New background indoor air levels of Volatile Organic Compounds (VOCs) and Air Phase Petroleum Hydrocarbons (APHs) in office buildings and schools

Rich Rago

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Indoor air background

"Background IA sources can be broken down into several categories …

- household activities
- consumer products
- building materials and furnishings
- ambient air pollution."

(NJDEP, VITG 2013)

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Indoor air background

- “Numerous materials found in buildings, such as carpeting, fabrics and wallpapered gypsum board, can act as "sinks" that retain IA pollutants and subsequently release them over a prolonged period of time.” (Won et al., 2001)
- “Outdoor air typically enters a building through infiltration, natural ventilation and mechanical ventilation. Yet, studies have shown that common organic pollutants are 2 to 5 times higher inside a building compared to levels in the ambient air.” (USEPA, 1988)

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Indoor air background

- VOCs are very common in personal, indoor air (Gordon, et al, 1999; Clayton, et al, 1999; Sexton, et al, 2004; Bradley, et al, 2004, RIOPA, 2005, Rago, et al, 2007; EPRI, 2007; MT DEQ, 2012), and ambient sources (EPA, 1988; EPA, 2000)

- Common VOCs identified in new (finished and operational, but unoccupied) pre-fabricated and site-built houses (Hodgson, et al, 2000)

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Indoor air background

- Higher background levels of VOCs have been observed in homes with attached garages (Kurtz, 2004; Graham, et al, 2004)
- Even from LSP and MassDEP garages
  - Attached Garage > Garage, Not Attached > No Garage (McCafferty, 2006)

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Indoor air background (continued)

- VOCs are also commonly encountered in office buildings (Girman, et al, 1999; Daisey, et al, 1994) and schools (Adgate, et al, 2004)
- Obvious potential for overlap of site contaminants from subsurface sources and personal, indoor, and ambient sources to residential and non-residential indoor air
- Requires careful consideration in vapor intrusion (VI) assessments

Indoor air background sources

Indoor air background sources

benzene
toluene
ethylbenzene
xylenes
naphthalene
aliphatics
tetrahydrofuran
acetone
methyl ethyl ketone
diethyl ether
alkyl benzenes
aliphatic alcohols
methyl butyl ketone
methyl isobutyl ketone
1,1,1-trichloroethane
tetrachloroethylene
methylene chloride
1,4-dichlorobenzene

One drop of BTEX in a basement

$$\left(0.05\ mL\ * 0.87\ \frac{g}{ml} * 1000\frac{mg}{g} * 1000\frac{\mu g}{mg}\right)/300\ \text{m}^3$$

$$= 145\ \mu\text{g/m}^3$$

One drop of TCE in a basement

$$\left(0.05\ mL * 1.46\ \frac{g}{ml} * 1000\ \frac{mg}{g} * 1000\ \frac{\mu g}{mg}\right)/300\ \mathrm{m}^3$$

$$= 243\ \mu\mathrm{g/m}^3$$

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Indoor air background references – offices

- EPA Building Assessment Survey and Evaluation (BASE) Study (1999)
- California Health Buildings Study (1994)

Building Assessment Survey and Evaluation (BASE) study

- Conducted over a five-year period (1994-1998)
- 100 public and commercial office buildings in the U.S.
- 37 cities in 25 states
- Goal of study was “to address a significant data gap that existed regarding baseline IAQ and occupant perceptions in large public and commercial office buildings” (Girman, et al, 1999)

BASE study (continued)

- Particles (PM10, PM2.5), VOCs, formaldehyde, bioaerosols, radon, temperature, relative humidity, carbon dioxide/monoxide, sound, light
- Generally, three indoor sampling locations and one outdoor sampling location
- VOCs: multi-sorbent samplers analyzed by gas chromatography/mass spectrometry (GC/MS) and SUMMA canisters

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BASE study (continued)

- Assigned ½ Reporting Limit to Non-Detect Values
- Percentiles and I/O Ratios available
- http://www.epa.gov/iaq/base/index.html
  - BASE Raw Data available on CD
  - See also "Individual Volatile Organic Compound Prevalence and Concentrations in 56 Buildings of the Building Assessment Survey and Evaluation (BASE) Study" (Girman, et al, 1999)
    - Local co-author

