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Indoor Chemistry has Exposure Consequences that are (Potentially) Health-Relevant

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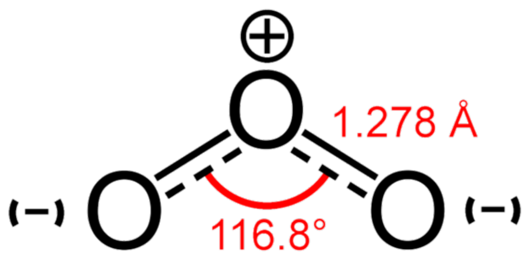
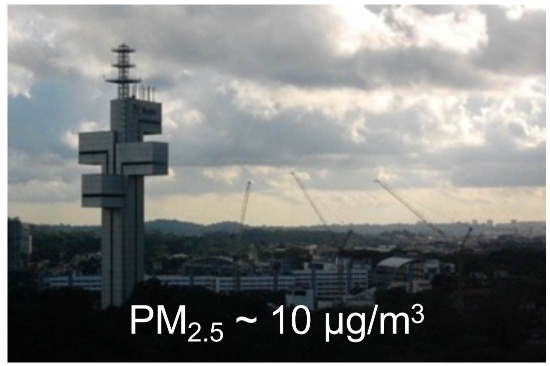
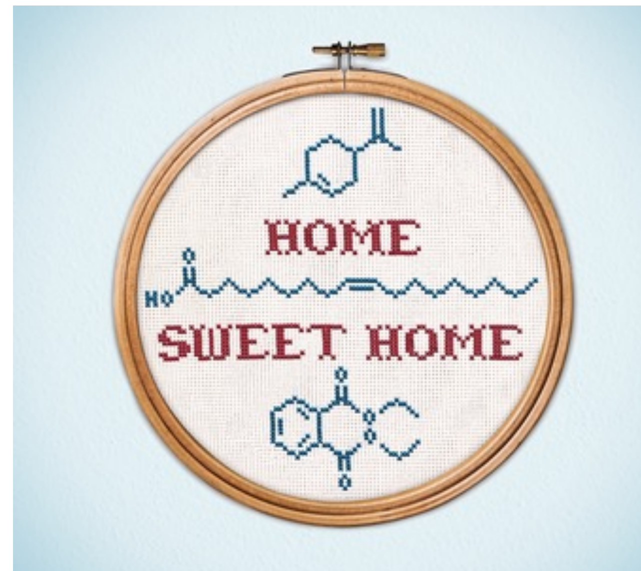
Committee on Emerging Science on Indoor Chemistry
Board on Chemical Sciences and Technology
Division on Earth and Life Studies

Some health-relevant air pollutants: O_3, PM, organics



Ozone (O_3)





Organics sampler of indoor interest (from top): Limonene, oleic acid, diethyl phthalate

Images: (a) Ozone from Wikipedia; (b) haze photographs from Singapore (WWN); (c) organic needlework sampler from C&E News, 24 November 2019.

Health-relevance indicators for PM and ozone

Air pollution is a major contributor to premature mortality

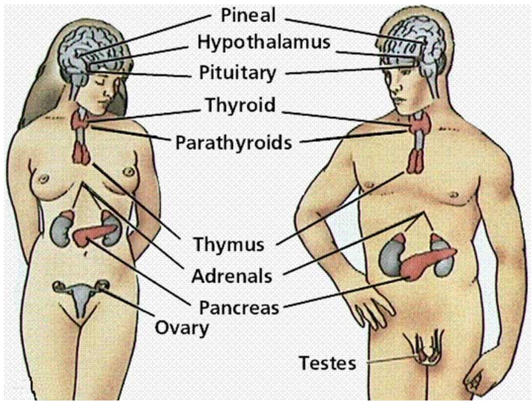
Cause	2016 deaths (millions)
All deaths	55.5
All risk factors	32.7
Air pollution	6.1
Ambient particulate matter pollution	4.1
Ambient ozone pollution	0.2

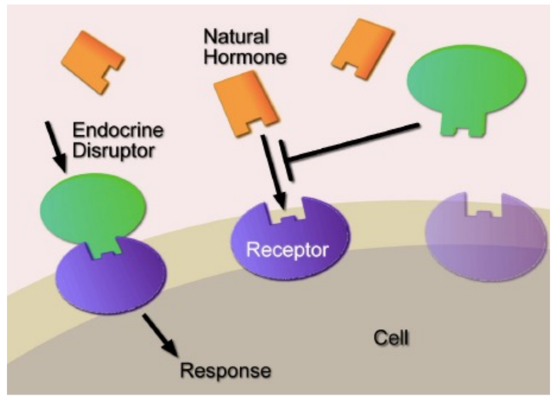
For context, the COVID-19 pandemic is estimated to have caused 2.7 million deaths globally as of 23 March 2021.

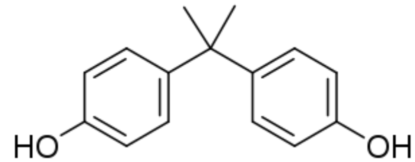
Atmospheric chemical reactions contribute substantially to ambient fine particulate matter (PM) and are the entire source of ambient ozone (O_3).

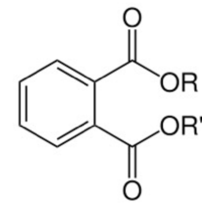
References: (a) Our World in Data (on-line); (b) Global Burden of Disease (2016) results from *Lancet* **390,** 1345-1422, 2017; COVID-19 statistic from NY Times (23 March 2021).

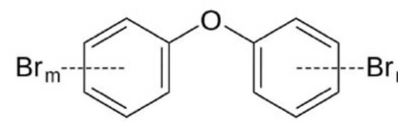
Health-relevant concern: Endocrine disrupting compounds

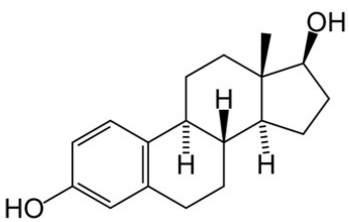


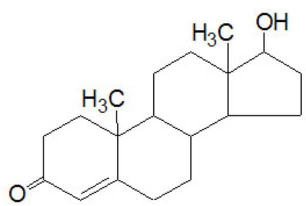


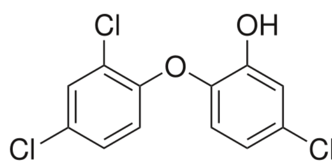

Bisphenol A


Phthalates


PBDE


Estradiol

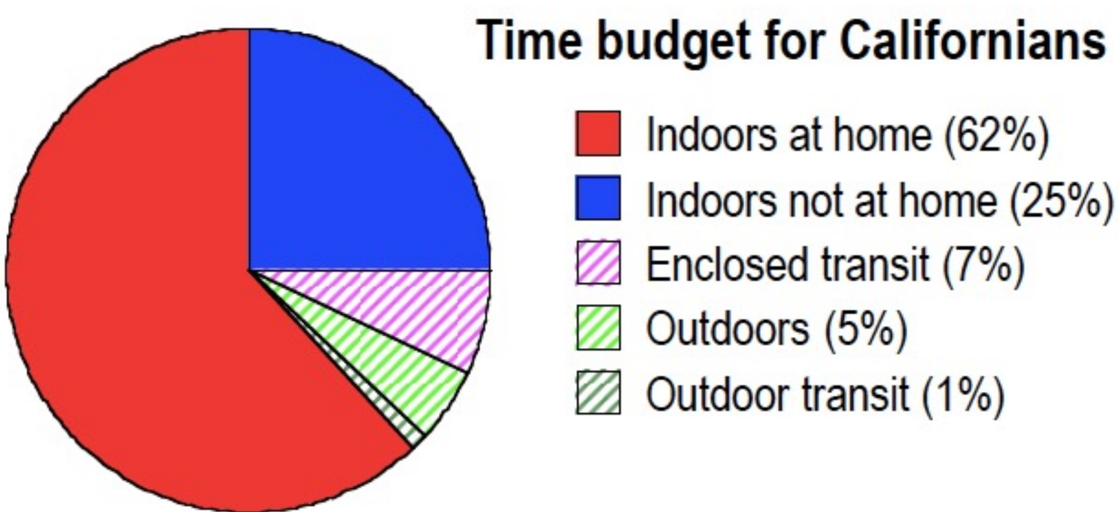

Testosterone


Triclosan

- Abundant mimics
- Promiscuous receptors
- Potent effects

Reference: RA Rudel, LJ Perovich, Endocrine disrupting chemicals in indoor and outdoor air, *Atmos. Environ.* **43**, 170, 2009.
Images: http://metabodymind.files.wordpress.com/2012/02/endocrinediagramsexes1.jpg;
https://epthinktank.eu/2012/07/05/health-threats-from-endocrine-disruptors-a-scientific-and-regulatory-challenge/.

