An Important 2nd-Look at the Lab-reported Indoor Air Total Petroleum Hydrocarbon Concentrations

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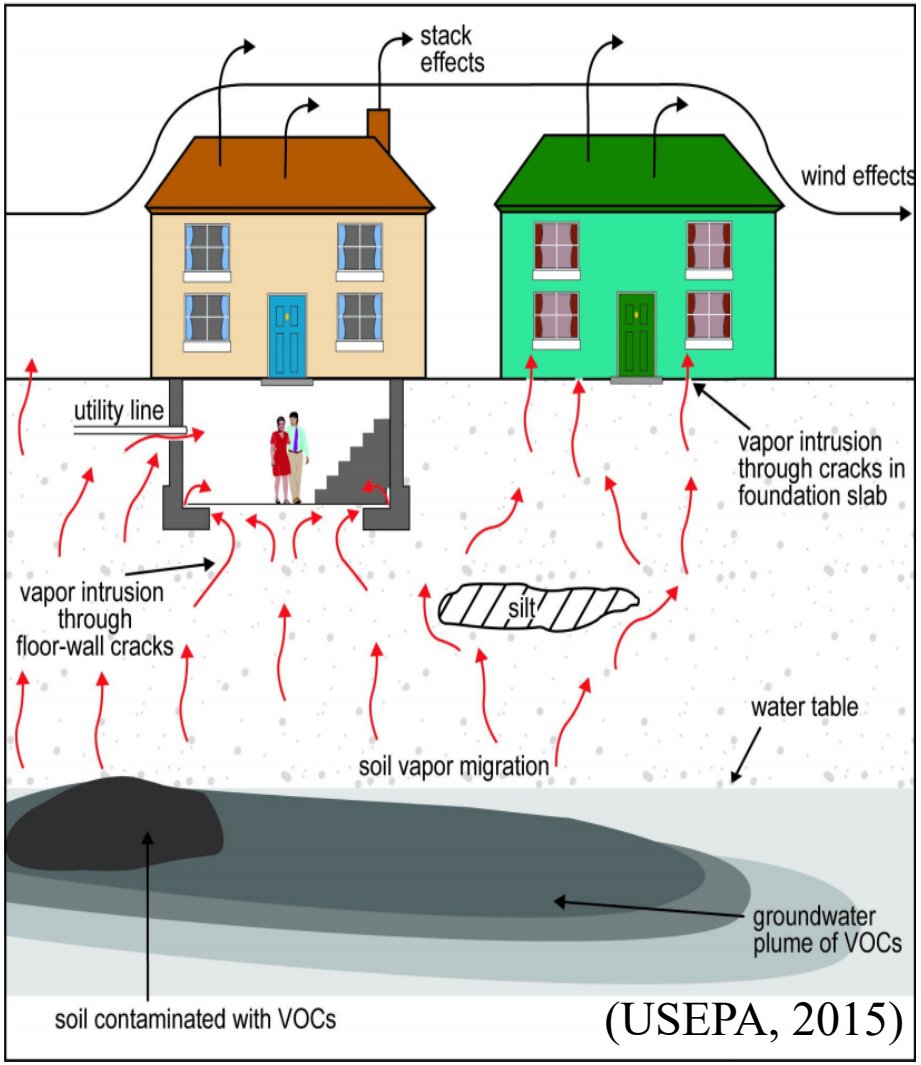
Outline

- Background:
  - ✓ Vapor Intrusion (VI)
  - ✓ Importance of indoor air (IA) chemical analysis in VI
- Indoor air chemical analysis in VI
  - ✓ Current IA analytical methods and limitations
  - ✓ Field causes for IA analysis limitations
- Case study:
  - ✓ Site information
  - ✓ Problem encountered in IA data
  - ✓ Solution
- Lessons learned and remaining questions

What is Vapor Intrusion (VI)?

