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Emerging and Impactful Research Needs: Insights Regarding Sources

Why Indoor Chemistry Matters Workshop 2: Prioritizing Indoor Chemistry Research
National Academy of Sciences

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Motivation: major exposure location

- Time spent indoors
- Close proximity to source emissions we generate through activities
- Limited ventilation
- A complex and evolving mix of chemicals, from:

human activities
consumer products
building materials
chemical reactions
biological processes
outdoor air

Unfortunately, one challenge is proprietary information about products

Why Indoor Chemistry Matters, NAS (2022) and references therein

Types of sources:

Primary - chemicals emitted directly (e.g., from cooking, volatile losses)

Secondary - emission of chemicals formed through indoor chemistry.

e.g., from oxidation of skin or surface films or gas phase

Sources to indoor air

Sources to outdoor air

Chemicals with higher indoor concentrations have indoor sources

VOCs:

TEAM Study	e.g.,	Wallace et al., *Atmos Environ*. 1985
NHANES		Su et al, *Atmos. Environ*., 2012
RIOPA Study		Su et al., *Environ. Res*. 2013

Chemicals with elevated indoor concentrations: WSOCg

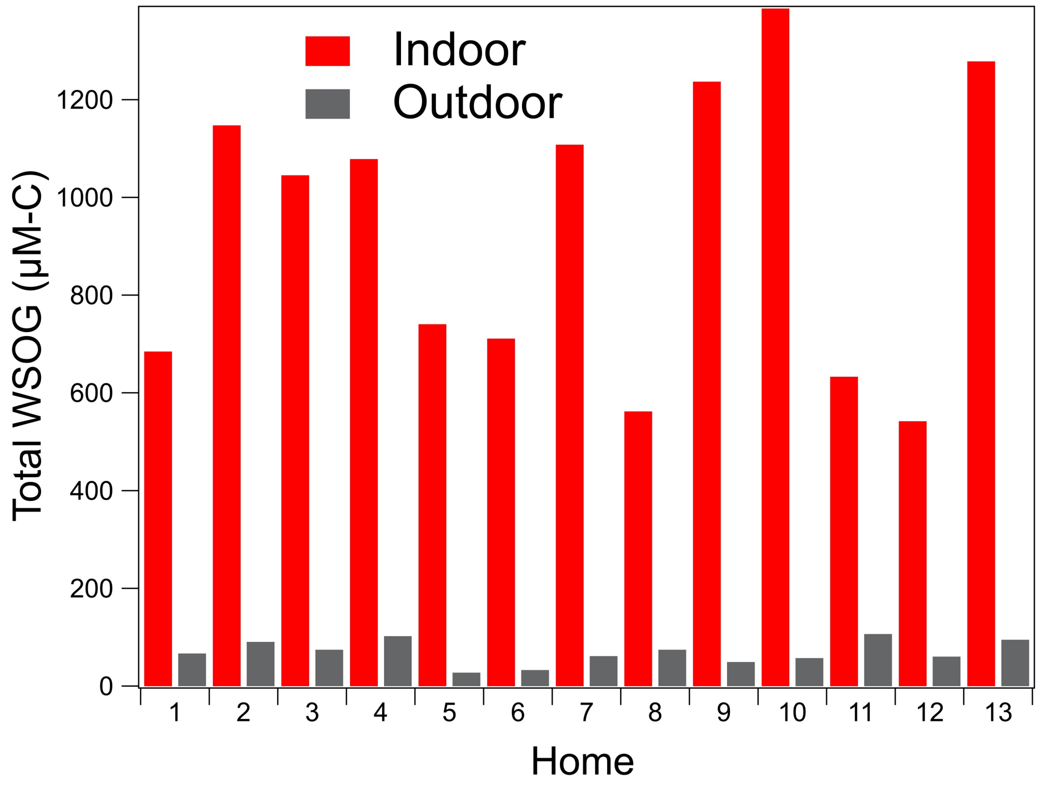
Water soluble organic gases

13 NC and NJ homes

few measurements of this type. Value of mass balance

What chemicals?
Major sources?
Primary or secondary (oxidation products)?

Total Water Soluble Organic Carbon (WSOCg)
~13 times higher inside



Means: 145 vs 11 μg-C/m^3

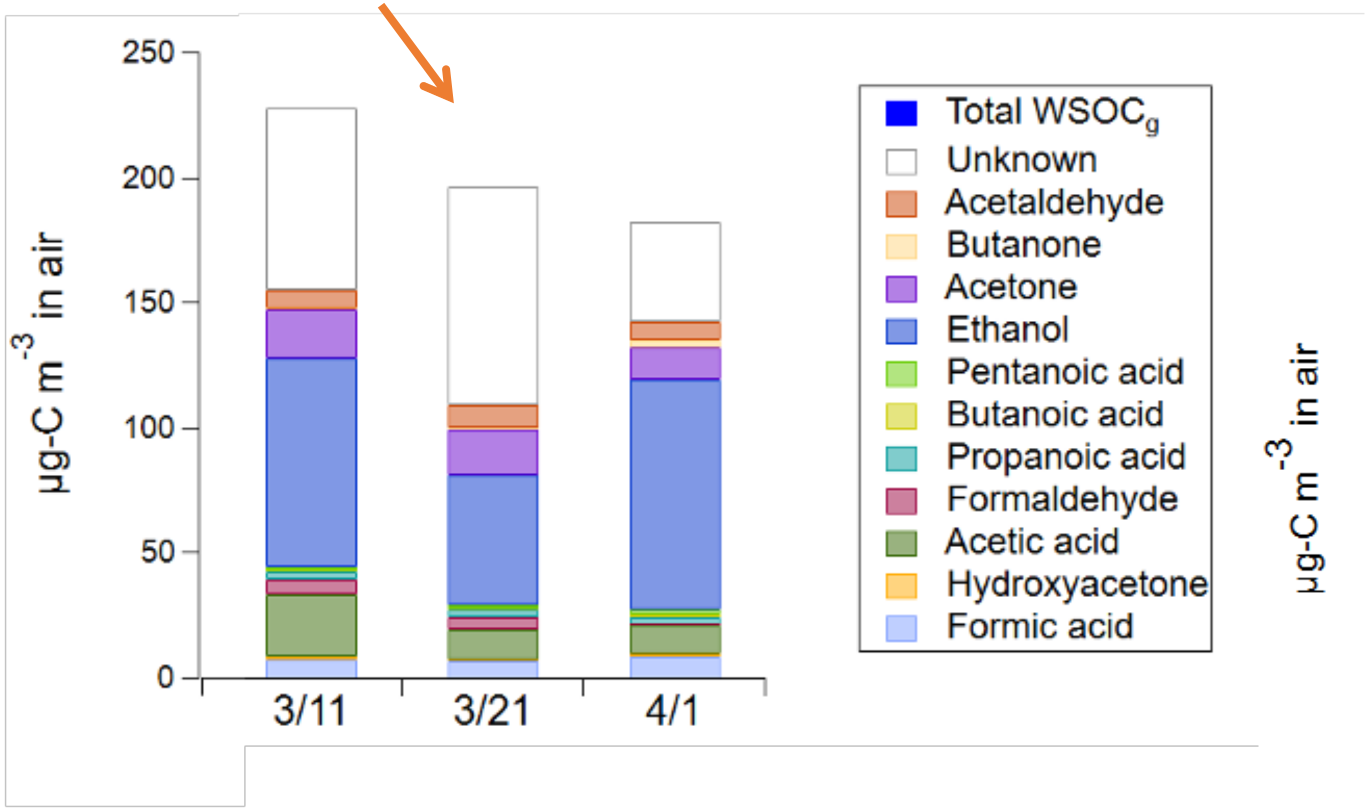
Duncan et al., *ESPI*, 2019

Value of species mass balance in identifying what is missing and do we understand the big picture