Exposure perspective asks: Where are the people?



- We spend ~ 90% of our time indoors.
- Most of the air we breathe is indoor air.
- Indoor air ≠ outdoor air.

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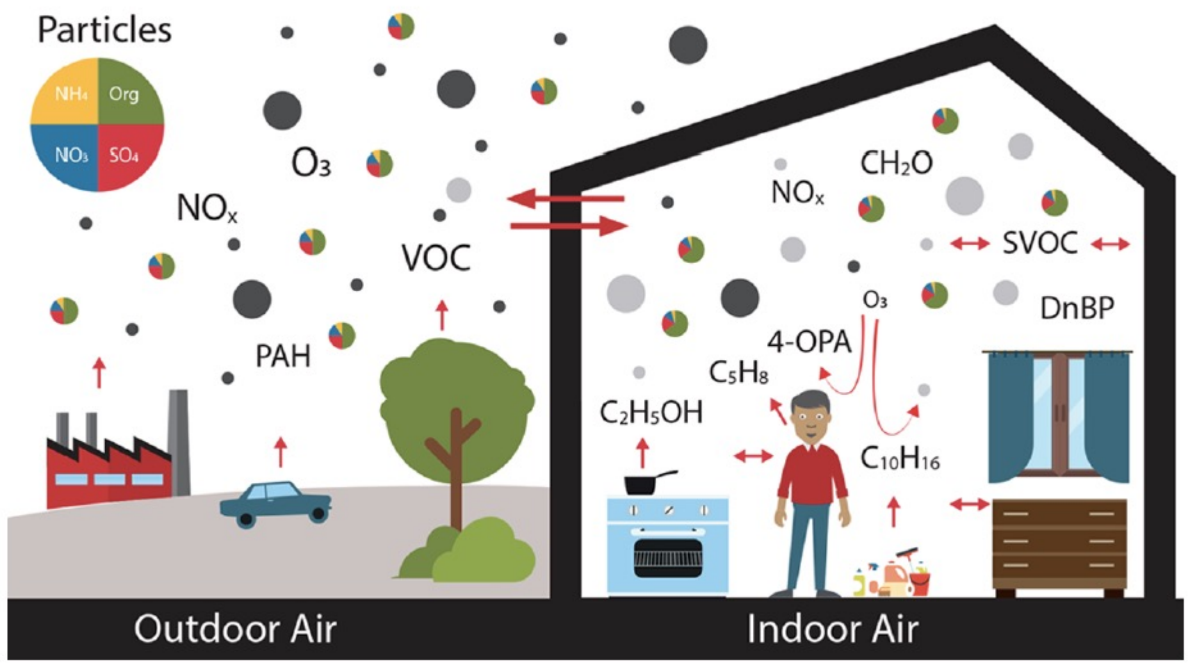
References: PL Jenkins et al., Activity patterns of Californians: Use of and proximity to indoor pollutant sources, *Atmos. Environ.* **26A**, 2141, 1992; NE Klepeis et al., The National Human Activity Pattern Survey (NHAPS): A resource for assessing exposure to environmental pollutants, *J. Expos. Analysis Environ. Epidemiol.* **11**, 231, 2001.

Indoor air ≠ outdoor air: O_3, PM, organics

Ozone
- Buildings partially protective
- Ozone drives oxidative chemistry

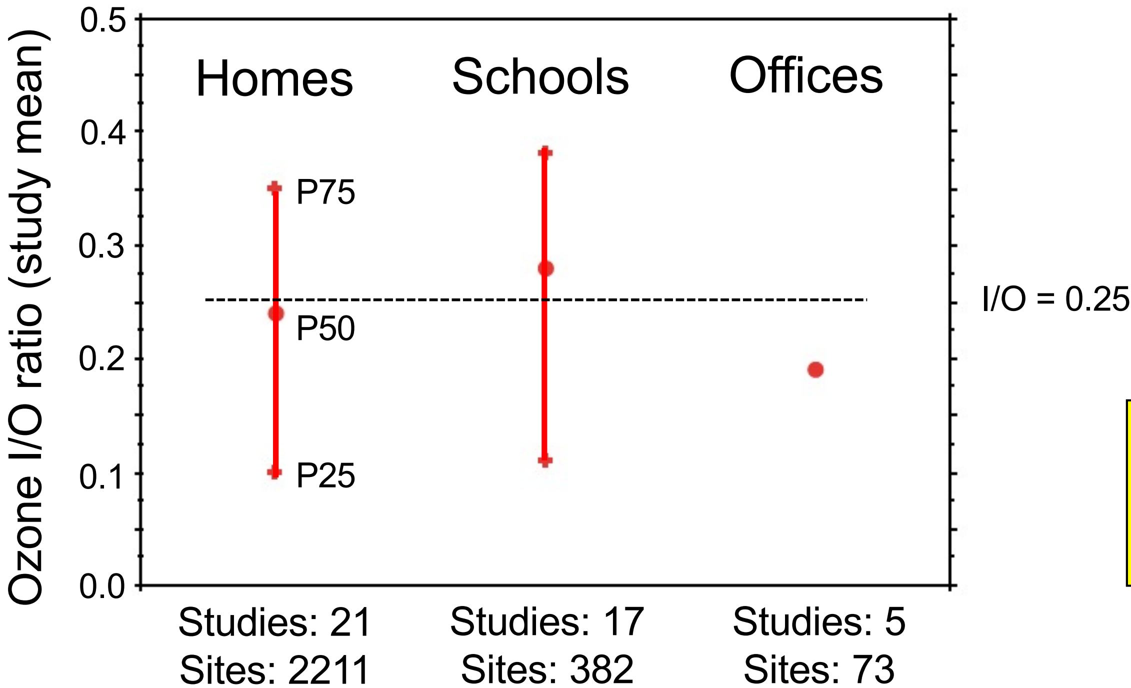
Particulate matter
- Buildings partially protective
- Size distribution altered
- Chemical composition shifts
- Indoor sources contribute

Organic compounds
- Indoor sources dominate
- Surface interactions modulate



Reference: AH Goldstein et al., How do indoor environments affect air pollution exposure? *Environmental Science & Technology* **55**, 100, 2021.

