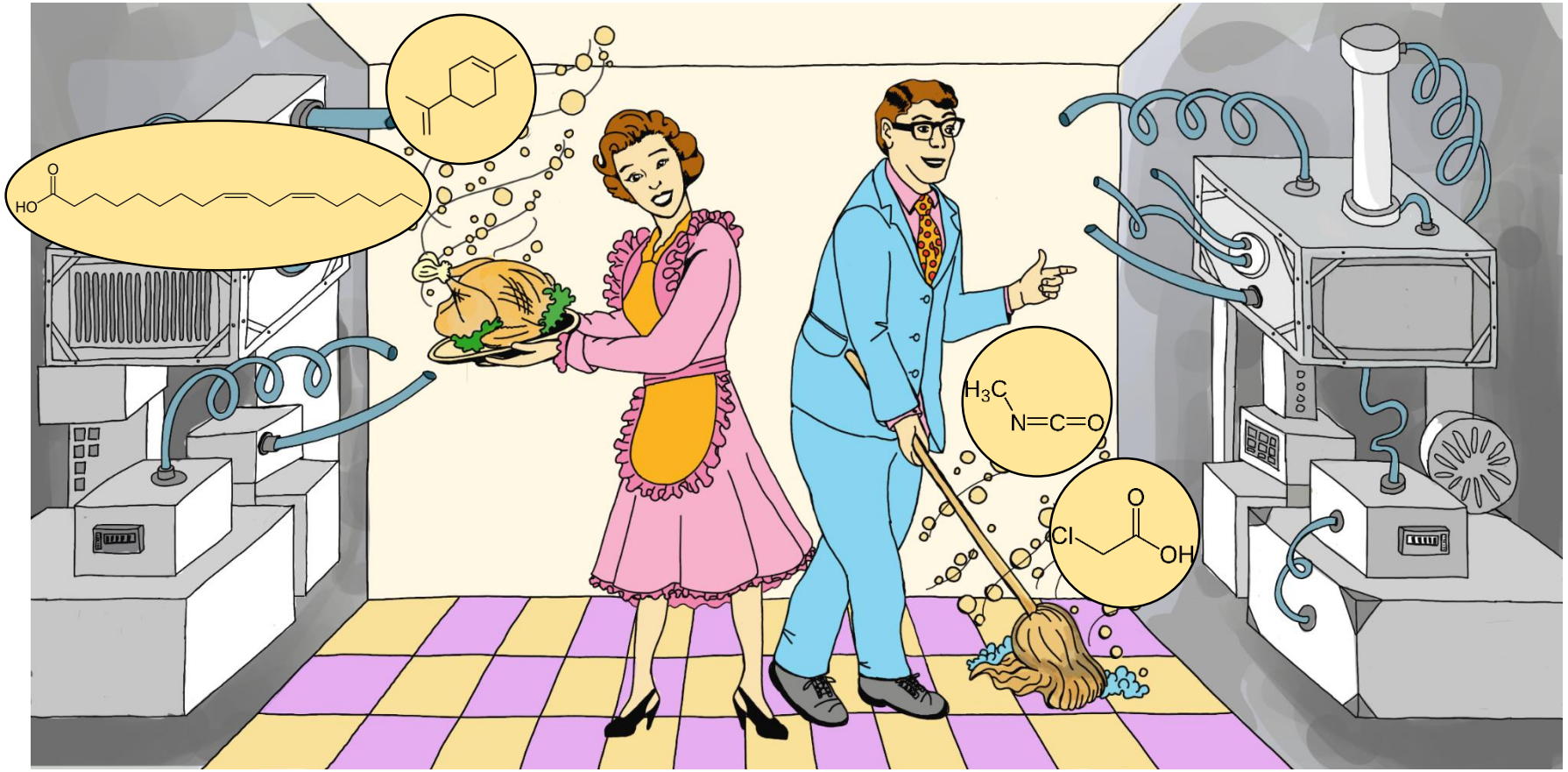
Everything but the kitchen sink: Understanding chemical complexity in our home



ALFRED P. SLOAN FOUNDATION

Delphine K. Farmer[1] + M. Vance[2], J. Mattila[1], A. Abeleira[1], E. Katz[3], P. DeCarlo[3], C. Wang[4], J. Abbatt[4], P. Stevens[5], A. Novoselac[6], P. Lakey[7], M. Shiraiwa[7] and the HOMEChem Science Team

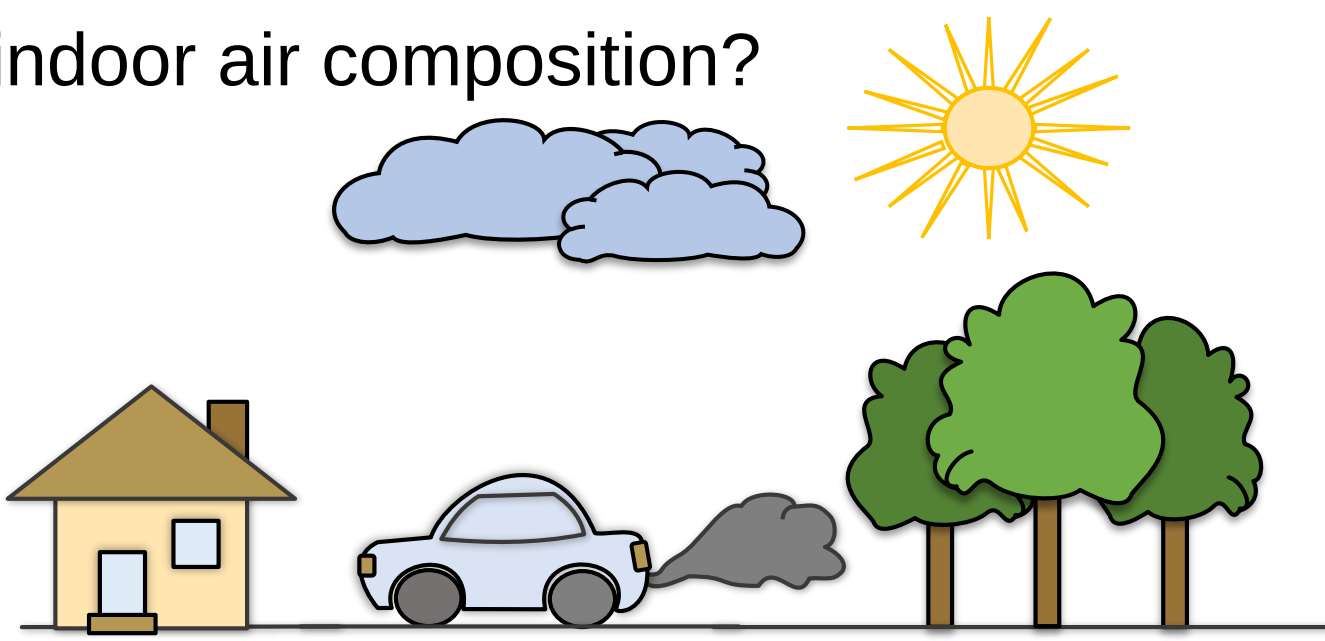
1. Colorado State University 2. University of Colorado Boulder 3. Drexel University 4. University of Toronto 5. Indiana University 6. University of Texas Austin 7. University of California Irvine

We spend 90% of our time indoors – but most air quality/health research has focused on outdoor air pollution