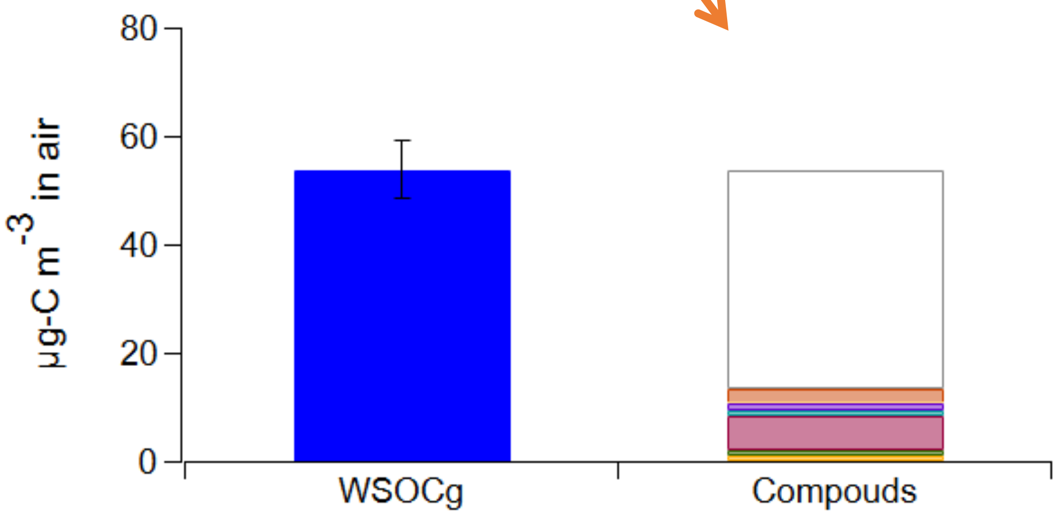
CASA Study

House background

Indoor WSOCg 20x outdoor



Infiltrated woodsmoke



Webb, Turpin, et al., *in preparation*

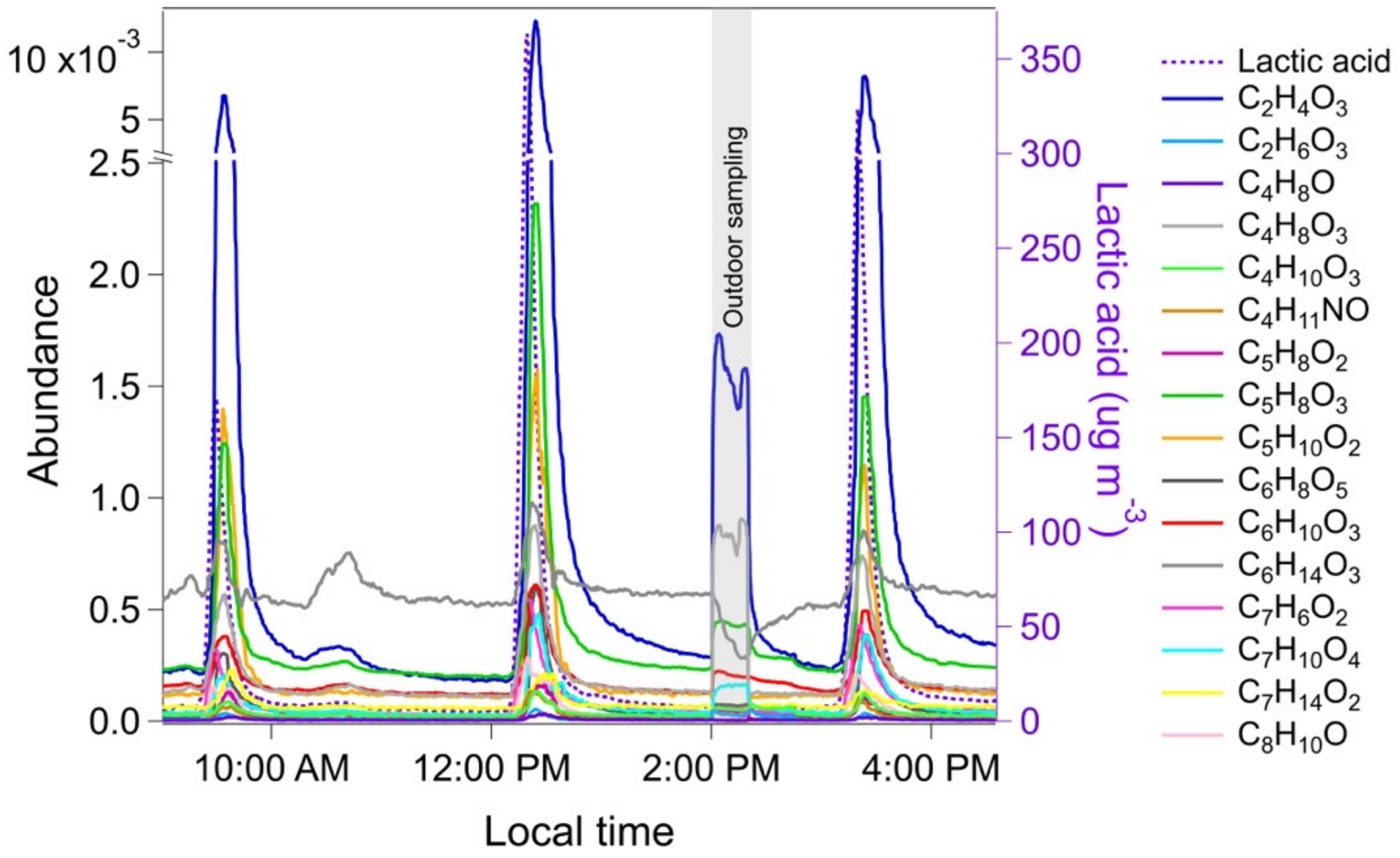
Value of real time measurements in locating (identifying) sources