Ozone indoors: Attenuated, but not eliminated

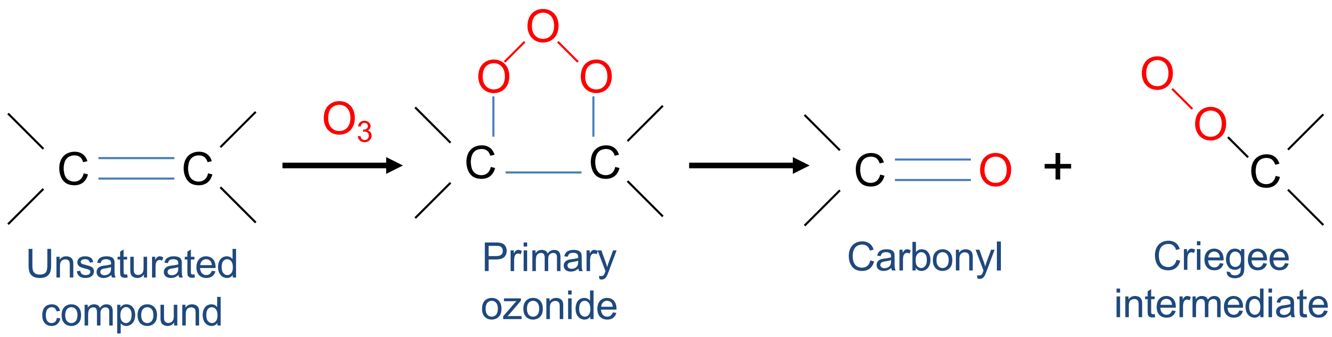


Indoor/outdoor ozone ratio:
- Almost always less than 1
- Central tendency ~ 25%

Reference: CJ Weschler and WW Nazaroff, Ozone-initiated indoor chemistry: A critical review, in preparation.

Ozone attenuated, chemical byproducts formed

Indoors, this illustrative chemistry mainly occurs on surfaces.

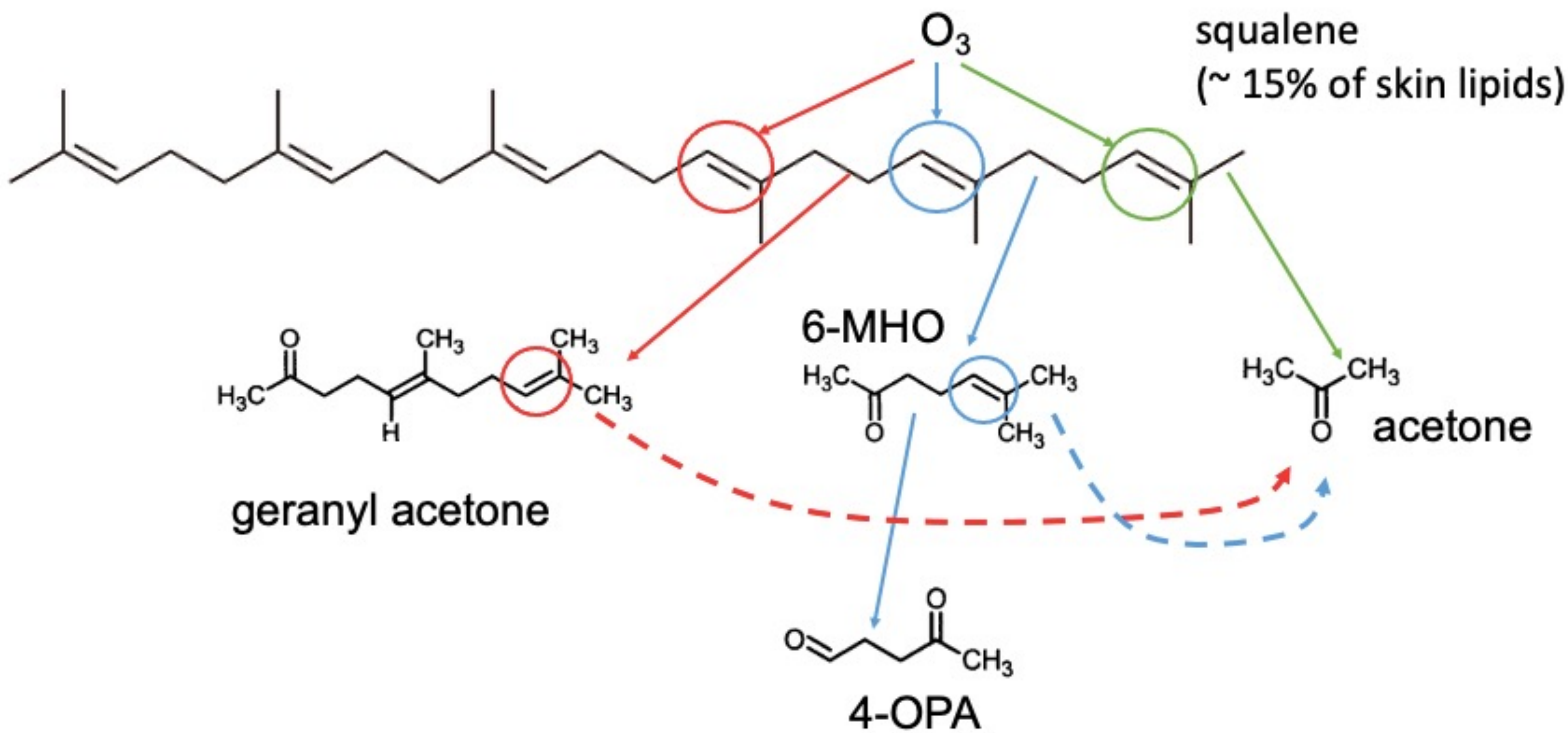


Some ozone-initiated chemical byproducts of concern

- Criegee intermediates
- Dicarbonyls
- Organic peroxides
- Secondary ozonides
- Organic nitrates
- Secondary organic aerosol
- Hydrogen peroxide
- Radicals: OH, HO_2, RO_2, NO_3

Reference: CJ Weschler and WW Nazaroff, Ozone-initiated indoor chemistry: A critical review, in preparation.

Ozone reacts with skin oil components, including squalene

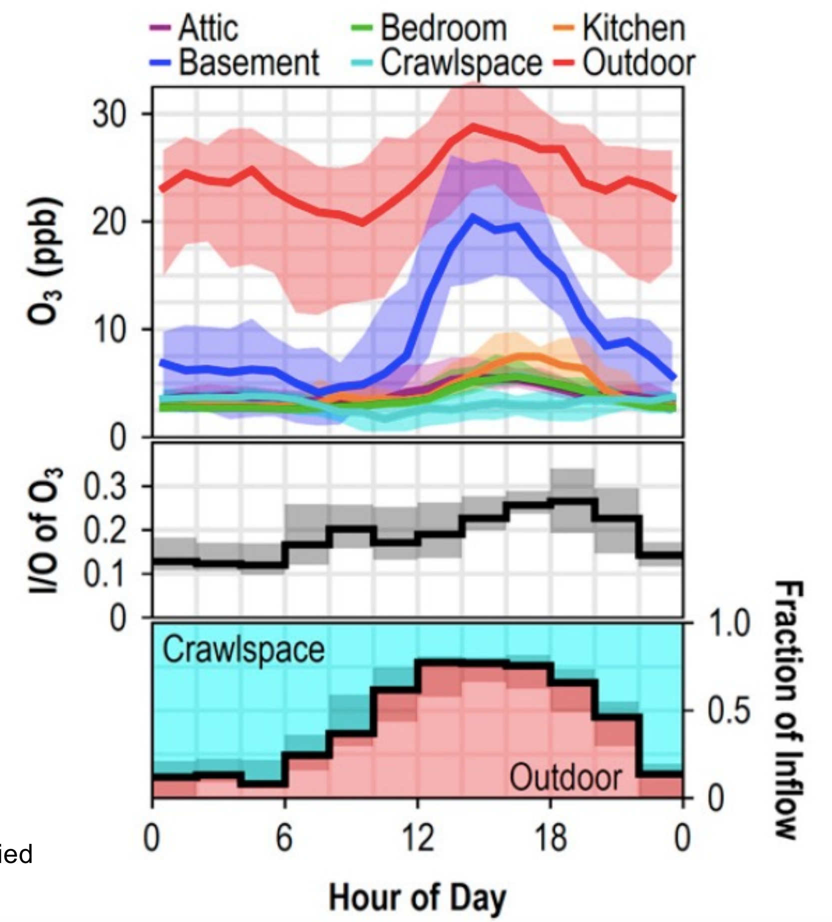


Graphic courtesy of Glenn Morrison; see also A Wisthaler, CJ Weschler, Reactions of ozone with human skin lipids …, *PNAS* **107**, 6568, 2010.