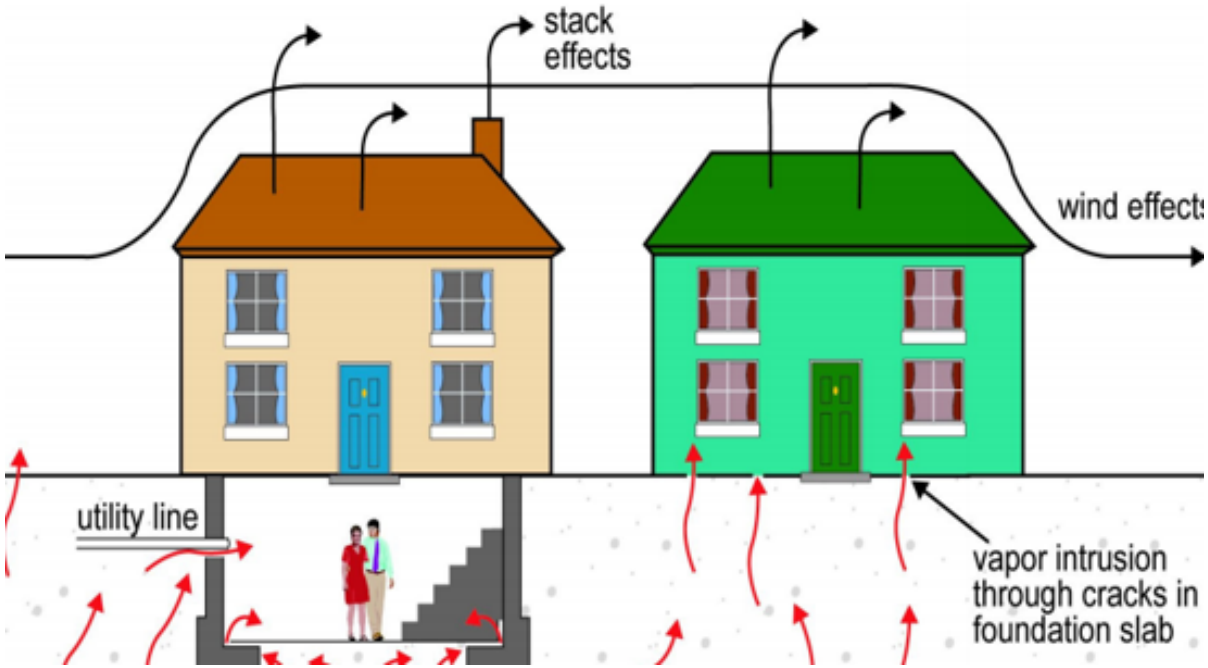
USEPA: The migration of volatile chemicals from contaminated soil and groundwater plumes into buildings.

- ✓ Not visible and most of the cases not noticeable;
- ✓ Long-term risk exposure and very low tolerance of risks
- ✓ A risk exposure pathway that needs to be evaluated at every site before closure/transfer **(Cannot escape!!!)**



(USEPA, 2015)

Importance of Indoor Air Analysis in VI



IA chemical concentrations are:

- A direct measurement of actual human exposure and basis for inhalation risk evaluation calculation
- Used to compare to established VISLs for screening site in/out (**$$$**)

Current IA Analytical Methods & Limitations

Target Analytes	Most Common IA Sample Collection Method	Most Common Lab Analysis Method	Common Limitations in VI Data Usage	Causes for Limitations
Individual VOCs	Summa Canister	EPA Method TO-15	Elevated RLs;	Unwanted presence of non-target compounds
TPH	Summa Canister	EPA Method TO-15 EPA Method TO-3	Elevated RLs; non-PHCs	Unwanted presence of non-target compounds; No subtraction of non-PHC
TPH/APH fractions	Summa Canister	TO-15 MassDEP-APH	Elevated RLs; non-PHCs	Unwanted presence of non-target compounds; No subtraction of non-PHC
SVOC	Active sorbent tubes	EPA Method TO-17	Elevated RLs; Overloaded sorbent tubes	Unwanted presence of non-target compounds; Wrong/No estimation of IA concentrations

Note:
VOC: volatile organic chemical; TPH: Total petroleum hydrocarbon;
SVOC: Semi-volatile organic chemical; RL: Reporting limit; PHC: Petroleum Hydrocarbons