Chemical Ionization Mass Spectrometry

Small number of real-time indoor studies <u>including:</u>

- HomeChem
- CASA

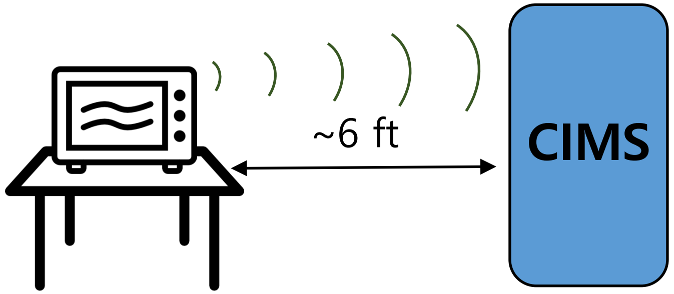
Cooking events: eggs and bacon

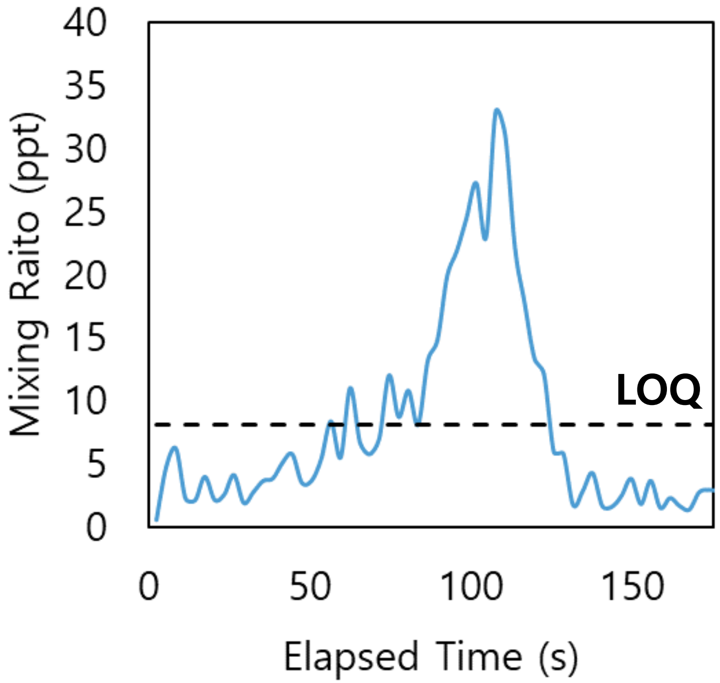


Duncan, *ES&T* 2019

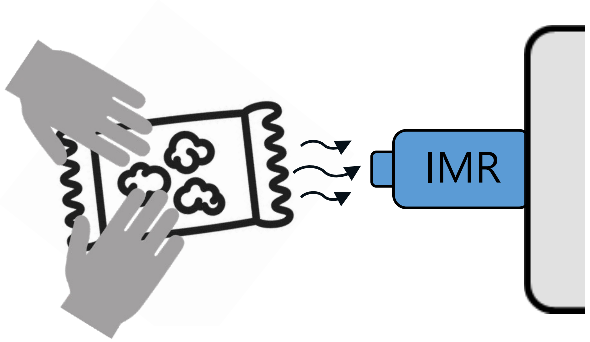
Locating sources

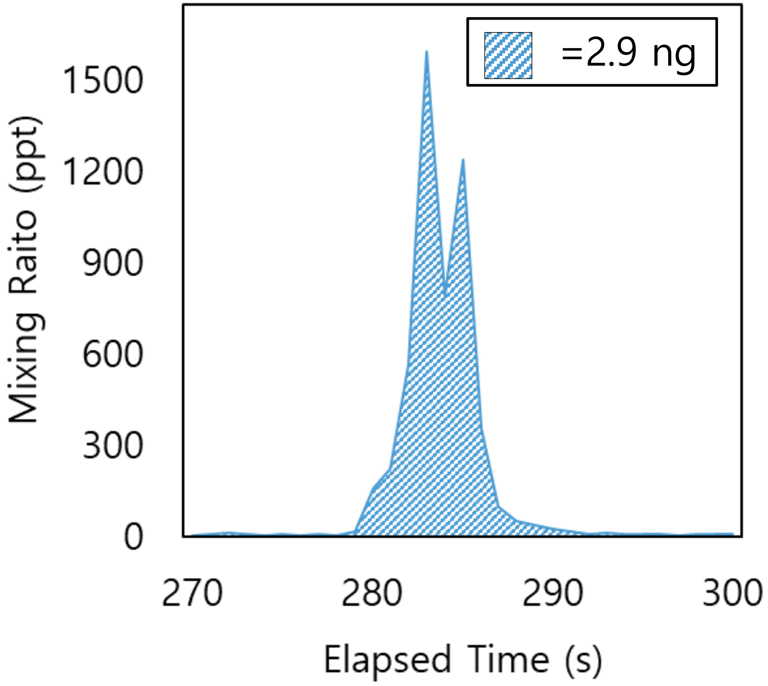
Real time mass spectral methods promising for emissions measurements even for low concentration species