Observing ozone chemistry in an occupied residence

Continuous time-resolved monitoring in occupied, single-family house in northern California during summer (8 weeks).

Diel means:
Outdoor O_3 = 20-29 ppb
Indoor O_3 = 3-8 ppb
I/O ratio = 0.1-0.3



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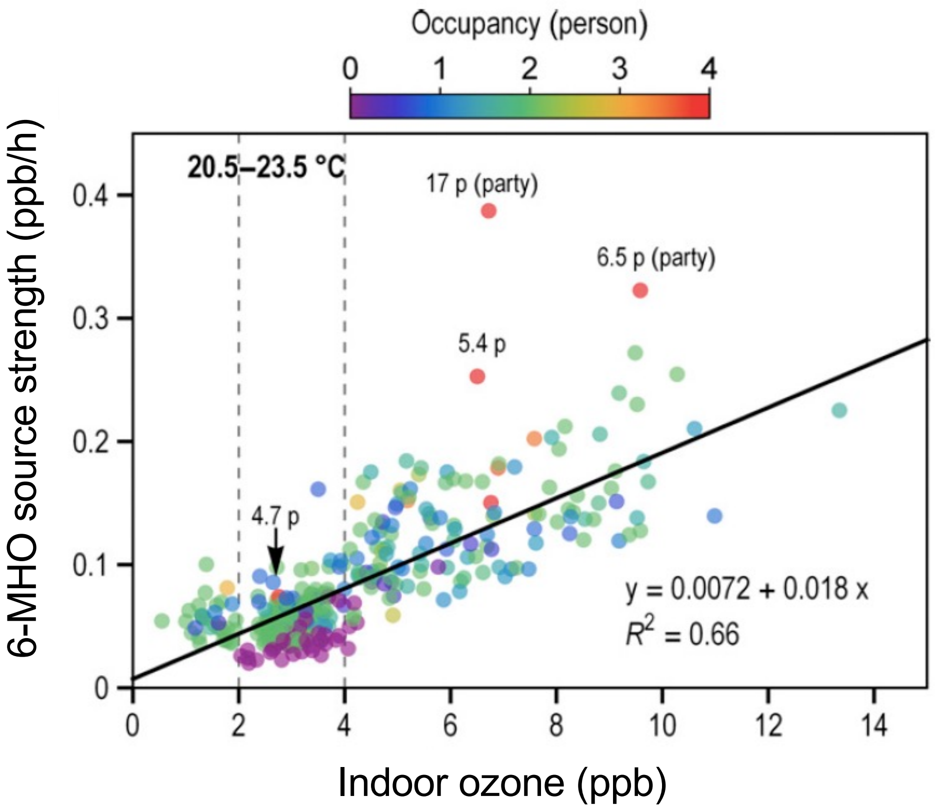
Reference: Y Liu et al., Observing ozone chemistry in an occupied residence, *PNAS* **118**, e2018140118, 2021.

Observing ozone chemistry in an occupied residence



- Emissions of 6-MHO increase with O_3.
- Emissions of 6-MHO increase with occupancy.
- Chemistry is observable even at low O_3 levels (< 10 ppb).

Reminder: 6-MHO is a byproduct of O_3 + squalene.

Reference: Y Liu et al., Observing ozone chemistry in an occupied residence, *PNAS* **118**, e2018140118, 2021.

Box model predicts high byproduct concentration indoors

$$[O_3]_{indoor} = \frac{a}{a+k} \times [O_3]_{outdoor}$$

$$[Byproducts]_{indoor} = Y \times \frac{k}{a+k} \times [O_3]_{outdoor}$$

a = air-change rate
k = ozone surface loss-rate coefficient
Y = gaseous byproduct yield

Typical residential values
$a = 0.5\ h^{-1}$
$k = 2\ h^{-1}$
$Y = 0.5$ (sum of gaseous byproducts)

Model predictions

$[O_3]_{indoor} = 0.2 \times [O_3]_{outdoor}$

$[Byproducts]_{indoor} = 0.4 \times [O_3]_{outdoor}$

$[Byproducts]_{indoor} = 2 \times [O_3]_{indoor}$

Reference: CJ Weschler and WW Nazaroff, Ozone-initiated indoor chemistry: A critical review, in preparation.

Other oxidants contribute to reactive indoor chemistry

Species	Sources	References
HOCl, Cl_2, chloramines …	Bleach, cleaning products, water	Wo17; Ma20
OH radical	Ozone-initiated chemistry	Sa02; Wa21
NO_3 radical	NO_2 + O_3	Wa15; Ar18

References

Wo17 — JPS Wong et al., Observations and impacts of bleach washing on indoor chlorine chemistry, *Indoor Air* **27**, 1082, 2017.
Ma20 — J Mattila et al., Dark chemistry during bleach cleaning enhances oxidation…, *ES&T Letters* **7**, 795, 2020.
Sa02 — G Sarwar et al., Hydroxyl radicals in indoor environments, *Atmospheric Environment* **36**, 3973, 2002.
Wa21 — N Wang et al., Total OH reactivity of emissions from humans …, *Environmental Science & Technol.* **55**, 149, 2021.
Wa15 — M Waring et al., [VOC] conversion by ozone, hydroxyl radicals, and nitrate radicals …, *Atmos Environ.* **106**, 382, 2015.
Ar18 — C Arata et al., Measurement of NO_3 and N_2O_5 in a residential kitchen, *Environ. Science & Technol. Letters* **5**, 595, 2018.

Indoor particulate matter: Multidimensional complexity

Particle size (diameter)
- Ultrafine (< 100 nm)
- $PM_{2.5}$ (mass < 2.5 μm)
- Coarse (2.5-10 μm)

Sources
- Outdoor air
- Indoor combustion & heating
- Mechanical generation
- Indoor chemistry

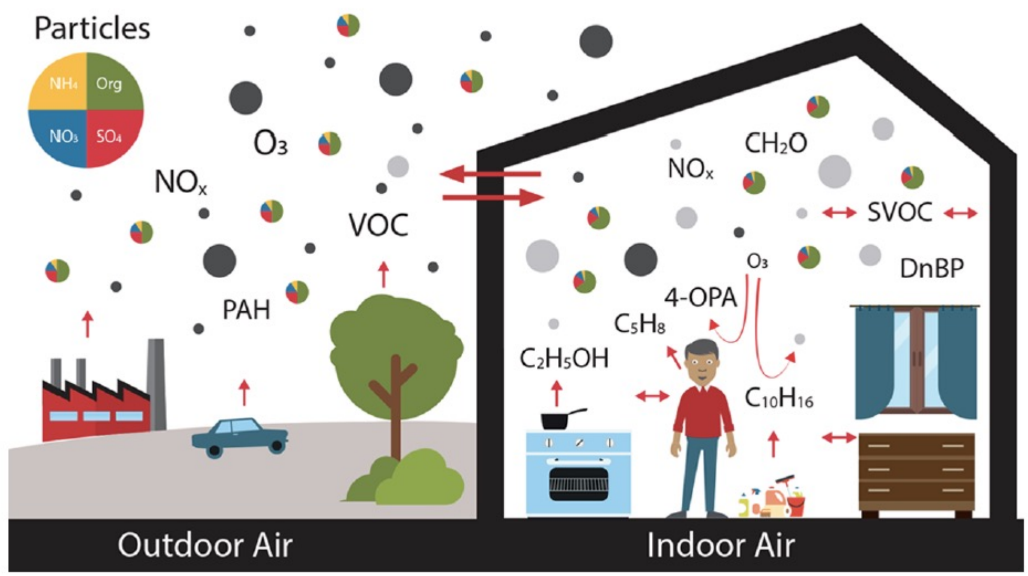
Chemical composition
- Crustal components and sea salt
- Inorganic ions (NH_4^+, NO_3^-, $SO_4^=$)
- Elemental carbon
- Organic carbon

Dynamic processes
- Emissions
- Ventilation and filtration
- Deposition and resuspension
- Phase change

What happens when outdoor PM comes indoors?