Top 3 most problematic IA data in the eyes of a VI expert:

#1: RLs>VISLs: no VI risk conclusions can be drawn with confidence

#2: Lump-sum TPH or TPH fractions: no idea what is in the numbers

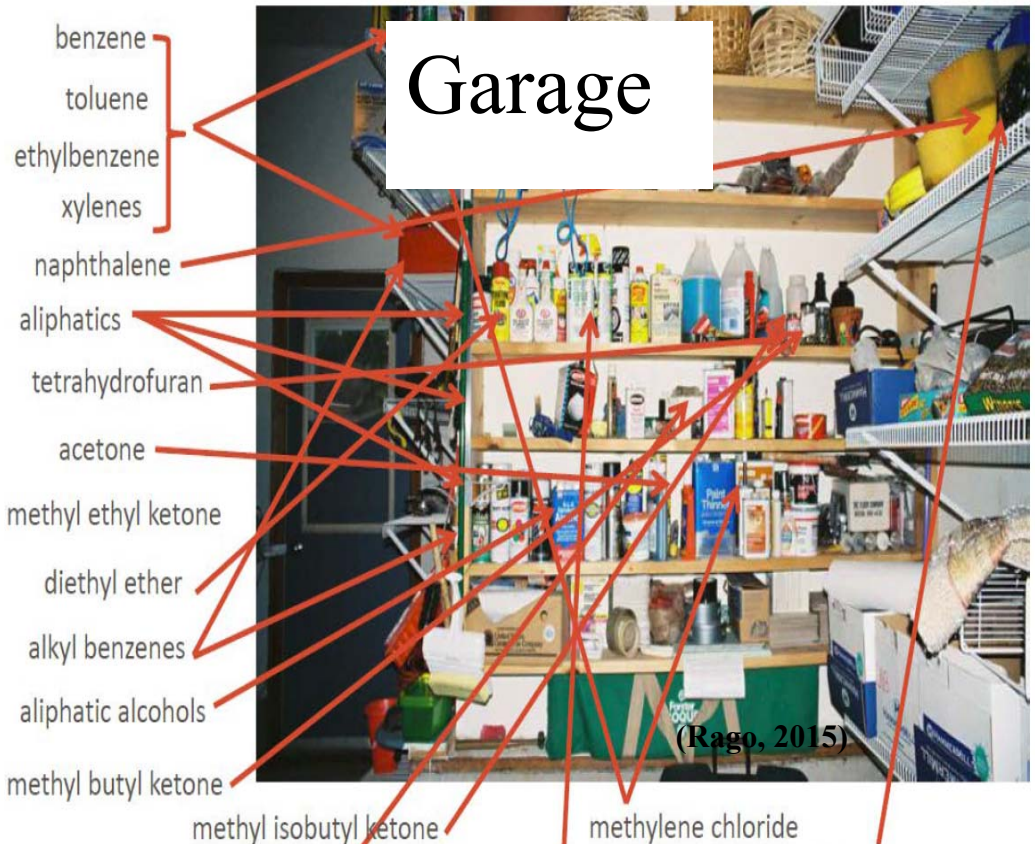
#3: Sorbent tube overloaded: no valid data available for risk evaluation

Low to Ultralow IA Screening Levels

Parameter	Frequency of detection	50th percentile Concentrations	95th percentile concentrations	Common TO-15 Lab RLs (no dilution, 6 L)	EPA (TR=1E-06/ THQ=1.0) RSLs
1,2-dichloroethane	100%	0.17	1.20	2.0	0.11
Benzene	98%	0.9	12	1.6	0.36
Ethylbenzene	94%	0.78	6.00	2.2	1.1
C5-C8 Aliphatic	**90%**	**81**	**414**	**~12**	**58***
C9-C12 Aliphatic	**84%**	**33**	**196**	**~10**	**68***
Naphthalene	80%	0.36	1.30	5.2	0.083
Xylene	66%	2.70	24.00	2.2	100
C9-C10 Aromatics	**40%**	**<9.2**	**38.00**	**~12**	**10***
1,2-dibromoethane	0%	<0.83	<1.3	3.8	0.0047
Unit: ug/m^3					
* MassDEP Residential Indoor Air Threshold Values					*(From MDEQ, 2012)*

- Low/ultralow ESLs make it hard to get RLs < ESLs
- Background concentrations > ESLs
  Background concentrations > RLs

Field Interference for IA analysis: IA sources?