6:2 FTOH emitted from Microwaving Popcorn

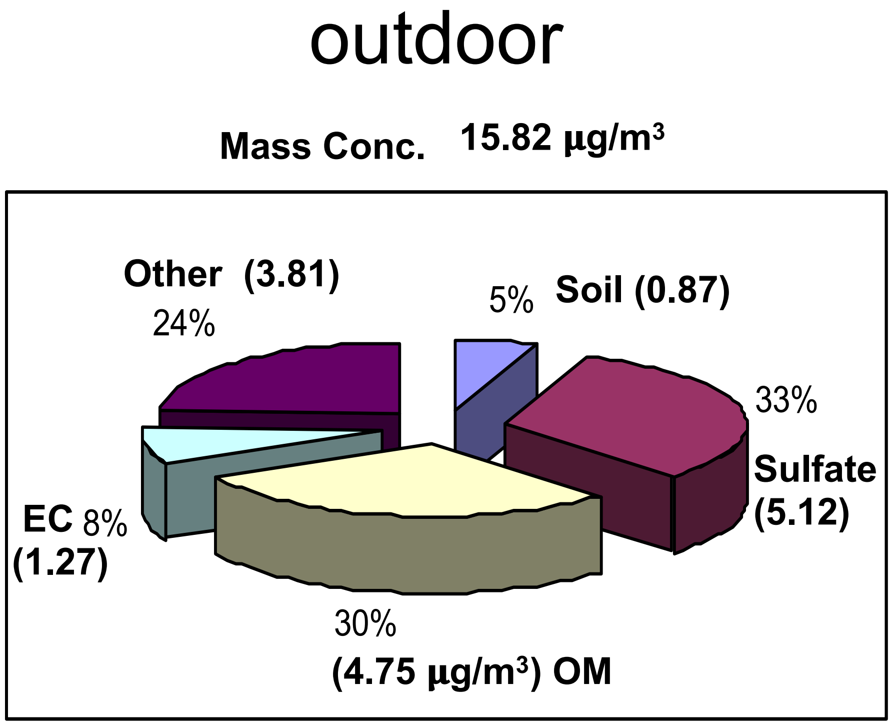


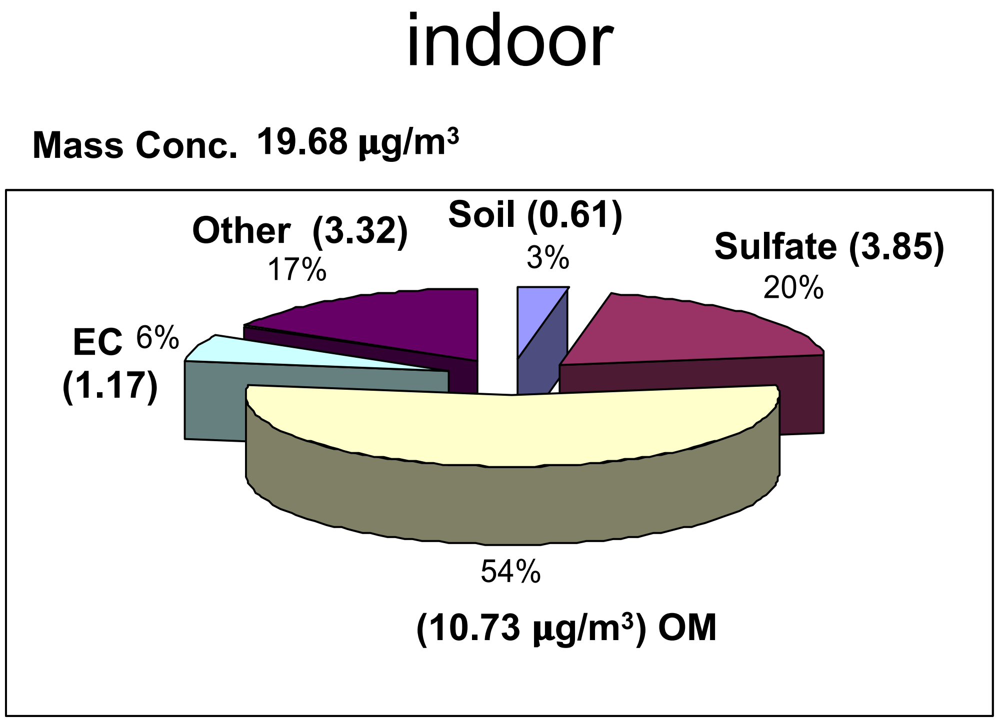


Davern et al submitted

Organic $PM_{2.5}$ twice as high indoors

RIOPA $PM_{2.5}$ Elizabeth, NJ, USA





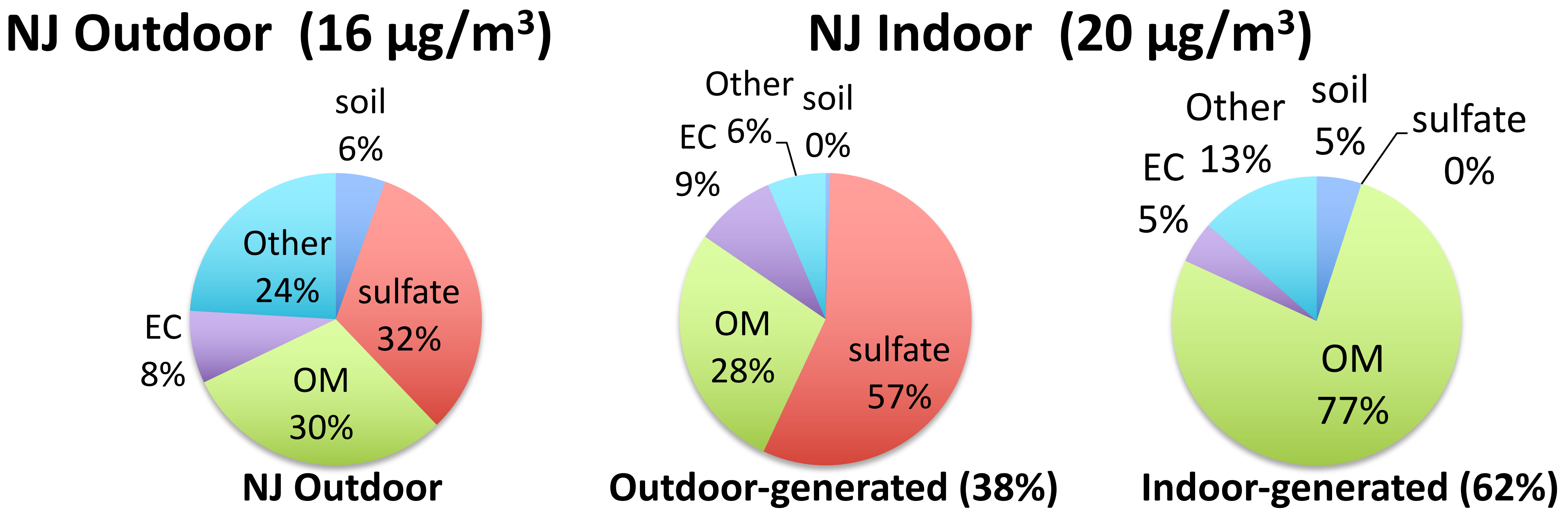
Mass balance assumptions:

$S = (NH_4)_2SO_4$ OM=1.4xOC

Soil = sum oxides

Polidori et al., *JEAEE 2006*

Indoor-generated $PM_{2.5}$ is largely organic



Derived from measurements of Polidori et al., *JEAEE 2006*

Potential implications (example)

<u>Example:</u>

Emitted organic PM could be a vehicle for transport of reactive or toxic chemicals, to the lower lung or to outdoor air.