Size-dependent chemical composition is altered by …

- Filtration and deposition (most efficient for ultrafine and coarse particles).
- Temperature and humidity changes (affects equilibrium partitioning for semivolatile species, including H_2O).
- Surface uptake and emissions of gaseous species (affects condensation to and evaporation from particles).
- Shifts in aerosol liquid water and pH (can alter size and composition).



Prominent semivolatile components of fine PM include NH_4NO_3 and organic compounds.

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Reference: AH Goldstein et al., How do indoor environments affect air pollution exposure? *Environmental Science & Technology* **55**, 100, 2021.

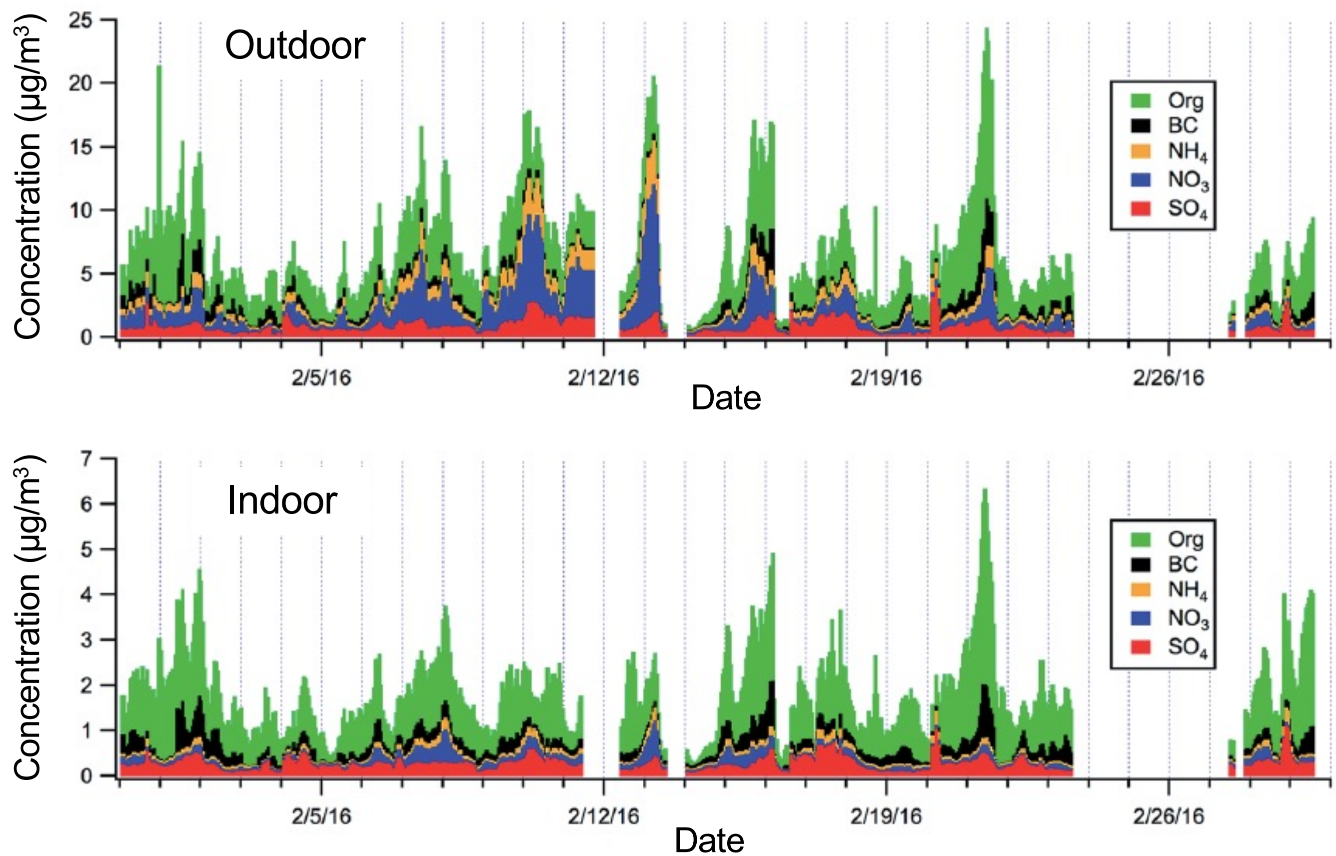
Submicron PM time series in a university classroom

Highlights
- Dynamic temporal patterns
- Dominant source: outdoor air
- Overall attenuation (I/O < 1)
- Stronger attenuation of NO_3^-

I/O ratios (ratios of means)

Organics (Org) — 35%
Black Carbon (BC) — 40%
Ammonium (NH_4) — 11%
Nitrate (NO_3) — 10%
Sulfate (SO_4) — 33%
Total — 28%

Reference: AM Avery et al., Seasonal variation in aerosol composition and concentration upon transport from the outdoor to indoor environment, *Environmental Science: Processes & Impacts* **21**, 528, 2019.