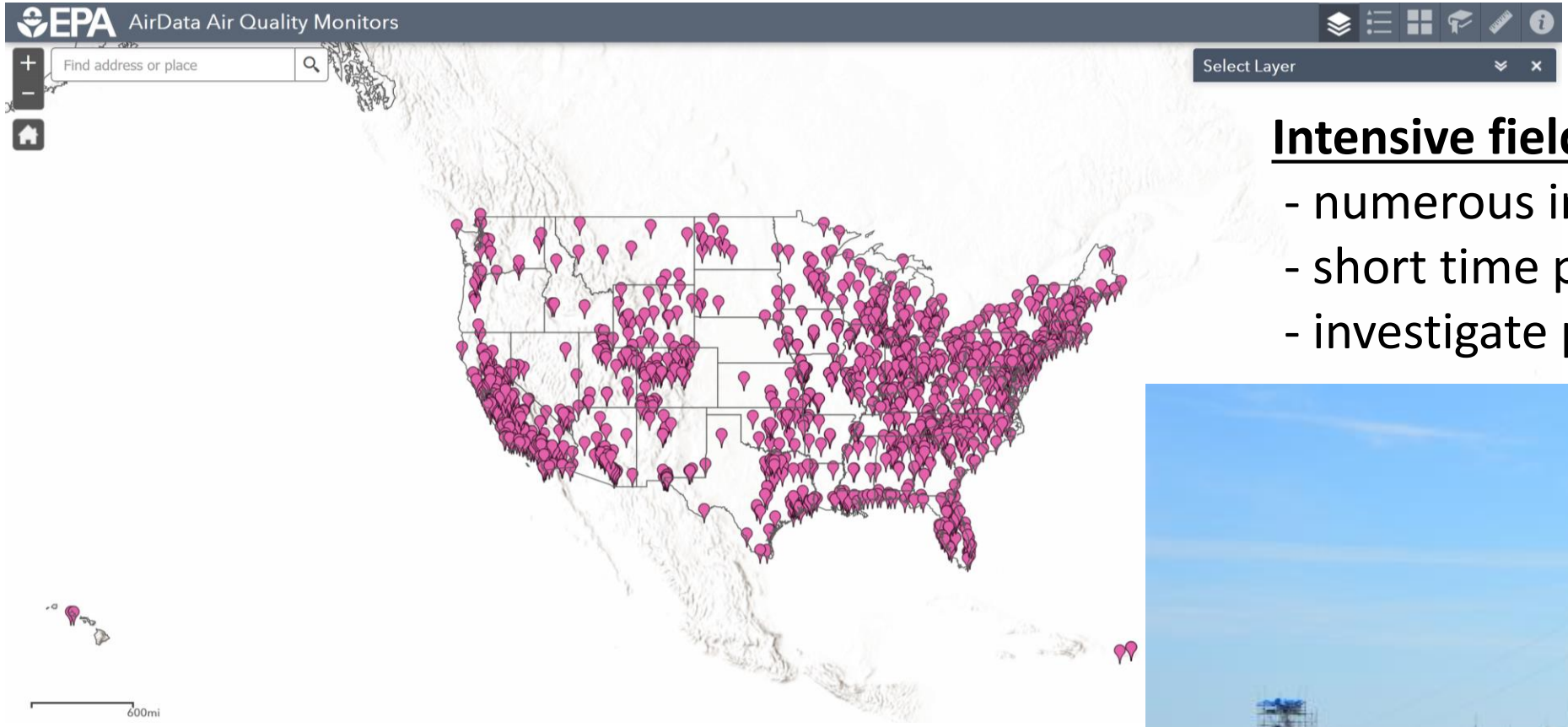
- How different is indoor chemistry to outdoor atmospheric chemistry?
  - Sources
  - Timescales
  - Surface Area : Volume
  - Low light

- What chemical processes control indoor air composition?

- What is the fate of indoor air?



How do we approach measuring indoor chemistry? Parallels to outdoors



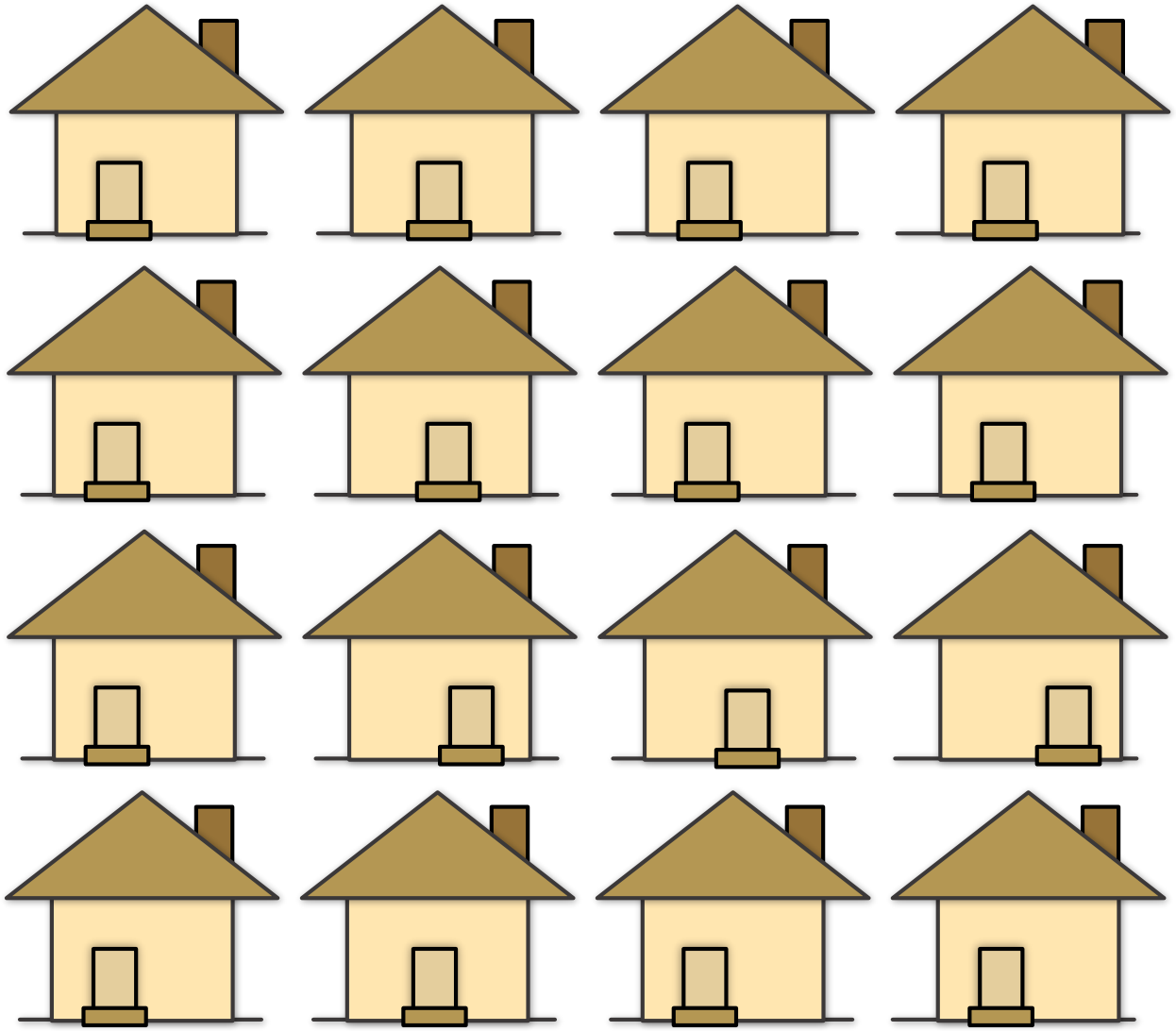
Large networks of monitors

- long-term measurements of consistent quality
- understand trends, patterns and variance
- but… limited target measurements and requires substantial effort and infrastructure