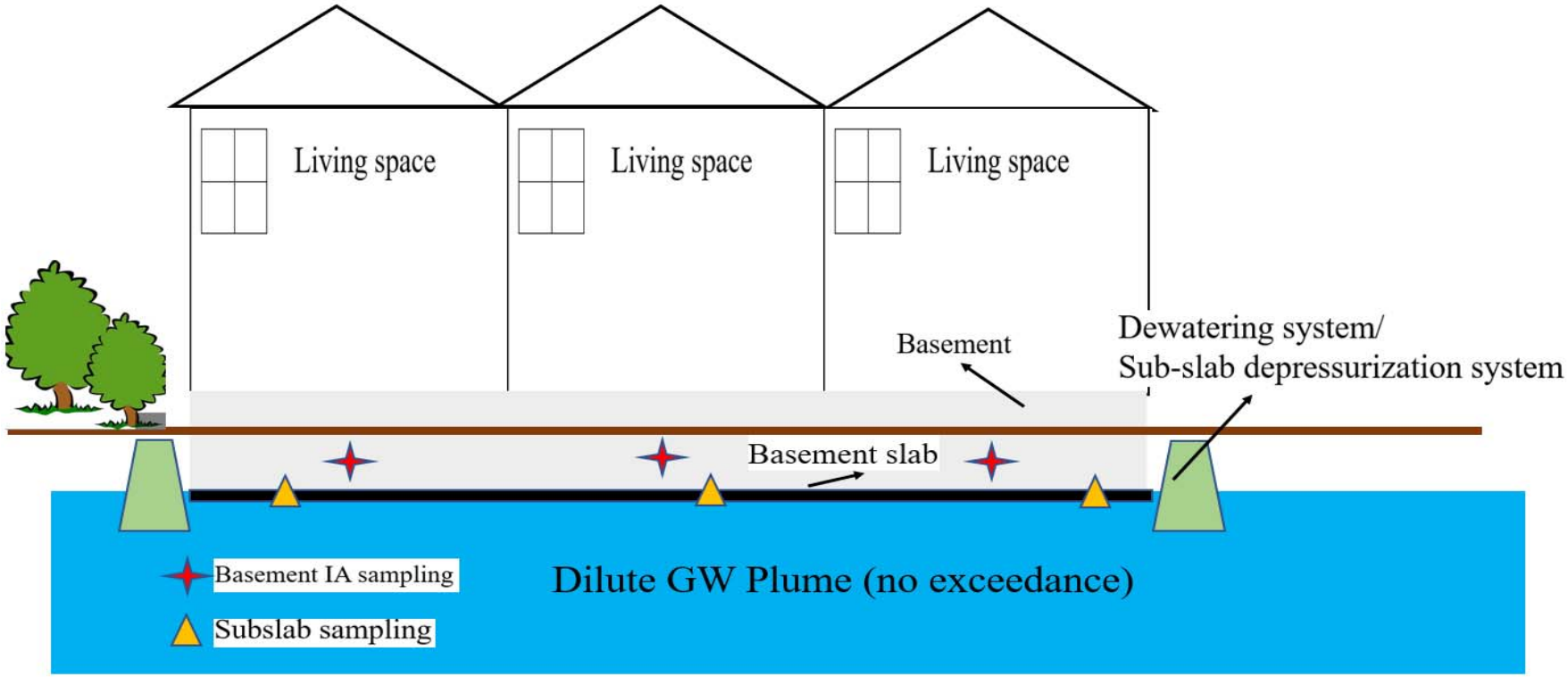


Sources of VOCs	Where in the house
Paints, paint strippers and other solvents	Garage, kitchen, bathrooms, newly remodeled homes
Wood preservatives	Living areas, garages, workshops
Aerosol sprays	Kitchen, garage, bathrooms, living areas
Cleaners and disinfectants	Kitchen, bathrooms, laudryroom
Moth repellents and air refreshers	Living areas, garage, bathrooms
Stored fuels and automotive products	Garage
Hobby supplies	Garage, workshop, living areas
Dry-cleaning clothing	Living areas
Building material and furnishings	Living areas, garages, workshops
Graphic and craft materials such as glues and adhesives, permanent markers	Living areas, home offices, garage