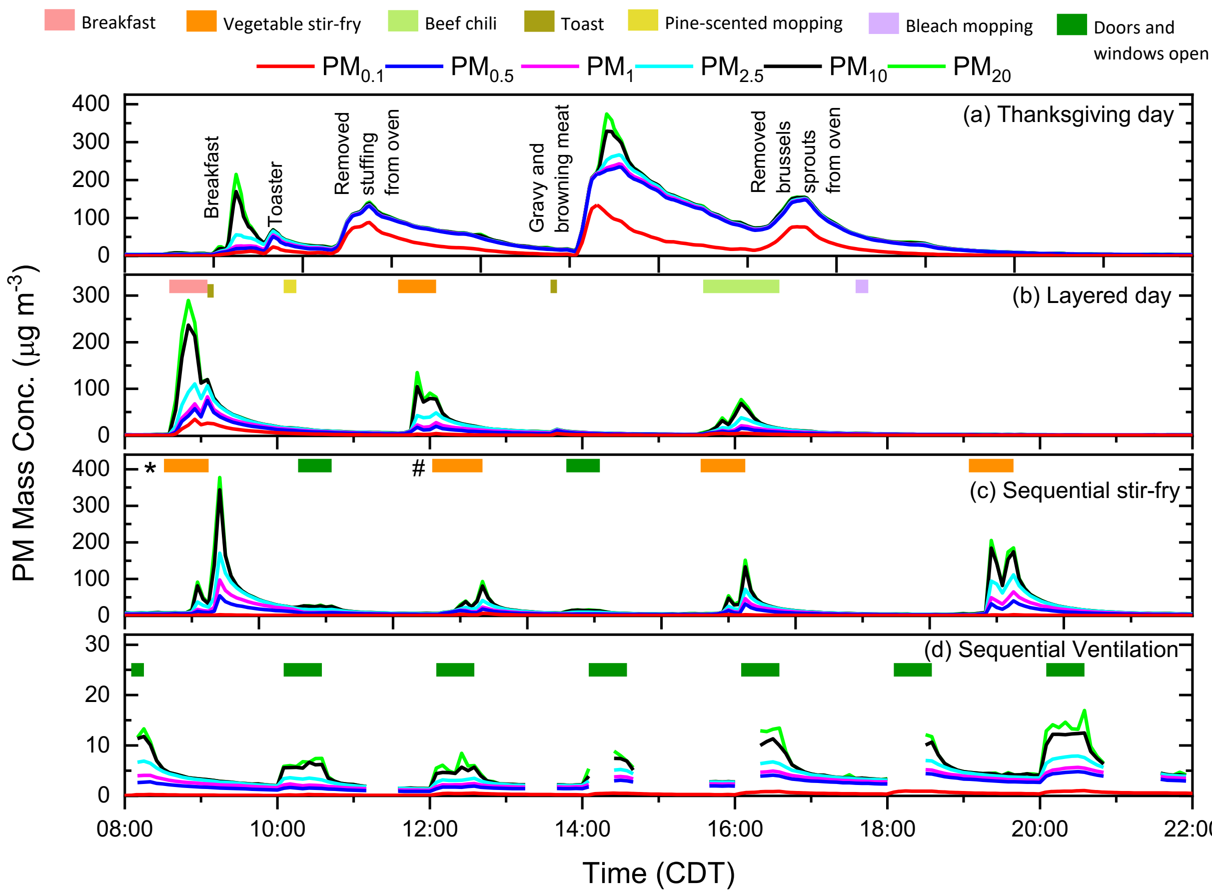


PM size-resolved time series during HOMEChem

Highlights
- Cooking: strong indoor source
- Absent indoor sources, I/O is higher with windows open.

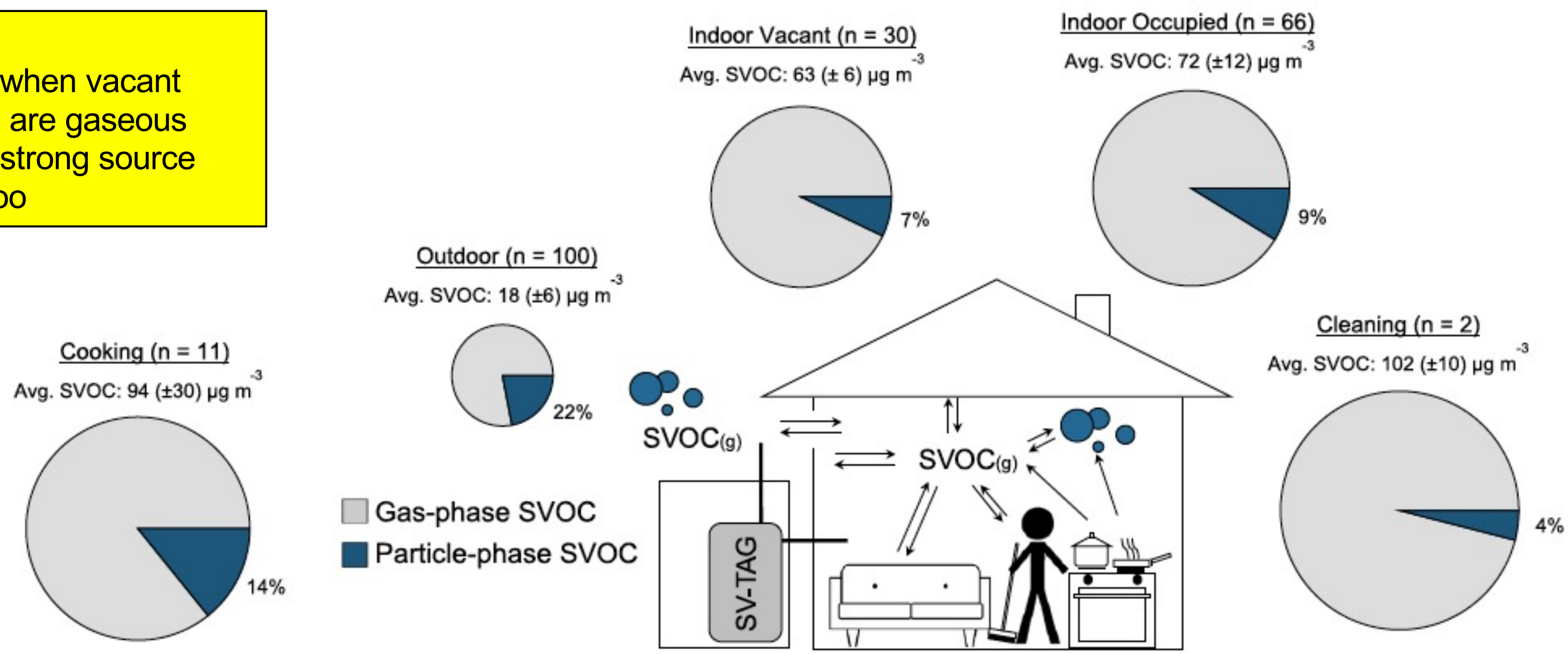
$PM_{2.5}$ concentrations (µg/m³)
Thanksgiving day — 62
Layered day — 14
While cooking stir-fry — 25-30
During high ventilation — 6
Unoccupied background — 2.3

Reference: S Patel et al., Indoor particulate matter during HOMEChem: Concentrations, distributions, and exposures, *Environmental Science & Technology* **54**, 7107, 2020.



Semivolatile organic compounds (SVOC) in a residence

Highlights
- I/O > 1 even when vacant
- Most SVOCs are gaseous
- Cooking is a strong source
- Cleaning is too



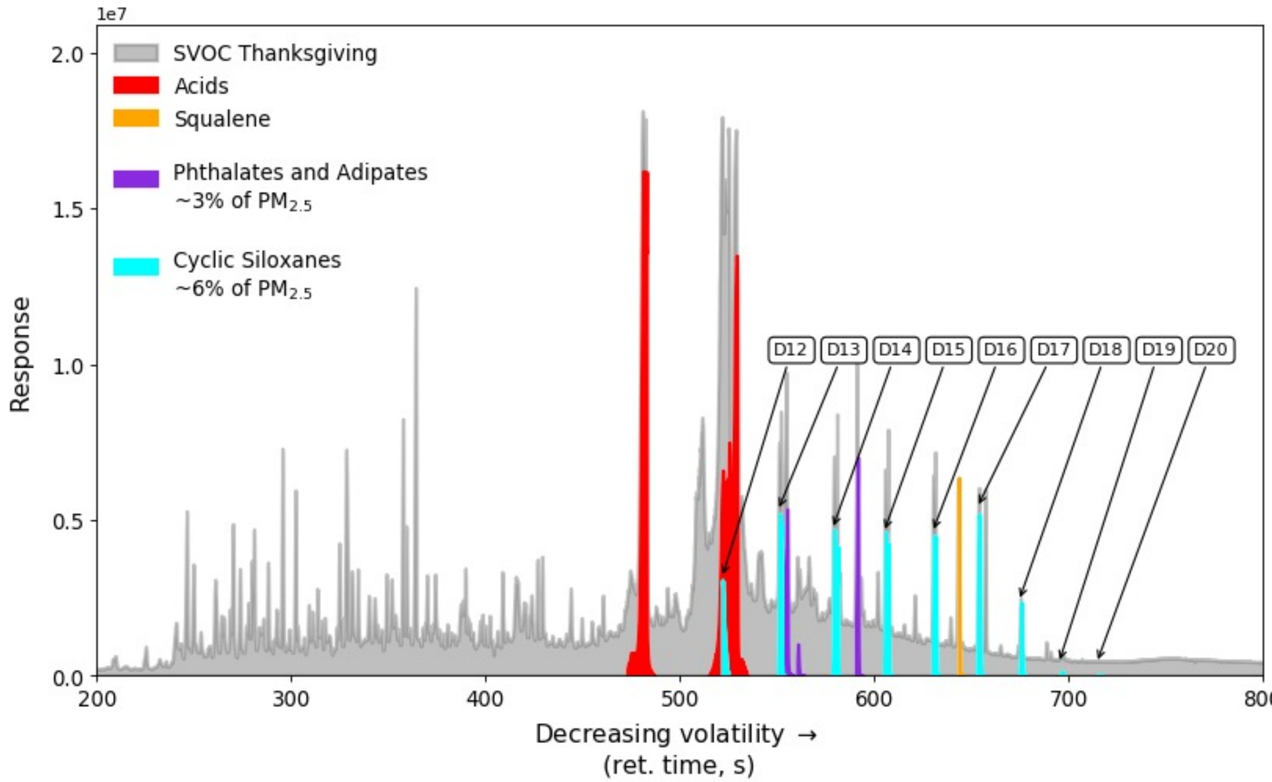
Study site is a wood-framed house built ~ 1950 in northern California. The 9-week wintertime monitoring campaign used semivolatile thermal desorption aerosol gas chromatography (SV-TAG).