- PAHs: Carbonaceous PM enhances partitioning of PAHs to particle phase

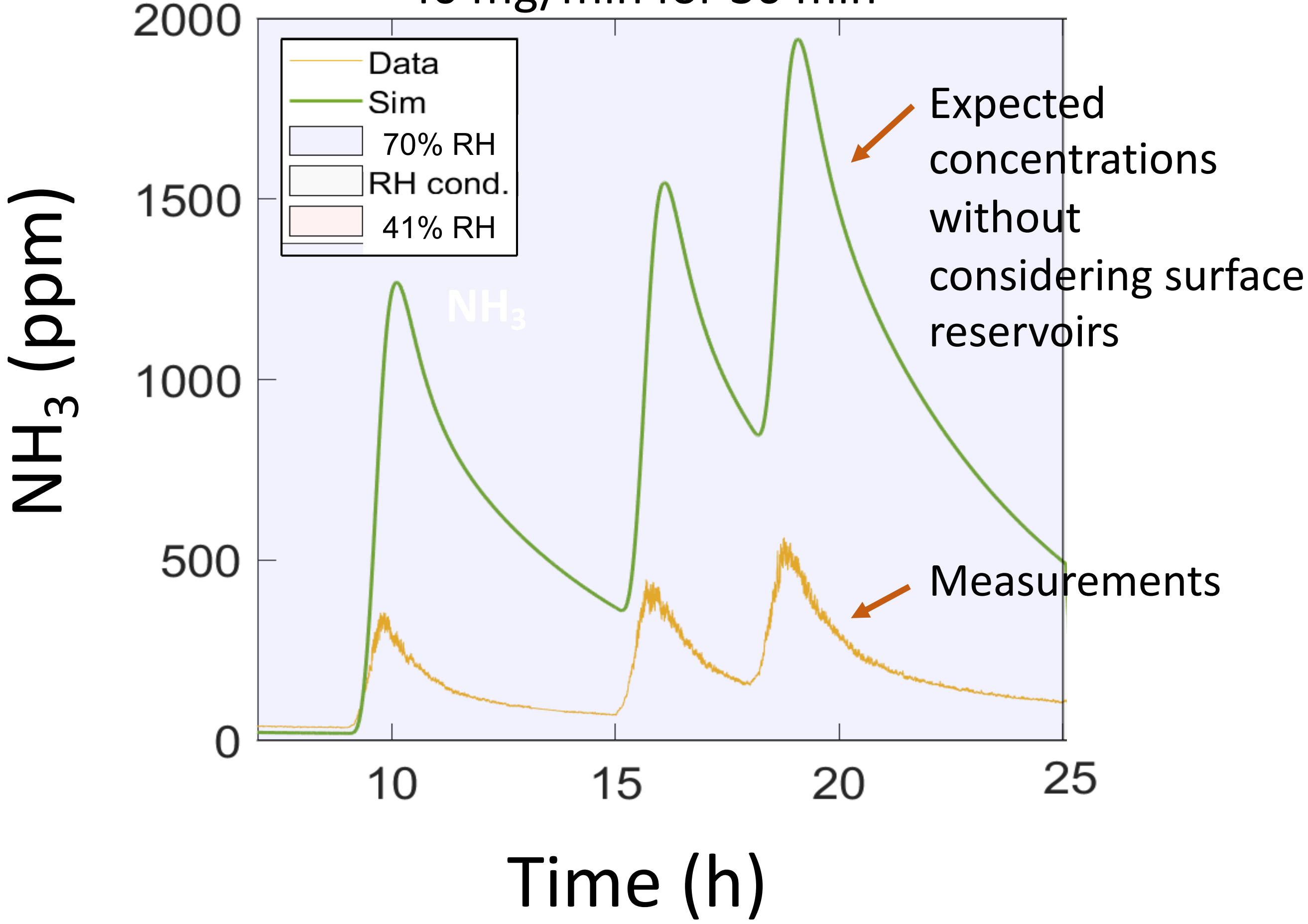
  Naumova et al., Atmos. Environ. 2003

- Does this effect exposure and dose of aerosol-associated ROS or toxic chemicals (e.g. PFAS) to the lungs or to outdoor air?

Ammonia: indoor/outdoor > 10 in homes

Ampollini, DeCarlo et al (HomeChem) ES&T 2019

CASA campaign
3 ammonia injections
40 mg/min for 30 min



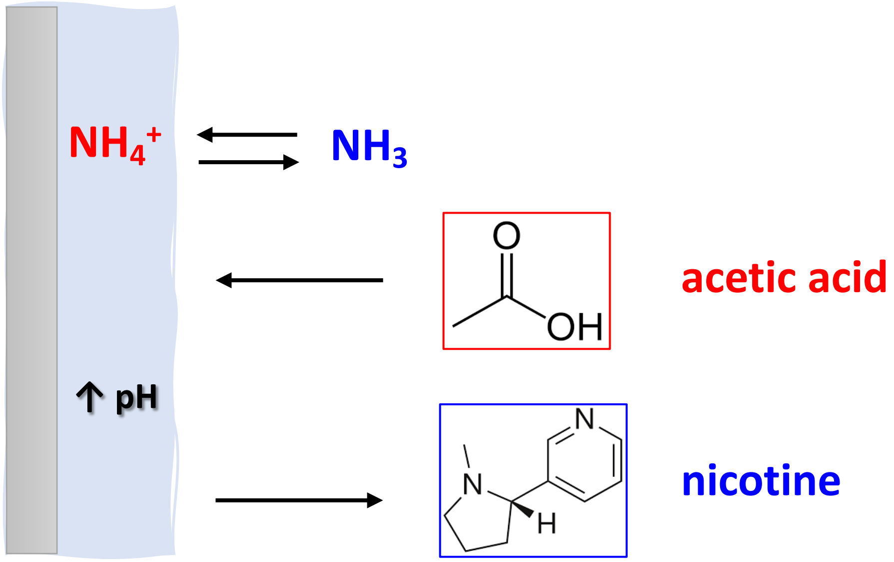
70-80% of injected NH_3 was located in house reservoirs at the 24 h time point

Best fit model including surface reservoirs with reversible uptake:

Reservoir 50% larger at 70% RH than at 41% RH

Webb et al, in preparation

Potential implications



- Indoors (30 to >1000 ppb); outdoors (1-5 ppb)
- Many known indoor sources
  (e.g. people, cleaning products, cooking)
- Water soluble base
- Increases pH in surface reservoirs
- Alters air concentrations of acids, bases

Ampollini, *ES&T* 2019,
Ongwandee & Morrison, *ES&T* 2008; Healthy Build 2006

Limited quantitative understanding of the impact of NH_3 on indoor air

Per- and polyfluoroalkyl substances are elevated indoors

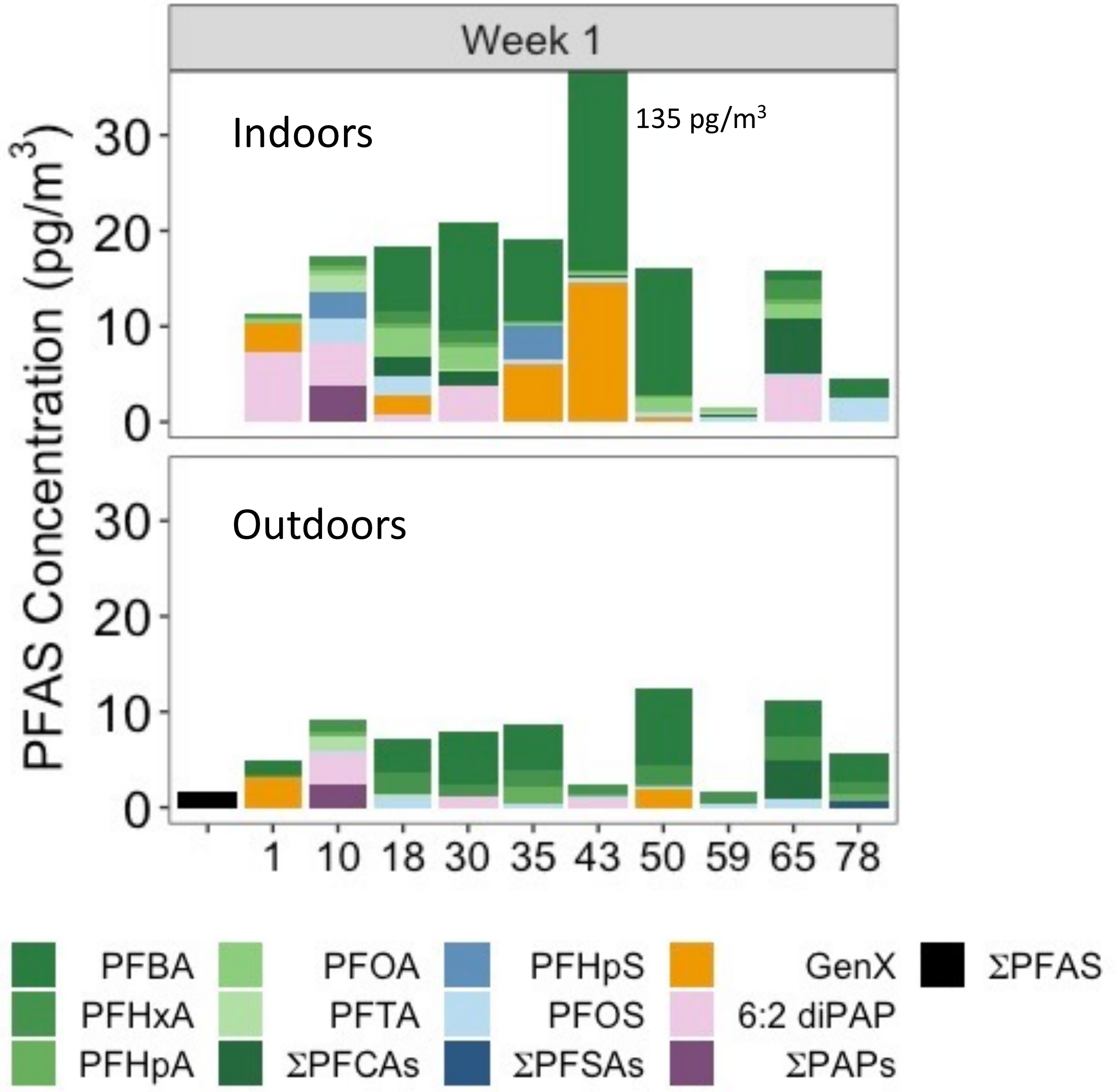
<u>26 Ionic PFAS:</u>

- Residential indoor 2-3 times larger than residential outdoor

- order of magnitude higher than regional background

<u>9 Neutral PFAS:</u>

- Indoor concentrations 1000 times higher than for ionic PFAS



Chang, et al., submitted
Eichler et al., ES&T 2023

PFAS: Many potential indoor sources, but which dominate?