Intensive field measurement

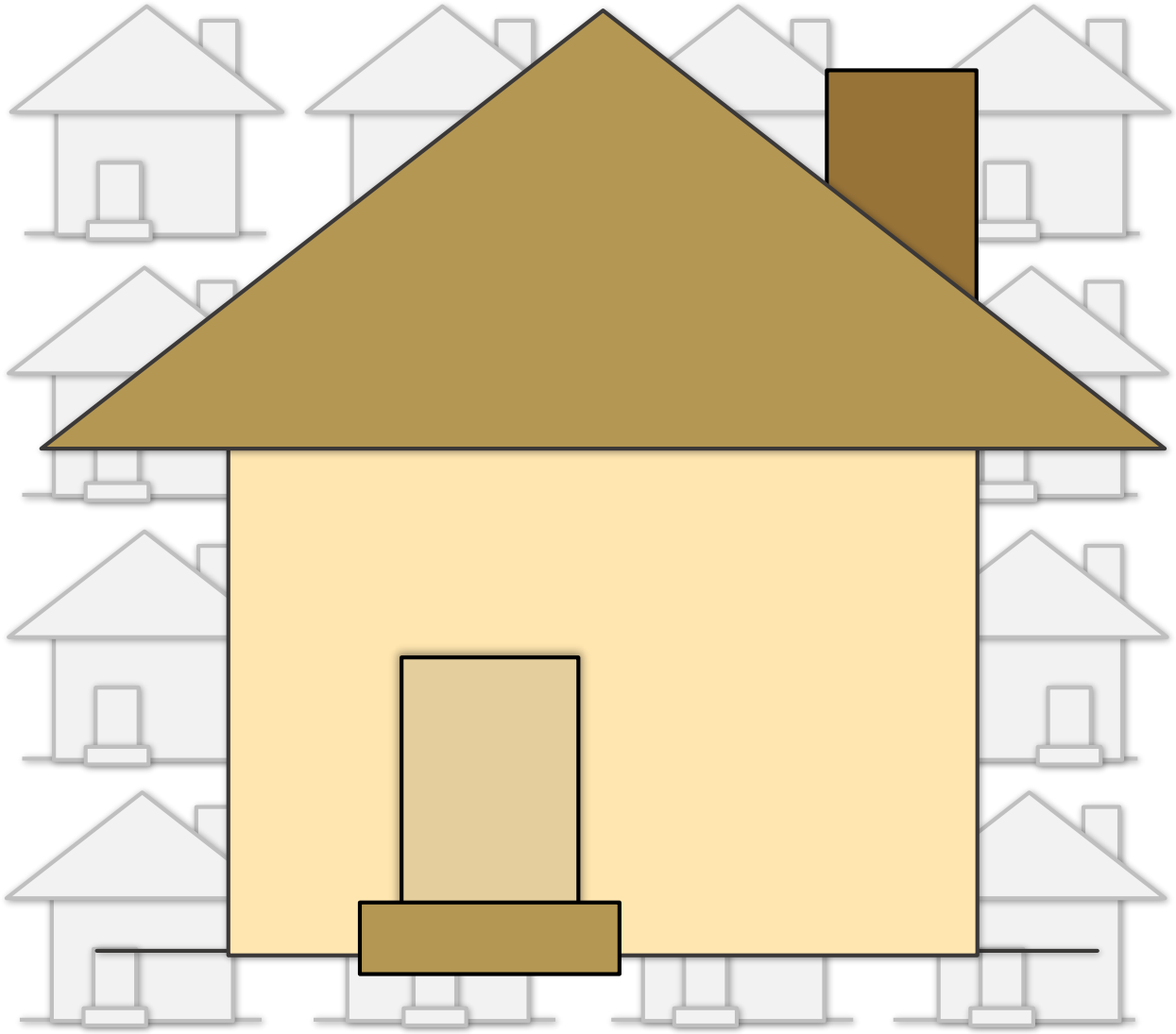
- numerous instruments & personnel
- short time periods, single site
- investigate processes, not trends

How do we approach measuring indoor chemistry?



Many buildings, few target compounds

How do we approach measuring indoor chemistry?



One test house with multiple measurements

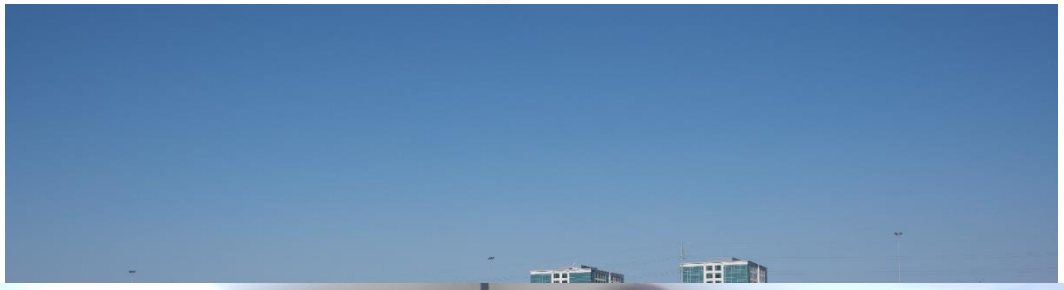
How do we approach measuring indoor chemistry?

One test house with multiple measurements

Controlled ‘perturbation’ experiment

HOMEChem: House Observations of Microbial and Environmental Chemistry

- 30+ state-of-the-art instruments from 13 universities plus industry & government
- 1-28 June 2018
- UTest House at the University of Texas Austin
- Goal: characterize aerosol and gas-phase chemistry during cooking, cleaning & occupancy



Colorado State University

University of Colorado Boulder

University of Toronto

The University of Texas

University of California, Berkeley

Drexel University

Indiana University

William & Mary

UC San Diego

Photo: Callie Richmond

HOMEChem: House Observations of Microbial and Environmental Chemistry

Two types of experiments

- **Sequential**
  - Replicated activities (stirfry; mopping)
  - Mop → Wait → Open/Close windows → Wait → Mop → Wait ….
- **Layered**
  - Multiple activities layered on top of each other
  - Cook → Wait → Pinesol Mop → Lunch → Wait → Dinner → Dishwasher → Bleach Mop