Reference: K Kristensen, et al., Sources and dynamics of semivolatile organic compounds in a single-family residence in northern California, *Indoor Air* **29**, 645, 2019.

Particle-phase SVOCs during HOMEChem Thanksgiving

Highlights
- Low volatility cyclic siloxanes (D12-D20) probably are from heated oven.
- Phthalates and adipates are likely from building materials and static contents with enhancement from high airborne PM levels.
- Squalene *may* be from turkey skin.

The HOMEChem study was conducted in a research house at UT Austin. This chromatogram represents organic compounds in airborne particles sampled during a simulated Thanksgiving-day event.

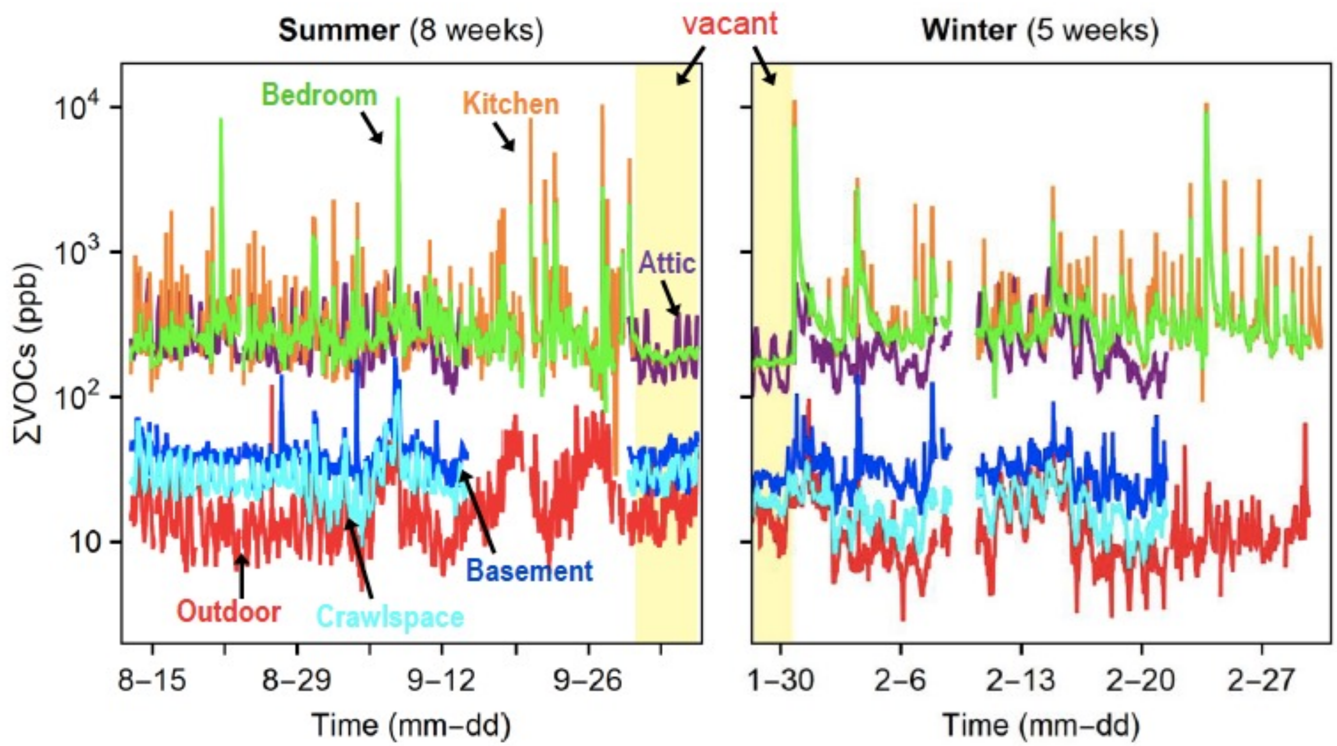


Reference: DM Lunderberg et al., Surface emissions modulate indoor SVOC concentrations through volatility-dependent partitioning, *Environmental Science & Technology* **54**, 6751, 2020.

Volatile organic compounds (VOCs): indoors >> outdoors

Highlights (summed VOCs)
- Living spaces ~ attic >> outdoor ~ subfloor (both seasons, vacant or occupied)
- Occupancy influences dynamics

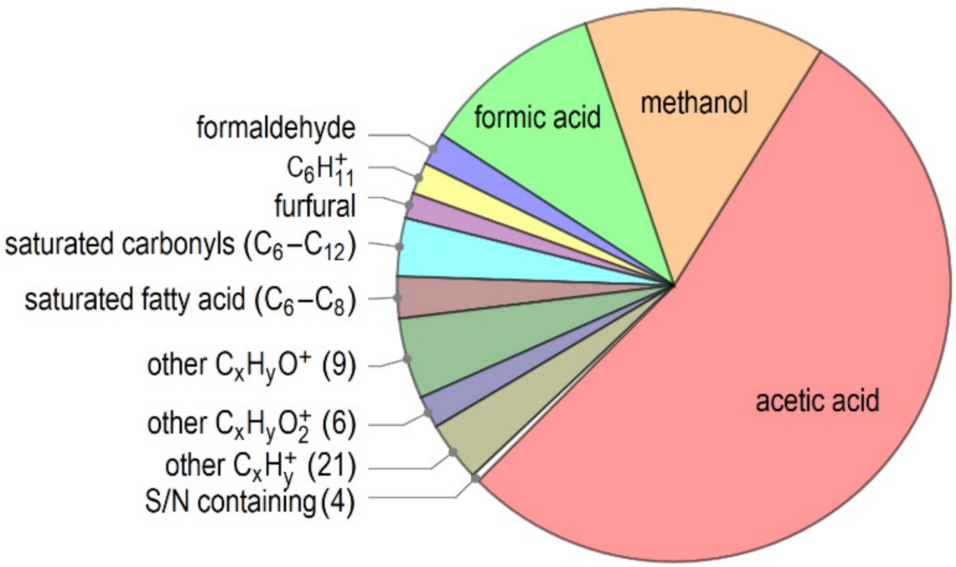
Continuous, time-resolved monitoring of volatile organic compounds in a normally occupied residence using proton-transfer reaction time-of-flight mass spectrometry. Study site is a 80-y old, wood-framed house (not recently refurbished) in northern California.