Used because of water, stain, and heat resistant properties

Photo Credit: https://www.sixclasses.org/videos/pfas

Challenges of evolving and proprietary product formulas,

Some of >10,000 PFAS species have been measured in many products

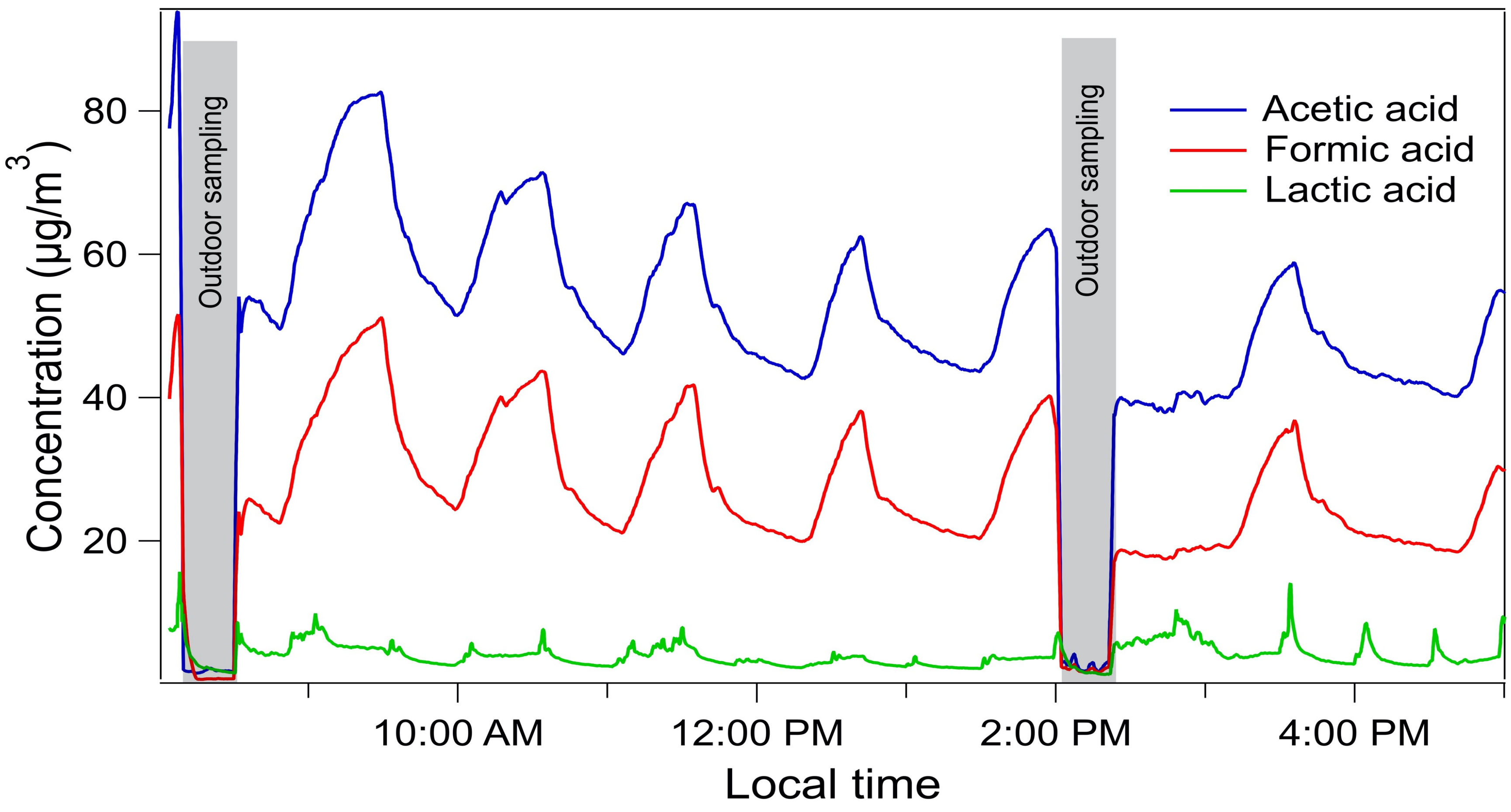
What are the major sources to indoor air?

What influences partitioning?

What processes and pathways drive indoor concentrations, exposures and emissions to outdoor air?

Surfaces can have a large impact on air concentrations
Large loss of WS gases to AC system; Rapid rebound from building reservoirs

Organic acids (CIMS)



Duncan, Turpin, et al., *ES&T* 2019

Indoor surfaces, surface soiling and surface associated water provide sinks/reservoirs and also sources of primary/secondary

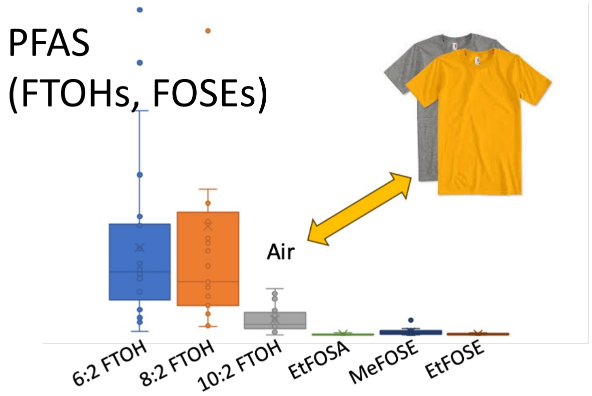
Higher surface-to-volume ratios indoors

Indoors: > 3 m^2/m^3

Outdoors: < 0.01 m^2/m^3

Singer et al. 2007

Morrison & Nazaroff, 2000



Eichler, et al., ES&T, 2023

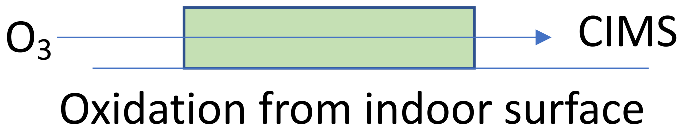
Surface reservoirs prolong residence time of chemicals indoors – time for reaction