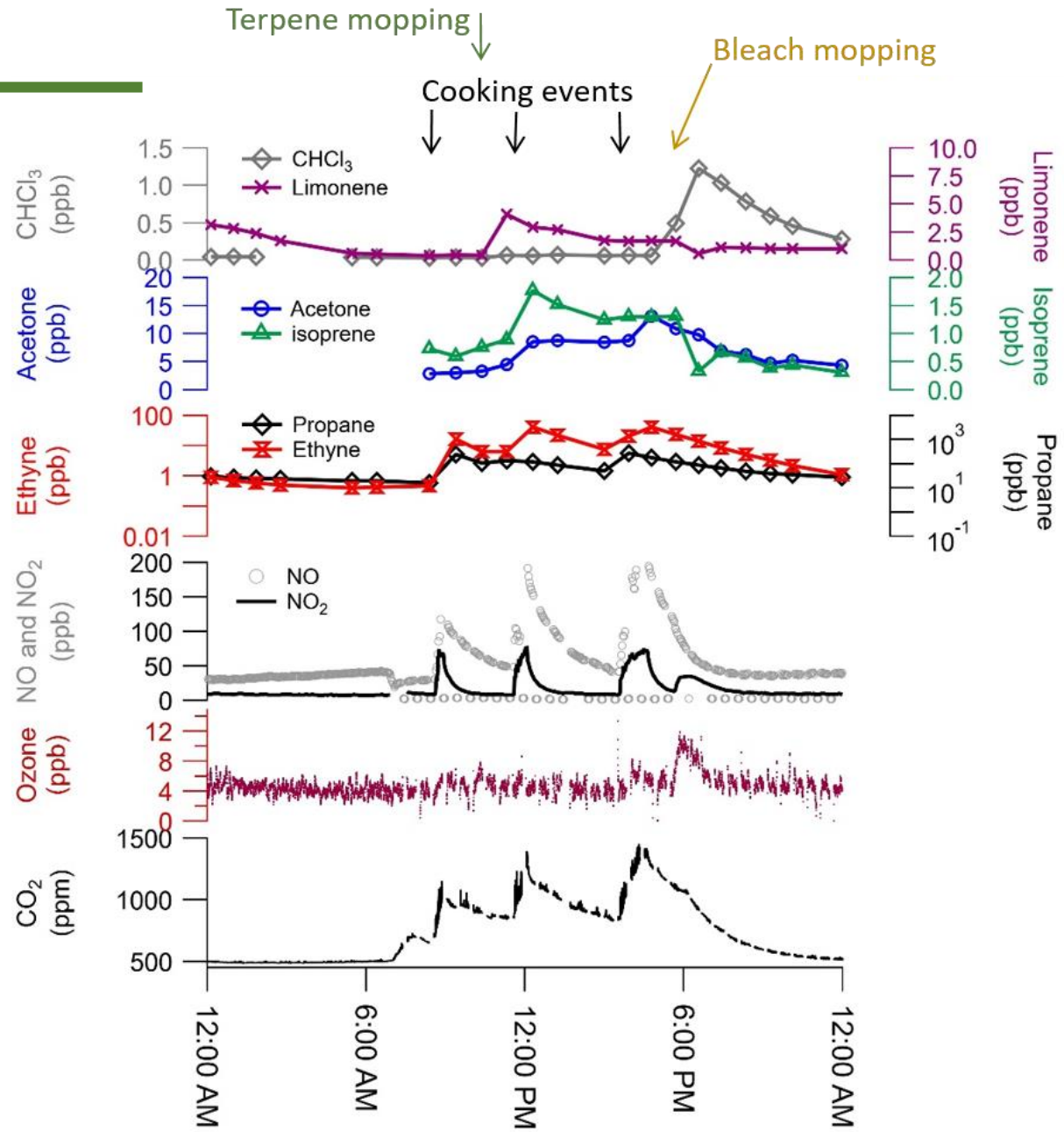
Sun	Mon	Tue	Wed	Thu	Fri	Sat
May 27	May 28	May 29	May 30	May 31	Jun 1	Jun 2
Instrument set-up					Shake-down day	Unoccupied background
Jun 3	Jun 4	Jun 5	Jun 6	Jun 7	Jun 8	Jun 9
AM: End of intercomparison. Inlets move	Response times	Sequential: Terpene cleaning I	Sequential: Stir-fry I	Sequential: Chlorine cleaning I	Layered I	house open 7 am - 1 pm House reset
Jun 10	Jun 11	Jun 12	Jun 13	Jun 14	Jun 15	Jun 16
Sequential: Chlorine cleaning II	Staggered occupancy 1	Sequential: Stir-fry II	Sequential: Natural Product Cleaning	am: house open AM: NPF on site 1-3: sci mtg	Unoccupied background	House reset
Jun 17	Jun 18	Jun 19	Jun 20	Jun 21	Jun 22	Jun 23
Sequential: Stir-fry III	Thanksgiving	Layered II	Sequential: Natural product cleaning	Layered III	OPEN HOUSE	House reset
Jun 24	Jun 25	Jun 26	Jun 27	Jun 28	Jun 29	Jun 30
Staggered occupancy 2	Layered IV	Sequential: Ammonia + Vinegar	Thanksgiving	Staggered occupancy 3	Instrument tear-down	

Science meetings

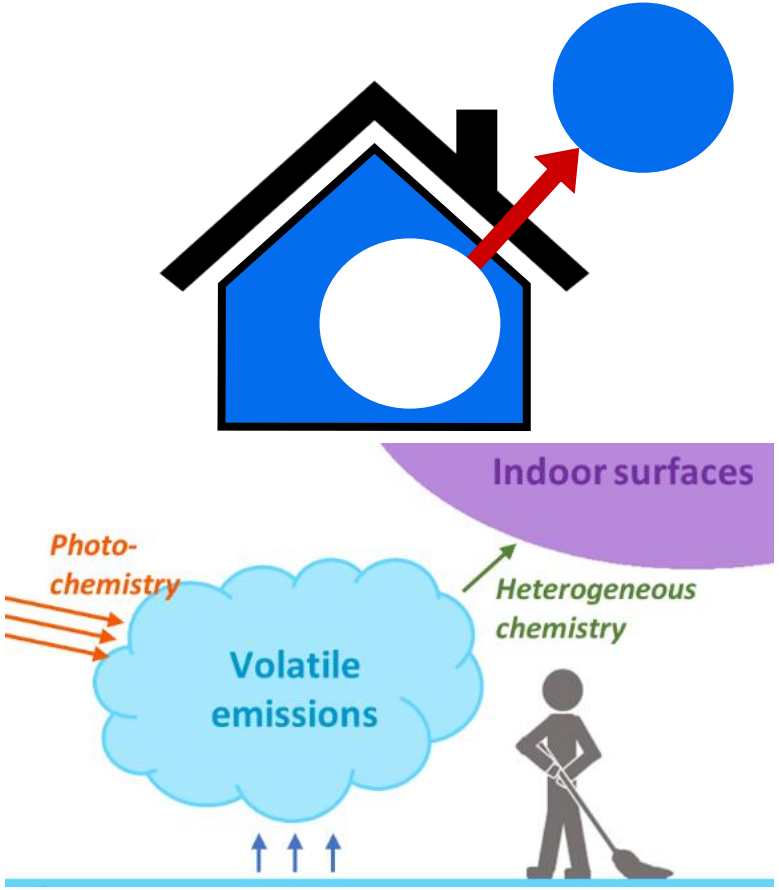
Most external researchers arrive Austin May 27 and depart July 1.
House Reset: Researchers allowed in the house for calibration
Unoccupied Background: No one allowed in house