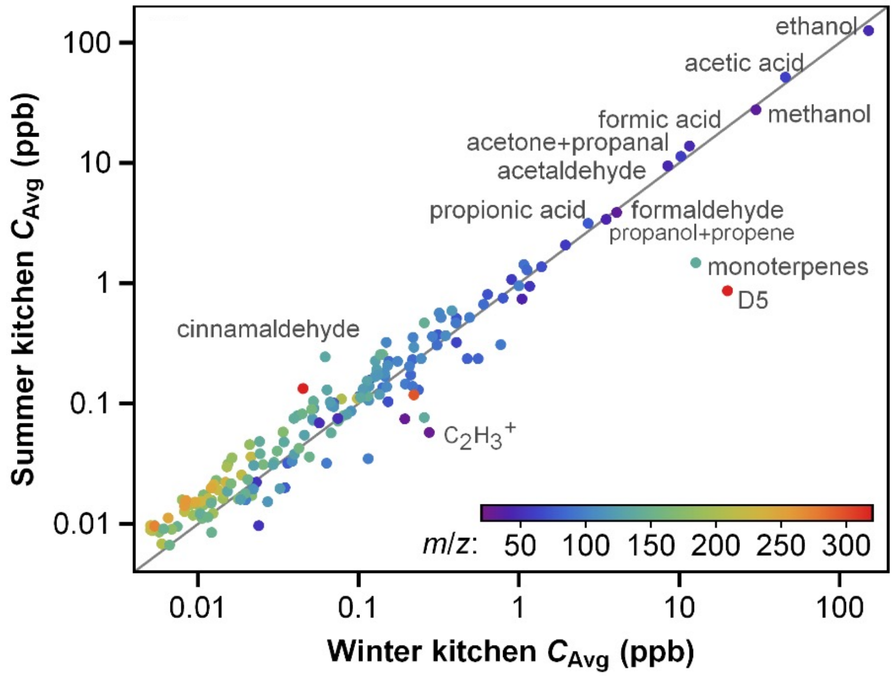
Reference: Y Liu, et al., Characterizing sources and emissions of volatile organic compounds in a northern California residence …, *Indoor Air* **29**, 630, 2019.

VOC emissions dominated by building and static contents

Apportionment of emission rate among 56 ions that meet the criteria for continuous sources. Total indoor emission rate = 37 mg/h (summer, average).



VOC composition is consistent across seasons.



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Reference: Y Liu, et al., Characterizing sources and emissions of volatile organic compounds in a northern California residence …, *Indoor Air* **29**, 630, 2019.

Semivolatile organics: Partitioning estimates

K_{oa} = octanol-air partition coefficient, an affinity indicator

*O** = volume of equilibrated organic condensed phase compartment (CPC) per volume air.
- Airborne organic PM: *O** ~ 5×10^{-12}
- Surface organic film: *O** ~ 4×10^{-8}
- Painted surfaces: *O** ~ 10^{-4}

Organic phase partitioning:
CPC/airborne ~ $K_{oa} \times O^*$

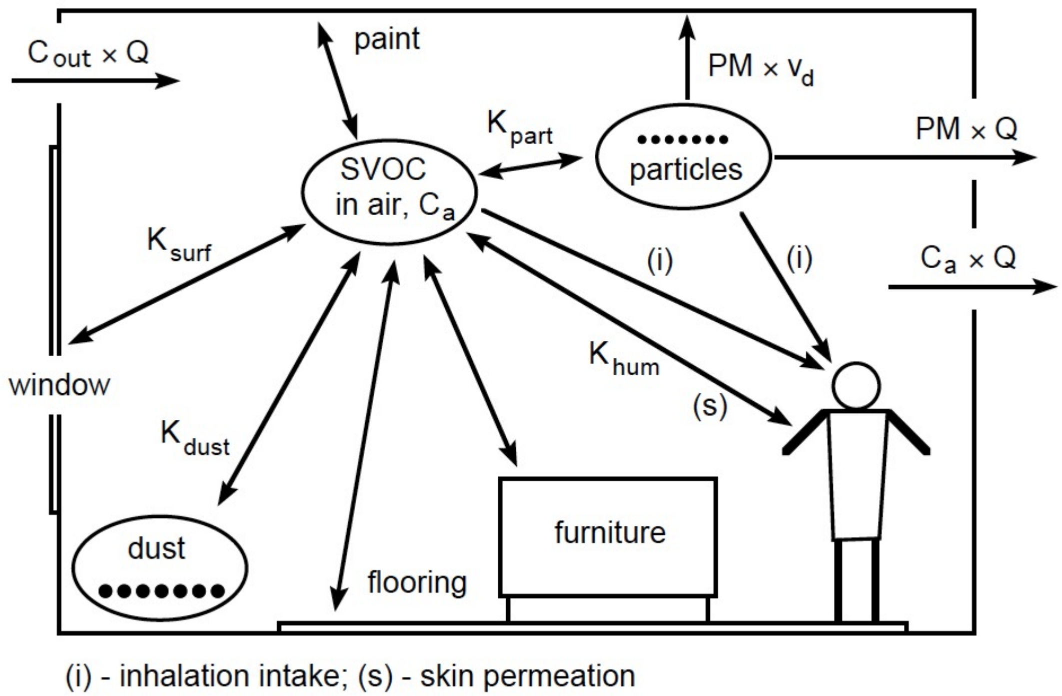
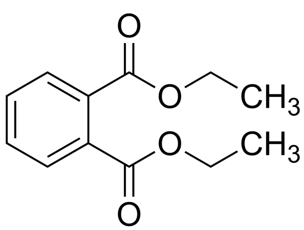


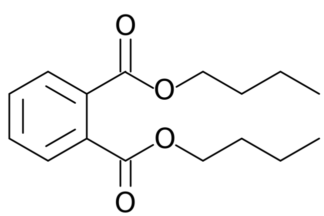
Image: CJ Weschler, WW Nazaroff, Semivolatile organic compounds in indoor environments, *Atmos. Environ.* **42**, 9018, 2008. Assumed values: organic PM ~ 5 μg m^{-3}; surface organic film thickness ~ 10 nm ; paint thickness ~ 64 μm; room dimensions = 3 x 4 x 2.5 m with painted walls and ceiling; surface-to-volume ratio of 4 m2/m3 covered with organic film.

Abundance ratios: Equilibrated condensed phase to air

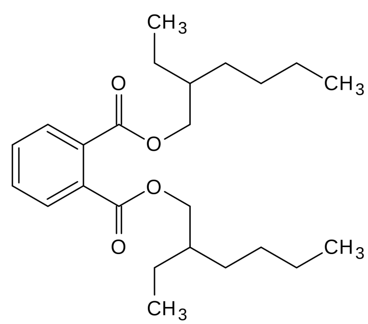
Compartment	DEP	DBP	DEHP
Airborne organic PM ($O^* = 5 \times 10^{-12}$)	5×10^{-5}	2×10^{-3}	20
Surface organic film ($O^* = 4 \times 10^{-8}$)	0.4	16	16,000
Painted walls and ceiling ($O^* = 10^{-4}$)	1000	40,000	4×10^{8}



Diethyl phthalate (DEP) log K_{oa} = 7



Dibutyl phthalate (DBP) log K_{oa} = 8.6



Diethyl hexyl phthalate (DEHP) log K_{oa} = 12.6

Legacy pollution: To remove DBP sorbed in paint by ventilation at an air-change rate of 0.5 h^{-1} would require 9 y (80,000 h).

Reference (K_{oa} values): P Schossler et al., Beyond phthalates…, *Science of the Total Environment* **409**, 4031, 2011; tabulated partitioning assumes equilibrium conditions.

Summary thoughts: Some future challenges and questions

• Utilize knowledge of indoor chemistry for effective air quality improvements (source control, air treatment, …).
• Advance knowledge about indoor chemistry across the built environment broadly (in addition to studying a few deeply).
• Would incorporating knowledge about chemical byproducts improve ozone health-risk assessments?
• Does PM chemical composition affect health risk?
• What are the important surface reservoirs for indoor organics? (How abundant are they? What controls exchange processes with indoor air?)

If the chemistry is too much, here are four key principles to guide efforts toward improving indoor air quality.

Image source: https://www.microbe.net/2013/09/16/four-principles-for-good-indoor-air-minimize-indoor-emissions-keep-dry-ventilate-protect-against-outdoor-pollution/; Reference: WW Nazaroff, *Indoor Air* **23**, 353–356, 2013.