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BASE study (continued)

- Benzene, Toluene, Ethylbenzene, Xylenes (BTEX), alkanes
  - 100 % detected (n=70)
  - Benzene: 1.1 µg/m^3_{5th} to 9.1 µg/m^3_{95th}

- Tetrachloroethylene (PCE)
  - 100 % detected (n=70)
  - PCE: 0.3 µg/m^3_{5th} to 18 µg/m^3_{95th}

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BASE study (continued)

- Trichloroethylene (TCE)
  - 66 % detected (n=70)
  - TCE: $<LOQ_{5th}$ to 2.6 $\mu g/m^3{}_{95th}$

- 1,2-dichloroethane (1,2-DCA)
  - 4.6 % detected (n=87)
  - 1,2-DCA: $<LOQ_{5th}$ to $<LOQ$ $\mu g/m^3{}_{95th}$

California Healthy Buildings Study

- Phase I papers 1990, 1991, and 1993
- Measured 39 VOCs in 12 northern California city and county office buildings (excluding jails, hospitals, police stations, and fire stations)
- Major objective of study was "to investigate the prevalence of various occupant symptoms and perceptions of thermal comfort"… "and test hypotheses about health symptoms and features of the building…" (Daisey, et al, 1994)

California Healthy Buildings Study (continued)

- VOCs: multi-sorbent samplers (eight-hour intervals) and analyzed by gas chromatography/flame ionization detector
- Measurements made in “32 areas” of the 12 buildings
  - 2 – 4 samples/building
- Three different ventilation types
  - Natural
  - Mechanical
  - Air Conditioning

California Healthy Buildings Study (continued)

- Means, ranges, and I/O Ratios available
- Hydrocarbons dominant class of VOCs
  - Attributed aromatics and alkanes to vehicle emissions and outdoor air
- Highest total VOCs in 2 buildings with "wet process" copiers
  - See also "Volatile Organic Compounds in Twelve California Office Buildings: Classes, Concentrations and Sources" (Daisey, et al, 1994)

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California Healthy Buildings Study (continued)

- Benzene range: <0.1 µg/m^3 to 2.7 µg/m^3
- PCE range: 0.1 µg/m^3 to 2.0 µg/m^3
- TCE range: 0.23 µg/m^3 to 6.9 µg/m^3
- Ethanol range: 6.4 µg/m^3 to 130 µg/m^3
- Total VOCs: 230 µg/m3 to 7,000 µg/m3
  - Also identified a Freon leak

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Indoor air background references – schools

- “Exposure to Multiple Air Toxics In New York City” (Kinney, et al, 2002)
  - Part of “TEACH” study
  - Characterized “urban air toxics” for inner city high school students in New York City and Los Angeles
  - Examined personal, indoor, and outdoor air for 17 VOCs
  - NYC paper focuses on 46 high school students in West Central Harlem
- “Outdoor, Indoor, and Personal Exposure to VOCs in Children” (Adgate, et al, 2004)

Adgate, et al (2004)

- Part of the School Health Initiative: Environment, Learning, and Disease (SHIELD) study (University of Minnesota Research Subjects' Protection Program Institutional Review Board: Human Subjects Committee)
- Examined school children exposures to VOCs and other chemical and biological agents (Sexton, et al. 2003; Sexton, et al. 2000).
- Measured VOC exposures for children in two inner-city schools in MN; winter 2000 (January-February) and spring (April to mid-May) 2000
- VOCs (TCL=15) measured using 3M 3520 Organic Vapor Monitors (OVMs)

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Adgate, et al (2004) (continued)

- Samples collected in 4 locations (outdoors (0), indoors at school (S), indoors at home (H), and personal (P) samples)
- H and P=48 continuous hours; S=31 hours over 5 days; 0 measurements collected at school from Monday morning to Friday afternoon (103 hours)
- Concentrations of most VOCs: O ≈ S < P ≤ H

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Adgate, et al (2004) (continued)

- Benzene (5 day average, Spring data omitted)
  - Winter 1.3 µg/m^3 $_{50th}$ to 2.2 µg/m^3 $_{90th}$
- PCE (5 day average)
  - Winter 0.2 µg/m^3 $_{50th}$ to 0.4 µg/m^3 $_{90th}$
- TCE(5 day average)
  - Winter 0.3 µg/m3 50th to 1.0 µg/m3 90th
- Note: 1,4-Dichlorobenzene (5 day average, home indoor)
  - Winter 344.6 µg/m3 90th and Spring 429.0 µg/m3 90th

