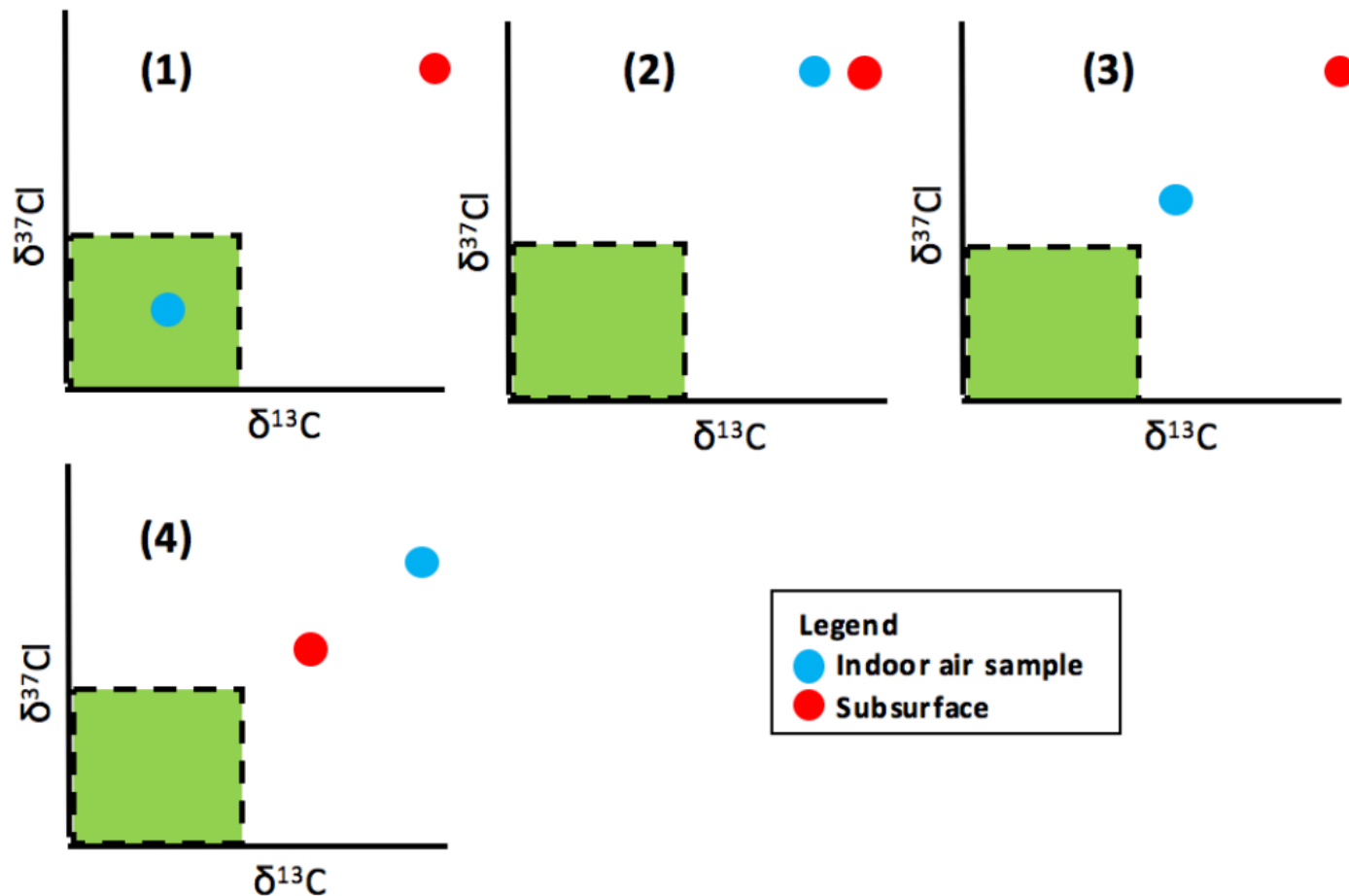
- The similarity of the subsurface and indoor air results
- Comparison to isotopic signatures of indoor sources (e.g., manufactured products)



A photograph of a white door with a brass handle and a blue-tinted glass panel. The text is overlaid on the lower half of the image.

Potential results and interpretations based on a two isotope ratios are illustrated hereinafter





- (1) Strong evidence that an indoor source is the primary source of VOCs in indoor air
- (2) Strong evidence that the subsurface source is the primary source of VOCs in indoor air
- (3) Evidence of mixed subsurface and indoor air sources
- (4) Evidence that the subsurface source is the primary source of VOCs in indoor air, additional enrichment in the heavy isotopes is likely occurring between the subsurface measurement point and the target building



## Conclusion

The strength of the overall conclusion should be weighted based on:

- The number of samples used to characterize the indoor air and subsurface source
- The consistency of the results with other lines of evidence





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