Strongest evidence for production (emission), is for ozone oxidation products

Why Indoor Chemistry Matters, NAS (2022)
and references therein

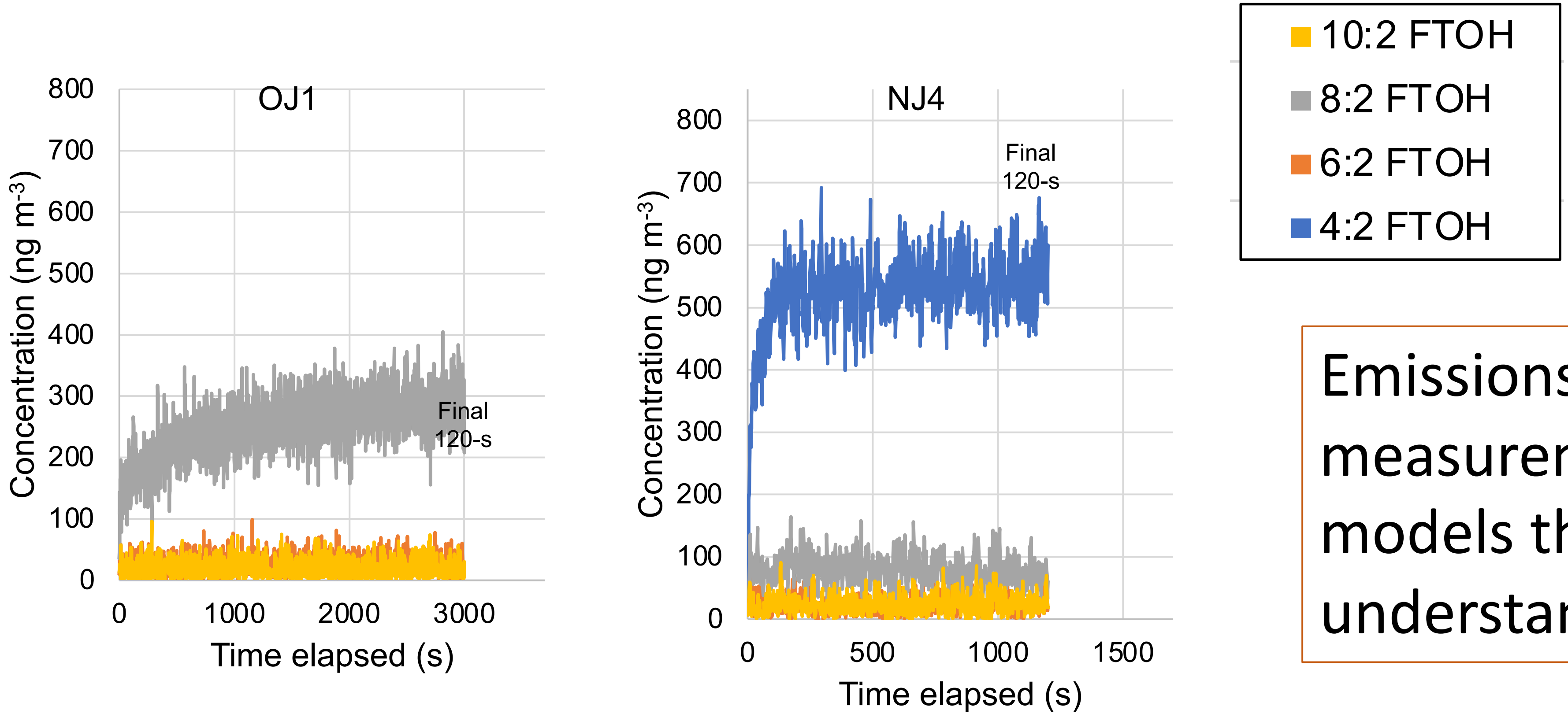
Soiling/Water alter partitioning. Their role in chemistry is incompletely understood.
Photosensitized reactions on soiled windows? Acid/base, hydrolysis, oxidation…
What are the secondary air emissions of volatile/semi-volatile products?

Potential for real-time mass spectral methods to measure emission rates with excellent sensitivity



Two Jackets

FTOH emission rates in the 10s to 100s of pg h^{-1} cm^{-2}



Emissions measurements feed models that test our understanding

An iterative process

- Hypothesis-building field campaigns in real buildings
- Controlled experiments, perturbation experiments, emissions measurements with some level of authentic complexity
- Model development and model-driven measurements
- Field campaigns designed to test physical/chemical understanding in models

Buildings are a source of chemicals to outdoor environment

<u>Example:</u> Volatile Chemical Products (VCP)
McDonald et al., *Science* 2018

PFAS

+OH → PFAAs

Ventilation of 9 neutral PFAS

Ventilation of 26 ionic PFAS

Dust removal (vacuuming)

Air exchange rates and cleaning/removal rates determined during the IPA Campaign

Eichler et al., *in preparation*
Chang et al., submitted

PFAS emissions from homes by ventilation: neutral > ionic

IPA Campaign: 10 NC homes

One home 

	9 neutral PFAS	26 ionic PFAS
One home	~ 39 mg yr^{-1}	~0.02 mg yr^{-1}

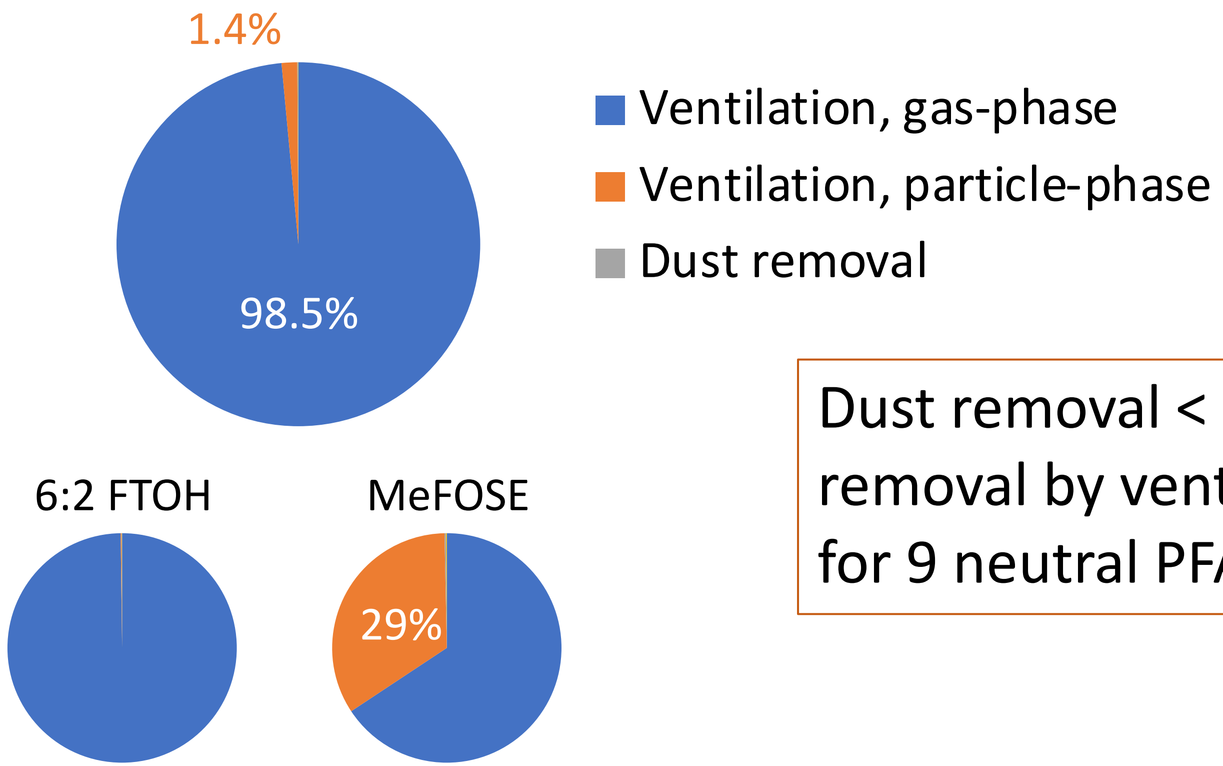
Neutral PFAS are:

- byproducts of manufacturing
- rarely reported by manufacturing facilities.
- likely have emissions from consumer materials and products (based on above)
- thus, **could be a major largely unmeasured source of PFAS from manufacturing facilities**

Eichler et al., *in preparation*
Chang et al., *submitted*

Neutral PFAS removal from homes: ventilation dominates over dust

IPA Campaign: 10 NC homes



Dust removal < 0.1% of removal by ventilation for 9 neutral PFAS

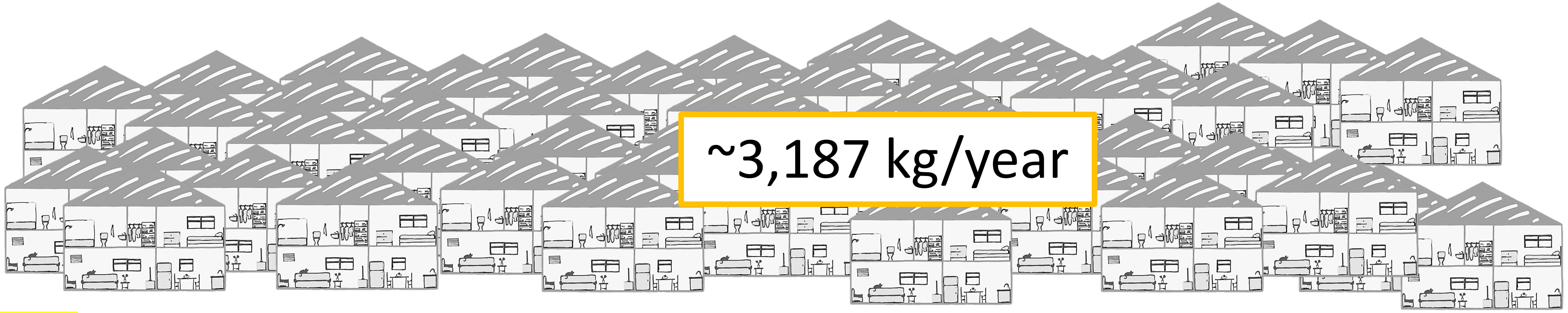
Eichler, Turpin, et al., *in preparation*

PFAS emissions from single-family, detached homes

- In Raleigh metropolitan, NC: ~**0.33 M** homes

~13 kg/year

- In the US: ~**82 M**



~3,187 kg/year

- Only 9 out of >10,000 PFAS

- PFAS manufacturing: generally does not report these compounds

total reported : ~109,393 kg/year total (mostly short chain ionic PFAS);

~19,700 kg/year long chain

a mass balance on total orgF would help understand the true impact

Eichler, Turpin, et al., *in preparation*

Summarizing Opportunities and Needs

- Progress in understanding drivers of chemical dynamics
- Progress developing tools, methods
- Developing a quantitative, actionable understanding of indoor environment benefits from an iterative process
- Test understanding with models in realistic settings
- Identify of sources, emission rates to test our understanding with models under realistically-complex environments
- What are we missing? Mass balance? Surface-associated oxidants, Secondary sources?
- Impacts on outdoor air?

Summarizing Opportunities and Needs

- An indoor challenge: complexity, heterogeneity
- An indoor advantage: can manipulate the system, while embracing complexity
- A challenge: proprietary and evolving chemical mixtures in products

Extra Slides

Indoor Challenges (homes)

Every indoor environment is different

And many buildings are exposure environments for only a few people

Challenges: every home is different

Population-based sampling (sensors, passive, other)

Convenience sample – with purposeful variations

to understand determinants (RIOPA example)

Intensive sampling in single home, **benchmarking**

Purposeful manipulation, controlled experiments

Sampling for model testing

Medians and extremes

Summarizing Opportunities

Every indoor environment is different

Population-based sampling; benchmarking; identifying critical factors; median and outliers

Loss processes of comparable timescale

Building manipulation to isolate a process

Real time measurements

Chemistry

observations in authentic buildings

hypotheses and model testing

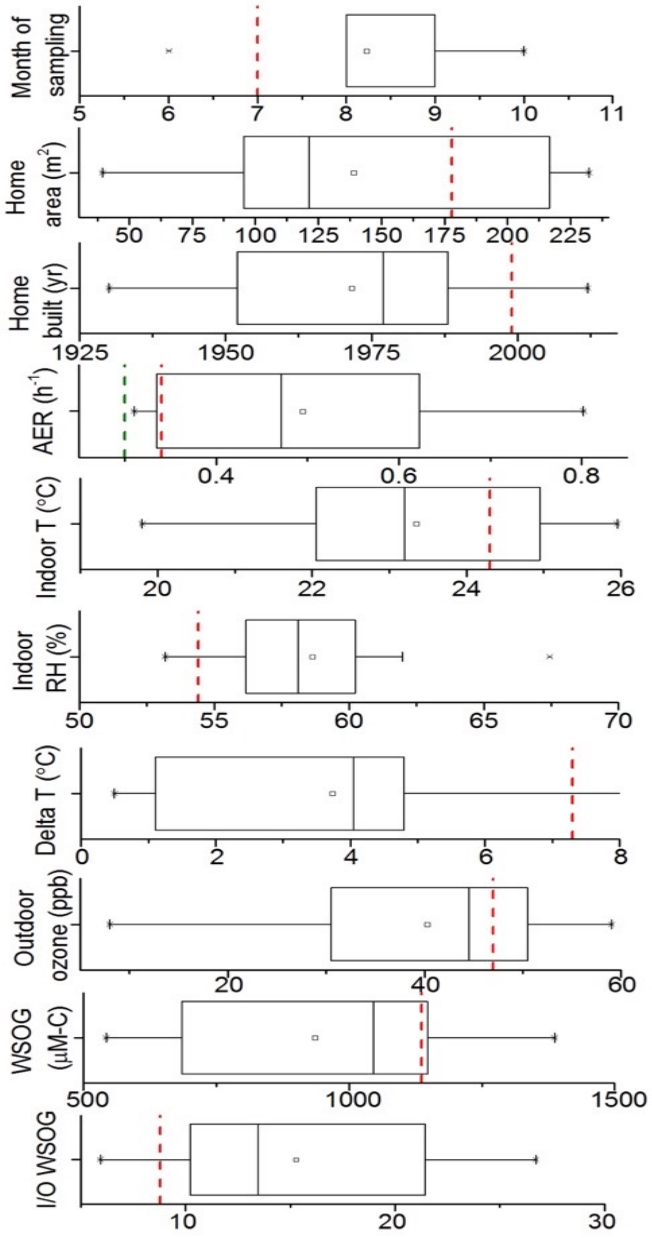
Controlled experiments (e.g. with authentic surfaces)

Characterization of indoor surfaces

Continued characterization; thermodynamic modeling; surface/multiphase chemistry

Benchmarking

N=13 NC/NJ homes



Sampling month

Floor area

Year built

AER (h^{-1})

Indoor temp. (ºC)

Indoor RH (%)

Indoor-outdoor temp. difference

Outdoor ozone (ppb)

WSOG (µM-C)

Indoor/outdoor WSOG

Duncan et al., *ES&T*