USA TODAY – "The Smokestack Effect"

- Obtained information relative to 127,800 schools
- Partnered with UMass-Amherst Political Economy Research Institute to examine modeling data
- Partnered with Johns Hopkins and University of Maryland School of Public Health to conduct monitoring (badges and active sampling)
- http://content.usatoday.com/news/nation/environment/smokestack/index
- Searchable by state or school
  - Milton: 86th percentile – "the air is worse at 111,022 schools"

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USA TODAY – “The Smokestack Effect”

Name	Street Address	Town	National Rank	Comment
Wilbur	816 Brayton Point Rd	Somerset, MA	2nd percentile	The air is worse at 916 schools across the nation
Montachusett Voc Tech	1050 Westminster Street	Fitchburg, MA	2nd percentile	The air is worse at 1,390 schools across the nation
The Montessori School	51 Bates Street	Northampton, MA	2nd percentile	The air is worse at 1,602 schools across the nation
Chicopee Comprehensive Hs National Rank	617 Montgomery Street	Chicopee, MA	2nd percentile	The air is worse at 1,602 schools across the nation
Lambert-Lavoie	99 Kendall Street	Chicopee, MA	2nd percentile	The air is worse at 1,946 schools across the nation
Springfield Central High	1840 Roosevelt Avenue	Springfield, MA	3rd percentile	The air is worse at 2,229 schools across the nation
Westall	276 Maple Street	Fall River, MA	3rd percentile	The air is worse at 2,291 schools across the nation
Springdale Education Center	1 Carando Drive	Springfield, MA	3rd percentile	The air is worse at 2,840 schools across the nation
Deaconess Home	Po Box 2118	Fall River, MA	3rd percentile	The air is worse at 2,840 schools across the nation
Seton Academy	PO Box 9658	Fall River, MA	3rd percentile	The air is worse at 2,840 schools across the nation

Source: http://content.usatoday.com/news/nation/environment/smokestack/index

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Existing literature data for non-residential buildings

- Older data sets
- Inconsistent sampling and analytical methods with higher detection limits
- Varying objectives, methodologies, geographies, statistics
- Consumer products and ambient air quality have changed over time (e.g., 1,2-dichloroethane)
- No data on petroleum hydrocarbon ranges

Residential vs. non-residential

- HVAC and air changes per hour (ACH)
    - $n = 60qV$
        - n=air changes/hour; q=fresh air flow (cfm); V=volume (ft^3)
  - Residential ACH may be much lower than non-residential
- Storage of products containing VOCs
  - Non-residential quantities may be larger?
  - Residential variety may be larger?
- One or the other may be more subject to episodic product usage?
- Transient nature of occupants

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Focus of new indoor air background study

- Sample population: offices and schools
  - Target 50 offices and 25 schools
- No known vapor intrusion
- Sample selection process:
  - interview and question period
  - access agreement/legal disclaimer/release

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Focus of new study (continued)

- Some sampling on multiple floors
- Samples collected in the breathing zone
- Phase I – winter 2013
  - All samples collected from offices and schools in Massachusetts (n=20)
- Phase II – 2014 -2015 (n=64)