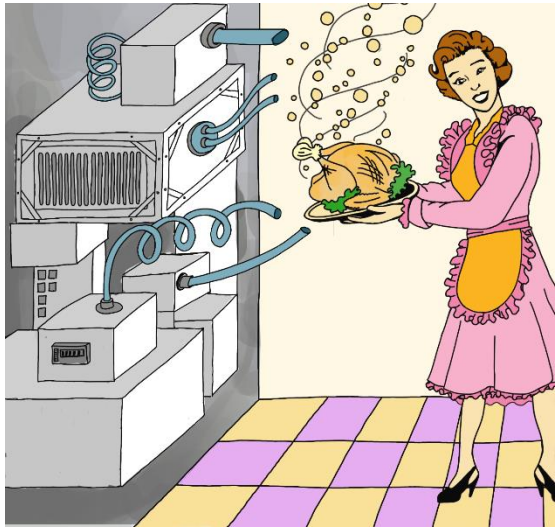
Layered Day example

- Most trace gases are very high relative to outdoors
- Exceptions: O_3, OH (& HO_2), a few VOCs
- Activities change concentrations rapidly and across a large dynamic range



[Farmer et al. ESPI. 2019]



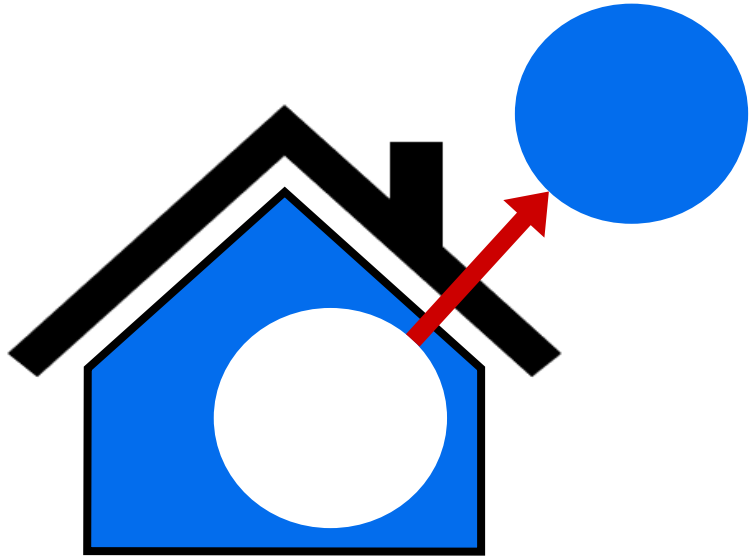


Indoor vs Outdoor Pollutants

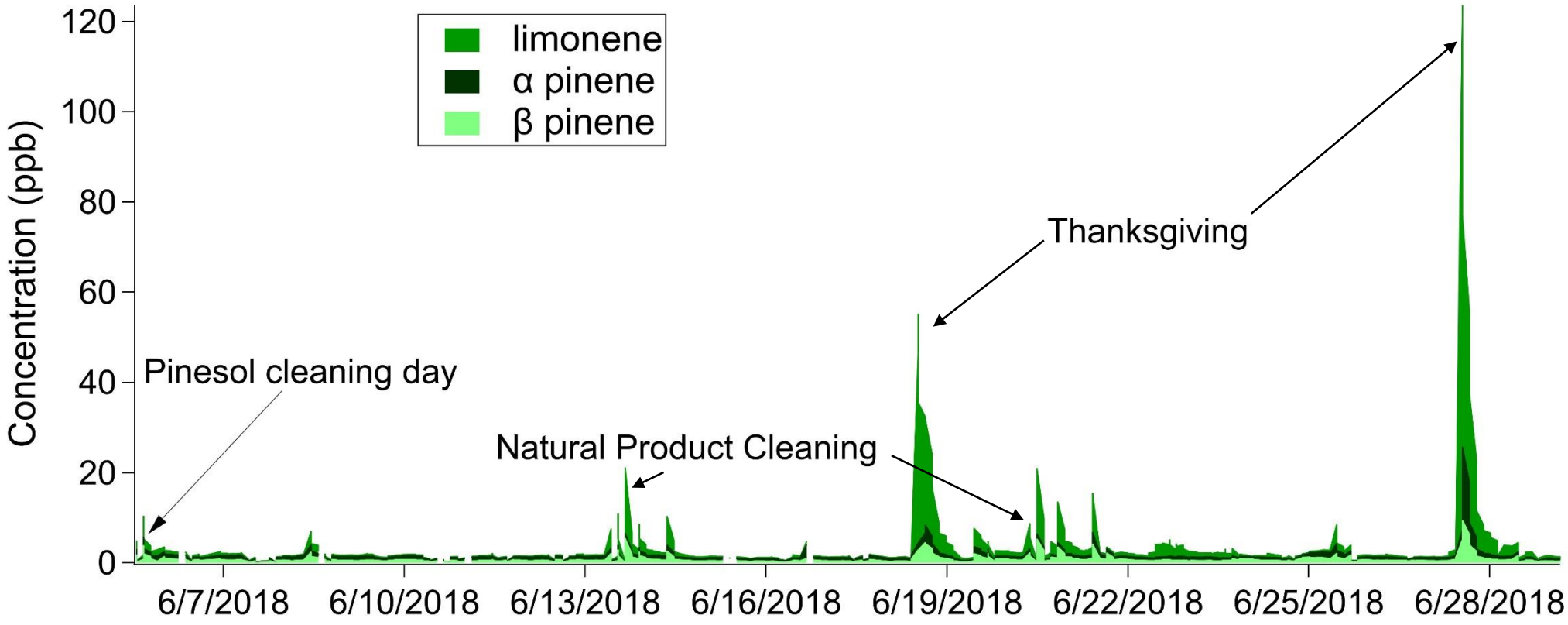
Bleach Chemistry & Equilibria

Instruments & Thanksgiving

How does indoor air contrast to the outdoor atmosphere?