Adapted from https://www.epa.gov/indoor-air-quality-iaq/volatile-organic-compounds-impact-indoor-air-quality

- **Most of them are not site COCs, but they causes elevated RLs and get into lump-sum TPH/APH fractions**

Case Study: Site Background



- Residential condo units with basement built offsite from a former UST site; Dilute GW, DTW very shallow;
- GW intrusion and potential VI have been controlled by dewatering trench system which also serves as an SSD;
- Basement IA APH fractions >MassDEP IA ESL since 2005;
- IA > Subslab soil gas sometimes

Case Study: Basement SG and IA APH Data

Sample Location	Date	Analytical Data	
		C5-C8 Aliphatics	C9-C12 Aliphatics
MassDEP Indoor Air Threshold Values		58	68
Unit A (unfinished-Basement IA)	August-15	63	<14
	April-16	31	<10
	April-17	NS	NS
	June-18	67.4	44.3
	June-18 (Subslab soil gas)	33.2	363
Unit B (finished-Basement IA)	August-15	63	74
	April-16	23	31
	April-17	180	110
	June-18	127	136
	June-18 (Subslab soil gas)	98.6	<12
Unit B (unfinished-Basement IA)	August-15	120	180
	April-16	25	68
	April-17	210	110
	June-18	81.4	60.3
	June-18 (Subslab soil gas)	98.6	<12
Equipment Blank	June-18	124	672
	June-18 (adjusted)	113	461

- Variable IA APH data & some IA APH>ESLs
- Subslab SG<IA sometimes
  -- Is this really VI?
- Equipment blank:
  -- not really blank!
- SSD was running and VI should not occur

What is really included in the reported IA APH values??

What is included in the reported IA APH Data??

Target Compounds				Qvalue
2) PROPENE	0.00	42	0	N.D.
3) DICHLORODIFLUOROMETHANE	0.00	85	0	N.D.
4) CHLOROMETHANE	0.00	50	0	N.D. d
5) FREON 114	0.00	85	0	N.D.
6) VINYL CHLORIDE	0.00	62	0	N.D.
7) 1,3-BUTADIENE	0.00	54	0	N.D.
8) BROMOMETHANE	0.00	94	0	N.D.
9) CHLOROETHANE	0.00	64	0	N.D.
10) VINYL BROMIDE	0.00	106	0	N.D.
11) ACETONE	6.11	58	850926	34.8859 PPBv # 100
12) TRICHLOROFLUOROMETHANE	0.00	101	0	N.D. d
13)				
14)				
15)				
16)				
17)				
18)				
19) CARBON DISULFIDE	0.00	76	0	N.D. d
20) TRANS-1,2-DICHLOROETHENE	8.03	96	3238132m	78.0935 PPBv
SAD (M7) 07/16/18				
21) 1,1-DICHLOROETHANE	0.00	63	0	N.D.
22) MTBE	0.00	73	0	N.D.
23) VINYL ACETATE	0.00	86	0	N.D.
24) IPA	6.36	45	1648418	12.2723 PPBv # 100
25) 2-BUTANONE(MEK)	0.00	72	0	N.D.
26) CIS-1,2-DICHLOROETHENE	0.00	96	0	N.D.
27) HEXANE	0.00	57	0	N.D. d
28) ETHYL ACETATE	0.00	61	0	N.D.
29) CHLOROFORM	0.00	83	0	N.D.
30) TETRAHYDROFURAN	0.00	71	0	N.D.

Non-APH eluted within the retention time of C5-C8 Aliphatic

What is included in the reported IA APH Data??