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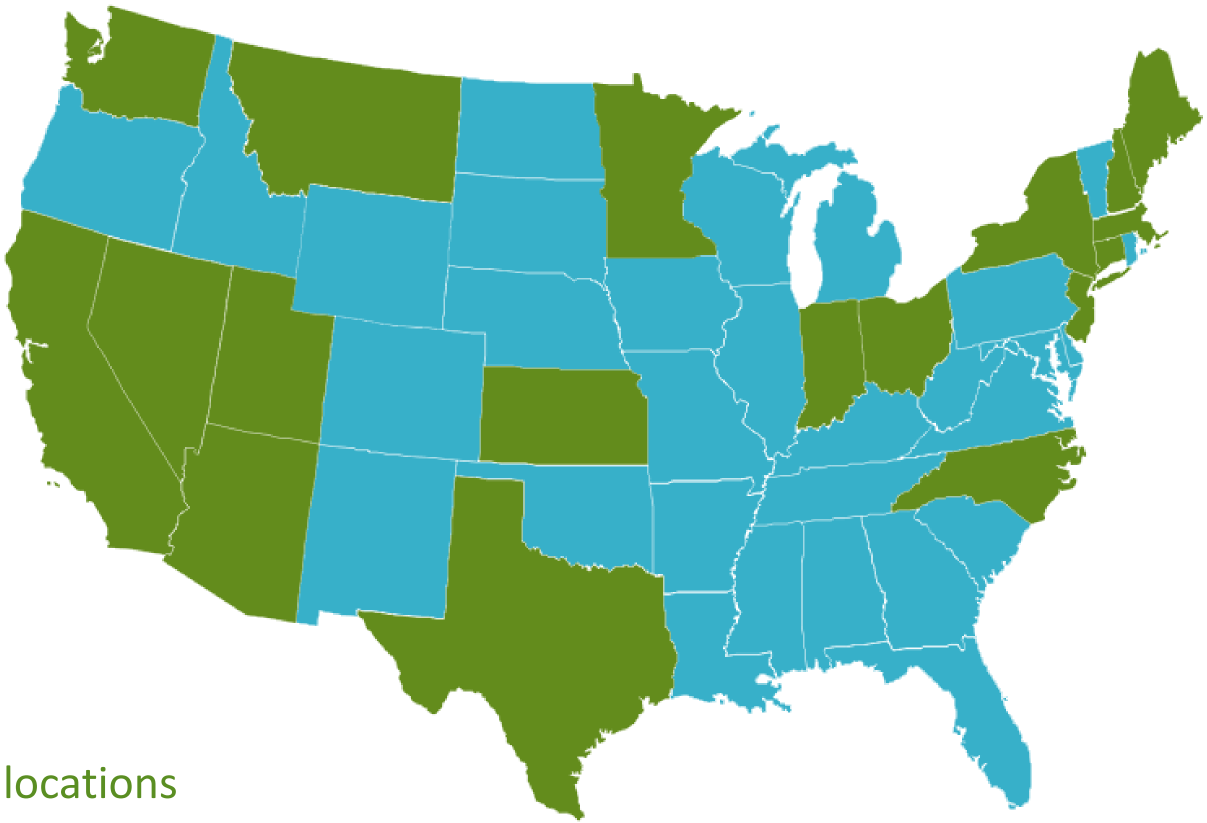
Focus of new study (continued)

- Sampling conducted using fused silica lined canisters fitted with 24-hour flow controllers
- USEPA Method TO-15 (acquired in full scan mode)
  - ~104 target VOCS
- USEPA Method TO-15 (subset acquired in SIM mode)
  - ~57 target VOCs

Focus of new study (continued)

- MassDEP Compendium Analytical Method for Air-Phase Petroleum Hydrocarbons (APH)
  - 1,3-Butadiene, Methyl tert-butyl ether, Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, Naphthalene
  - C5-C8 Aliphatics, C9-C12 Aliphatics, C9-C10 Aromatics

Indoor air background sampling locations



- Sample locations

59 office building samples (professional, academic, and municipal)

25 school building samples (K-8, middle and high school, university)

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Detected VOCs and APH

- Offices and schools
  - Full Scan: 57 VOCs detected (of 105 tested)
    - 105: slight target compound list variation
  - SIM: 37 VOCs detected (of 58 tested)
    - 4-ethyltoluene
- Offices
  - Full Scan: 56 VOCs detected (of 105 tested)
  - SIM: 22 VOCs detected (of 58 tested)
- Schools
  - Full Scan: 37 VOCs detected (of 105 tested)
  - SIM: 26 VOCs detected (of 57 tested)
- APH: 9/11 in offices; 6/11 in schools
    - methyl tert-butyl ether and 1,3-butadiene – not detected *by APH*

preliminary

Top 31 compounds detected

COMPOUND	FREQUENCY OF DETECTION
Acetone	100%
Butane	100%
Chloromethane	100%
Ethyl Alcohol	100%
Isopropyl Alcohol	100%
Methanol	100%
Toluene	100%
Acetone	100%
Carbon tetrachloride	100%
Ethylbenzene	100%
o-Xylene	100%