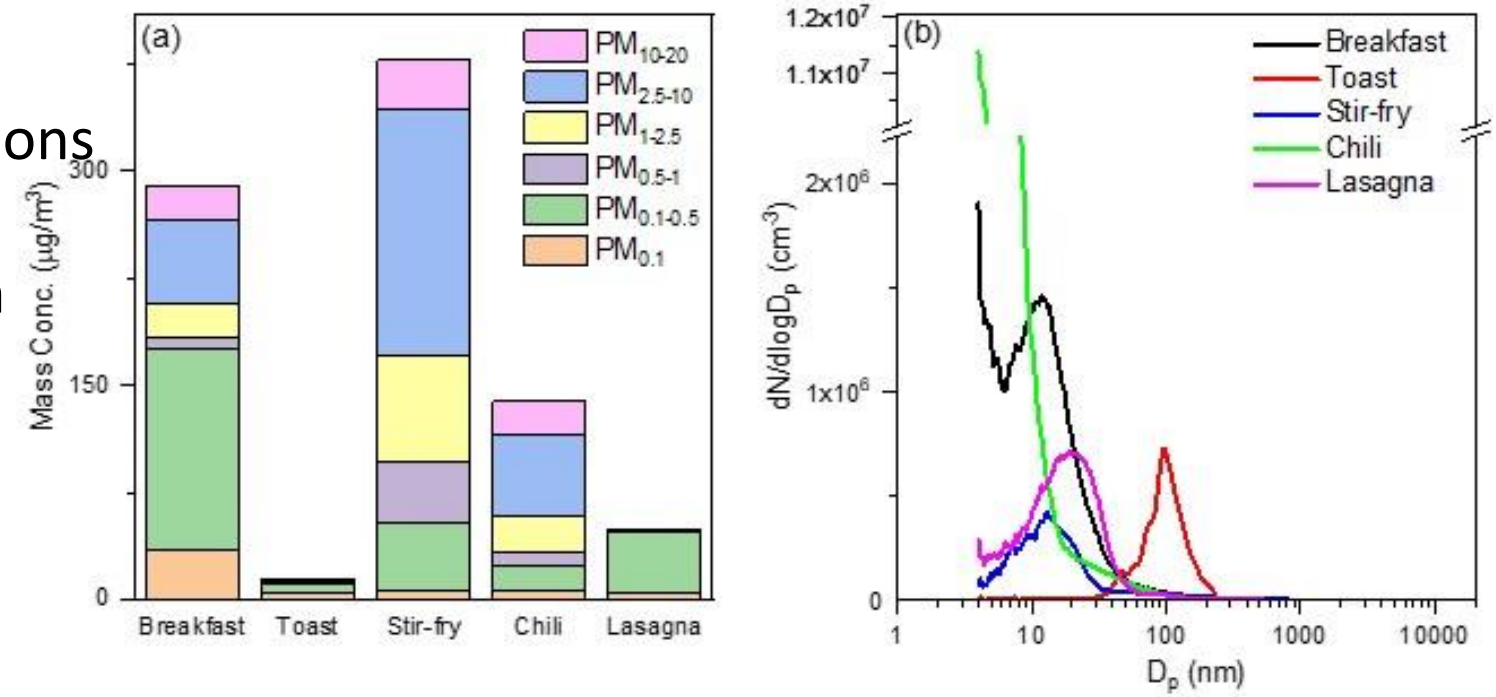
[VOCs] are high indoors

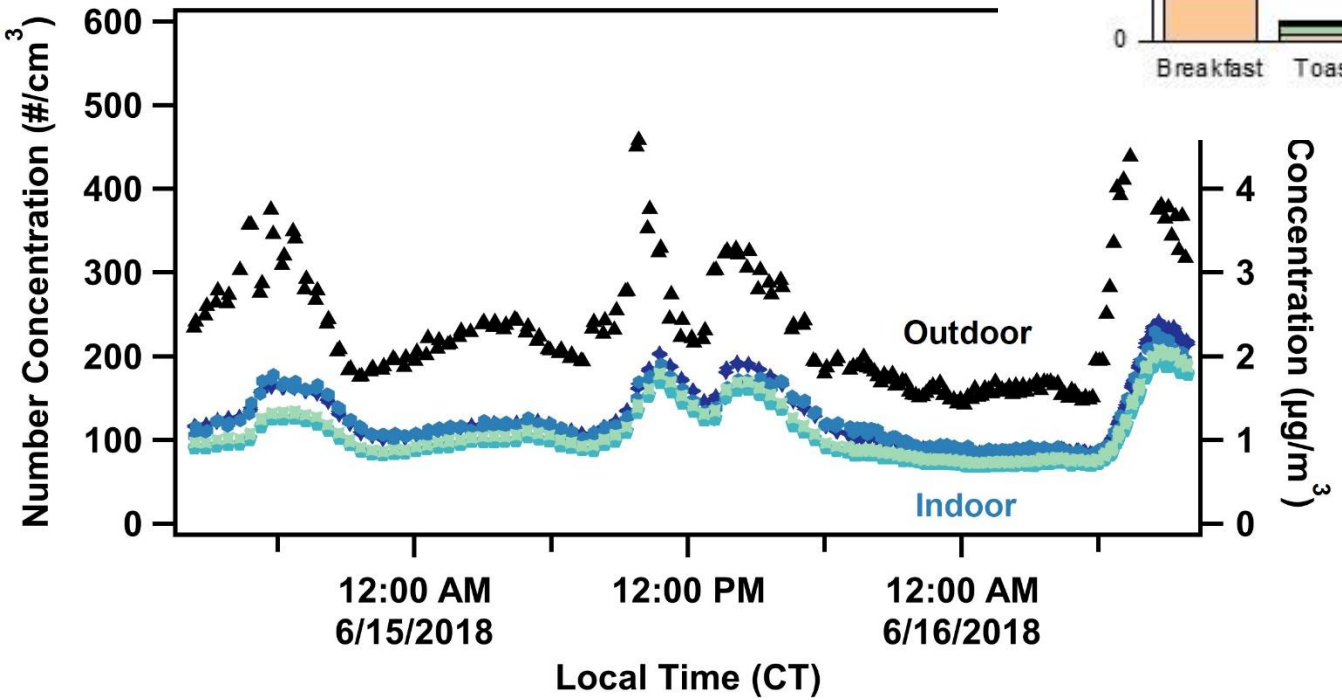


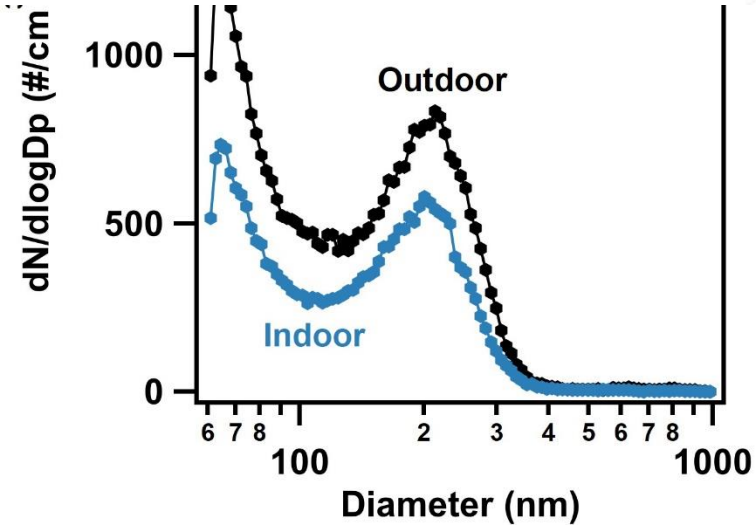
- Outdoor: <1 ppb total monoterpene during day
- Indoor monoterpene background similar to outdoors, dominanted by α- & β-pinene
- Cooking and cleaning causes up to 116 ppb limonene, 16 ppb α-pinene indoors!
    - Chemistry? Export outdoors?