Date analyzed	7/10/2018
C5-C8 Unadjusted	
C5-C8	87779260
TIC Internal Stnd areas	
Bromochloromethane	6307125
1,4-Difluorobenzene	6159356
Chlorobenzene-d5	6138335
Total IS area	18604816
C5-C8 Adjusted	
Non-petro	
Targets	
MTBE	
Benzene	
Toluene	1263655
Ethylbenzene	
M/P-XYLENE	
o-Xylene	
Total Targets	1263655
New C5-C8 area minus targets	67910789
C5-C8 Adjusted ug/m3	126.74
Final ug/m3 results	126.74

C9-C12 Unadjusted	
C9-C12	42919664
TIC Surrogate	
4-Bromofluorobenzene	4515346
C9-C12 Adjusted	
Targets	
Naphthalene	
Non-petro	
Total Targets	0
New C9-C12 area minus targets	38404318
C9-C12 Adjusted ug/m3	141.05
C9-C12 minus C9-C10	136.35
Final ug/m3 results	136.35

Only IS compounds areas were subtracted from the reported APH C5-C8 & C9-C12 Aliphatic values

What should be in the reported IA APH values?

Sample Location	Date	Analytical Data	
		C5-C8 Aliphatics	C9-C12 Aliphatics
MassDEP Indoor Air Threshold Values		58	68
Unit A (unfinished-Basement IA)	June-18	67.4	44.3
	June-18 (adjusted)	43.8	39.8
	June-18 (Subslab soil gas)	33.2	363
Unit B (finished-Basement IA)	June-18	127	136
	June-18 (adjusted)	65.9	104
	June-18 (Subslab soil gas)	98.6	<12
	Dec-18 (adjusted)	19	74
	Dec-18 (Subslab soil gas)	22.0	71
Unit B (unfinished-Basement IA)	June-18	81.4	60.3
	June-18 (adjusted)	47.4	46.4
	June-18 (Subslab soil gas)	98.6	<12
Equipment Blank	June-18	124	672
	June-18 (adjusted)	113	461
	Dec-18 (adjusted)	<10	<10

Non-APH compounds subtracted:

Acetone
Trans-1,2- DCE
IPA
PCE
MEK
Limonene
……

Along with other lines of evidence, regulator agreed that VI is not occurring at this site

In the MassDEP APH Method Manual

Table 7. List of Common Non-APH Compounds That Elute Within the APH Method Ranges

Hydrocarbon Range	Potential Non-APH Compounds
C_5-C_8 Aliphatic Hydrocarbons	Acetone may co-elute/interfere with isopentane. Isopropyl alcohol, methyl ethyl ketone, trichloroethene, tetrachloroethene, tetrahydrofuran, hexanal, 1-butanol, hexamethylsiloxane
C_9-C_{12} Aliphatic Hydrocarbons	Terpenes (e.g., a-pinene, d-limonene), phenol, benzaldehyde, n-chain aldehydes, 2-ethyl-1-hexanol, siloxanes, dichlorobenzenes
C_9-C_{10} Aromatic Hydrocarbons	Siloxanes, a-pinene, and d-limonene may slightly interfere if present at high concentrations (contribute to the area of ions 120/134)

11.2 Reporting Requirements for Non-APH Compounds

As described in Section 9.6.2, the contribution (i.e., area count) of compounds not meeting the regulatory definition of the aromatic and/or aliphatic hydrocarbons, defined in Sections 3.1.9, 3.1.10 and 3.1.11, that elute within the method-defined retention time windows for these hydrocarbon ranges, may be excluded from collective range concentrations **at the discretion of the data user,** providing the compound meets the requirements for positive **GC/MS identification** as described in Section 11.2.1.

Lessons Learned & Remaining Questions

1. Reported TPH/APH fractions values worth a 2nd look

- Understand the sources of the limitations of IA analytical data in vapor intrusion application;
- Subtracting out non-TPH and/or non-APH compounds is crucially important

2. Open discussion: How can we work together to eliminate the dreadful air phase data in vapor intrusion application?

- Avoid sorbent tube overloading?
- Achieve low RL<ESLs?
- Improve lab/consultant communication?

Thank you!
Questions?