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Top 31 compounds detected (continued)

COMPOUND	FREQUENCY OF DETECTION
p/m-Xylene	100%
Toluene	100%
Trichlorofluoromethane	100%
Chlorodifluoromethane	99%
Pentane	99%
Freon-113	99%
Dichlorodifluoromethane	99%
Propane	98%
Trichlorofluoromethane	98%
Chloromethane	98%

preliminary

Top 31 compounds detected (continued)

COMPOUND	FREQUENCY OF DETECTION
C5-C8 Aliphatics	98%
Dichlorodifluoromethane	97%
1,2,4-Trimethylbenzene	96%
Benzene	94%
Chloroform	92%
Styrene	87%
C9-C12 Aliphatics	85%
1,2-Dichloroethane	79%
2-Butanone	77%
Acetaldehyde	77%
C5-C8 Aliphatics	98%

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Detected compounds without available screening levels (and frequency detected)

Full Scan VOCs

1,3,5-Trimethylbenzene (46%)	n-Butylbenzene (2%)
2,2,4-Trimethylpentane (10%)	Octane (13%)
4-Ethyltoluene (5%)	p-Isopropyltoluene (2%)
Butane (100%)	Propane (98%$_{n=63}$)
Butyl Acetate (2%)	sec-Butylbenzene (2%)
Decane, C10 (33%)	tert-Butyl Alcohol (13%)
Dodecane, C12 (30%)	Undecane (23%)
Heptane (42%)	

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Summary of selected VOCs (µg/m^3)

Parameter	Frequency of Detection	Minimum Concentration	Maximum Concentration
VOCs by SIM			
Benzene	94%	0.319	24.8
Toluene	100%	0.803	242
Ethylbenzene	100%	0.109	45.6
o-Xylene	100%	0.104	51.3
p/m-Xylene	100%	0.243	157
1,3-Butadiene	39%	0.044	0.774
Methyl tert butyl ether	1%	0.151	0.151
Naphthalene	24%	0.267	5.18

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Summary of selected VOCs (µg/m^3)

Parameter	Frequency of Detection	Minimum Concentration	Maximum Concentration
APH Carbon Ranges			
C5-C8 Aliphatics	98%	15	3,000
C9-C10 Aromatics	10%	10	130
C9-C12 Aliphatics	85%	15	990

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Detection frequencies in schools and offices for selected compounds by SIM

Parameter	Frequency Detected in Schools (N = 25)	Frequency Detected in Offices (N = 59)
Benzene	96%	93%
Tetrachloroethene	64%	63%
Trichloroethene	4%	24%
1,2-Dichloroethane	76%	80%

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PCE/TCE by SIM

	PCE (µg/m³)	TCE (µg/m³)
Frequency of Detection	63%	18%
Minimum Concentration	0.136	0.107
Maximum Concentration	9.02	115
Residential Air RSL	11	0.48
Industrial Air RSL	47	3
Mass DEP Residential TV	1.4	0.40
MassDEP Commercial/Industrial TV	4.1	1.8

RSL – Regional Screening Level (January 2015)

TV – Threshold Values

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1,2-DCA by SIM

	1,2-DCA ($\mu g/m^3$)
Frequency of Detection	79%
Minimum Concentration	0.081
Maximum Concentration	0.704
Residential Air RSL	0.11
Industrial Air RSL	0.47
Mass DEP Residential TV	0.090
MassDEP Commercial/Industrial TV	0.44

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Some planned data set examination

- Continue careful review of data
  - Over 14,000 data points
  - Approximately 7,800 data points on the residential study
- Calculate Summary Statistics
- Examine relationships between compound types, building types, and between residential data
- Statistics for Censored Data using Kaplan Meier
  - Widely accepted to give more accurate statistical representations (Helsel, 2005)

Closing thoughts

- Indoor air background is building-specific and commercial product formulations can and do change
- Understanding background data can be of strategic importance in vapor intrusion data review, focusing investigations, mitigation decision making, and risk communication
- Carefully review background studies for focus, relationships, and ranges - do not simply rely on “bright lines” such as medians
- Look for this presentation, updates, and data summaries to be posted to: http://www.haleyaldrich.com/insights/publications

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