Indoor particle concentrations lower – unless you're cooking

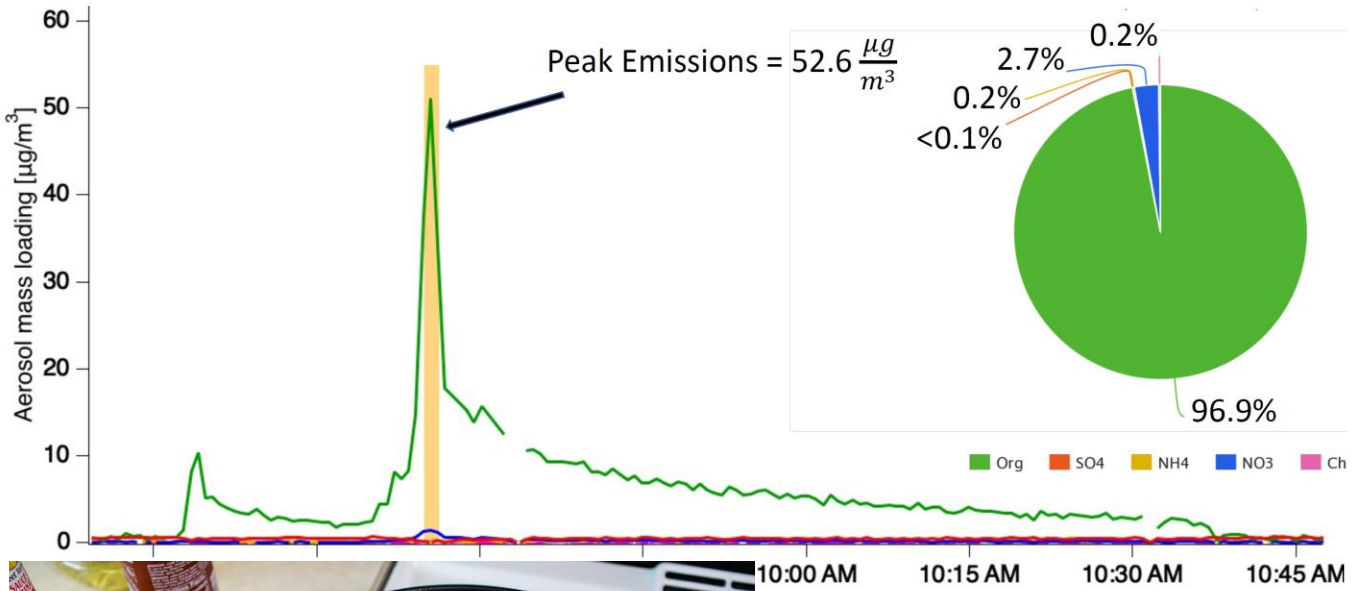
- Cooking causes high PM concentrations – but only for short periods of time
- Background PM_1 lower indoors than outdoors (similar size distribution)

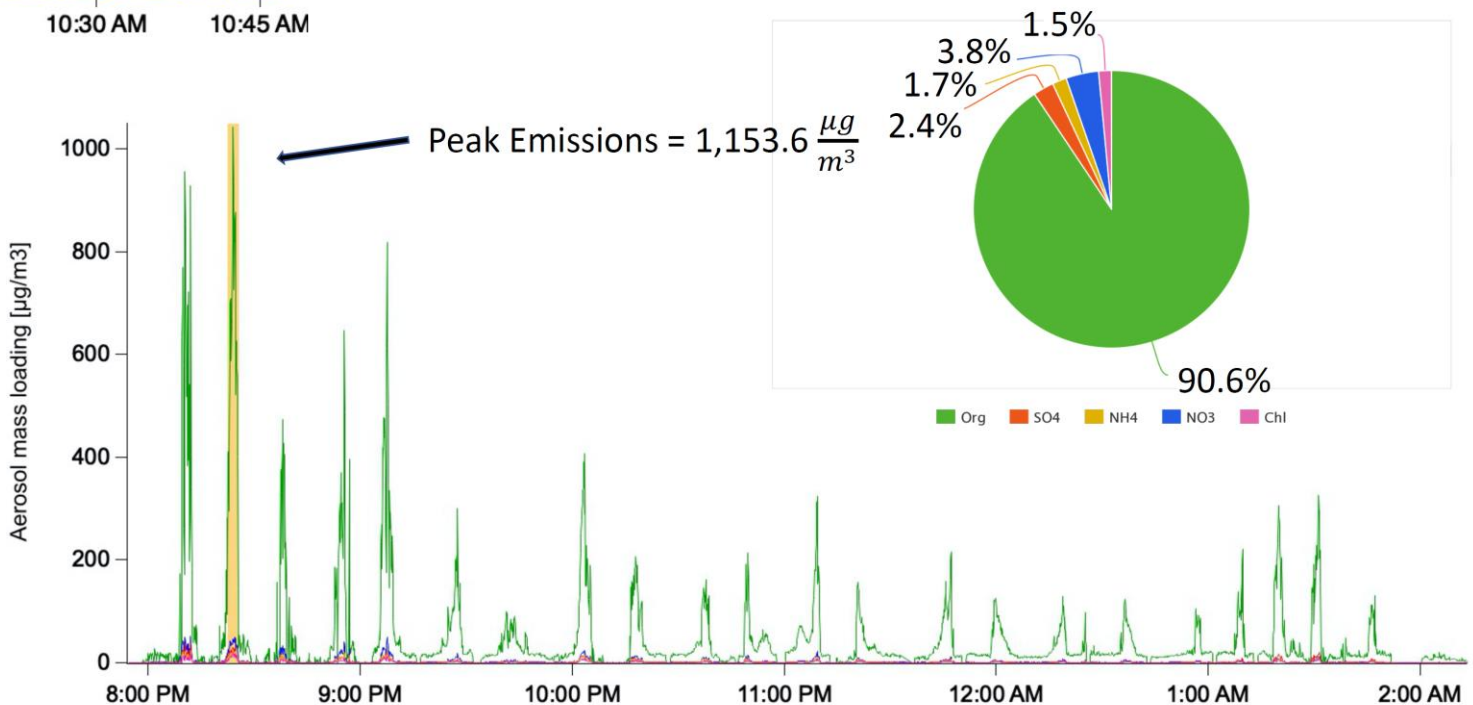






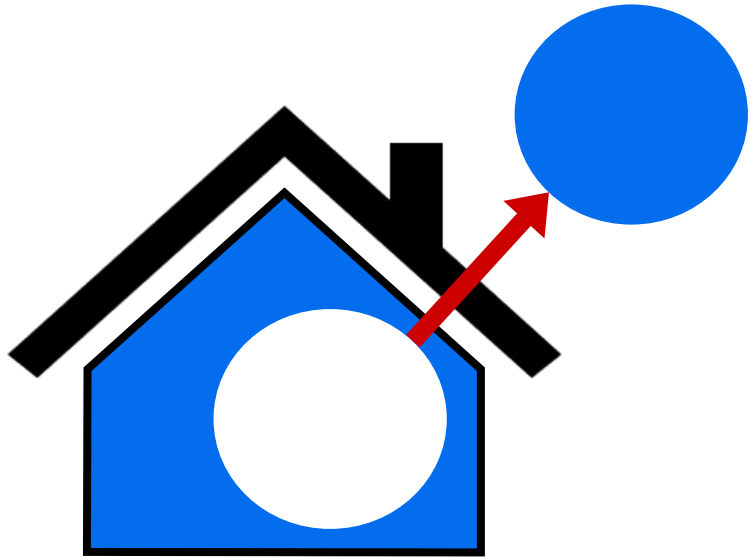
Cooking concentrations are high! (But not smoke-plume high)



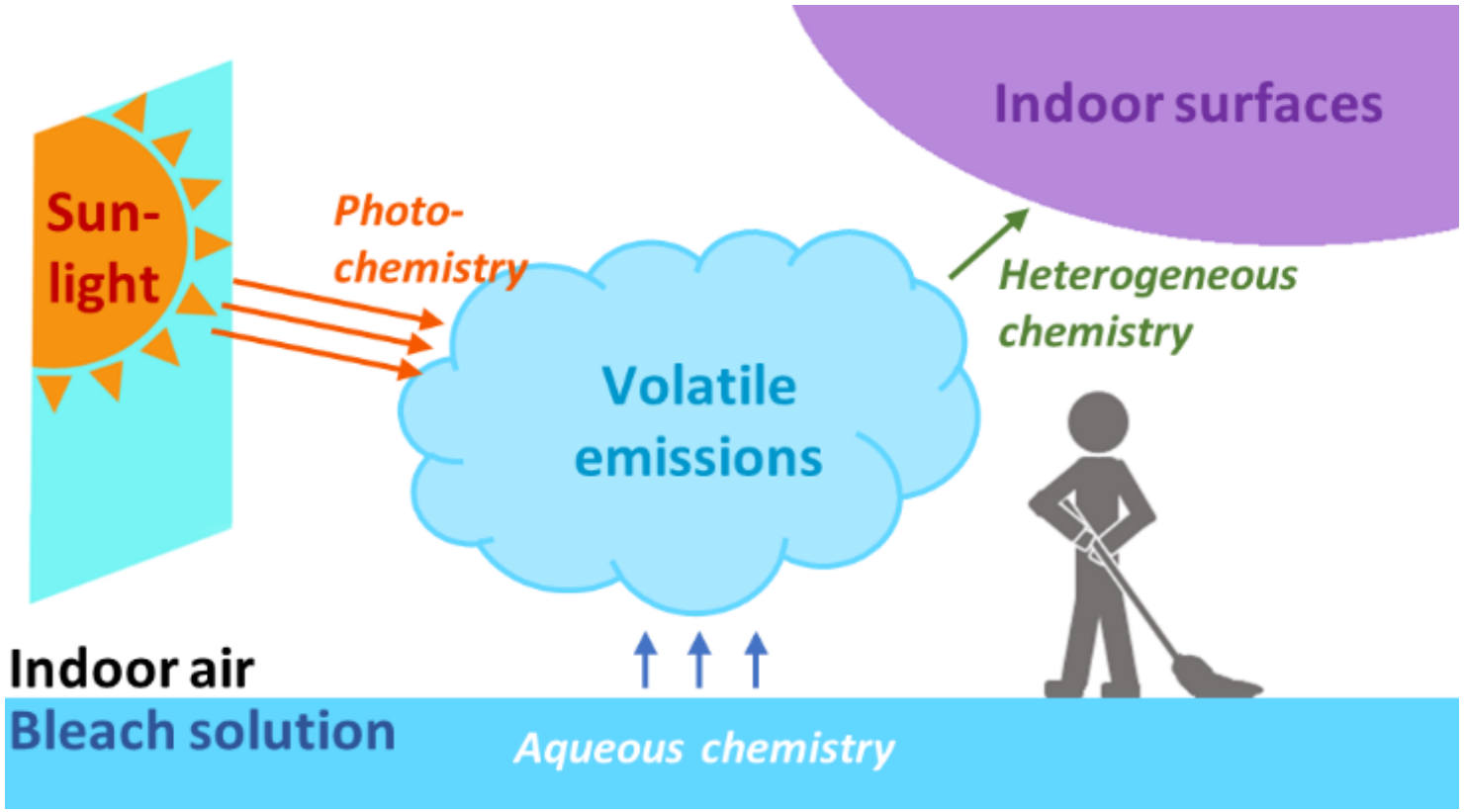


How does indoor air contrast to the outdoor atmosphere?

- High concentrations of VOCs
- Rapid changes in concentration
- Low oxidant loading, low light

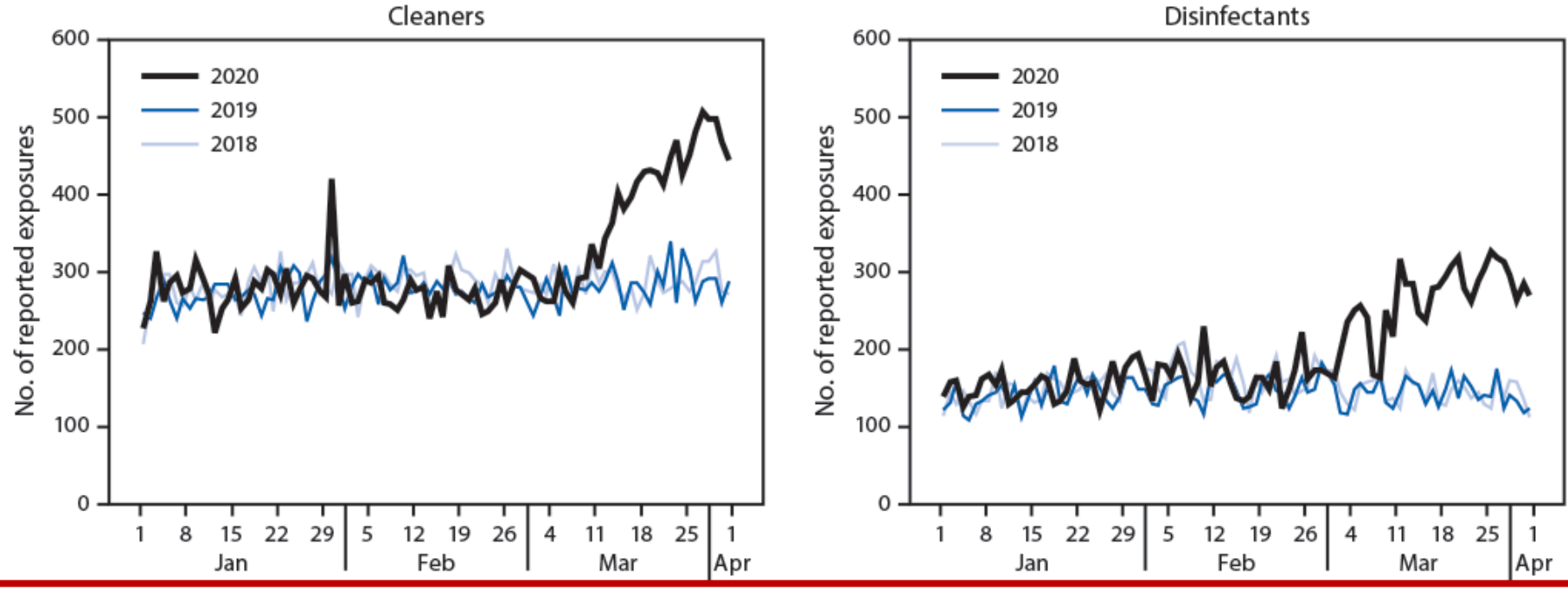


Are there chemical transformations indoors?



How does chlorine bleach cleaning impact indoor chemistry?

- Calls to U.S. poison centers about cleaner and disinfect exposures increased by 20% between Jan-Mar 2020 relative to previous years*

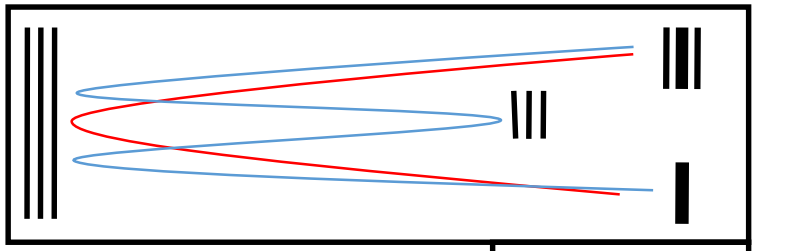


Case 1

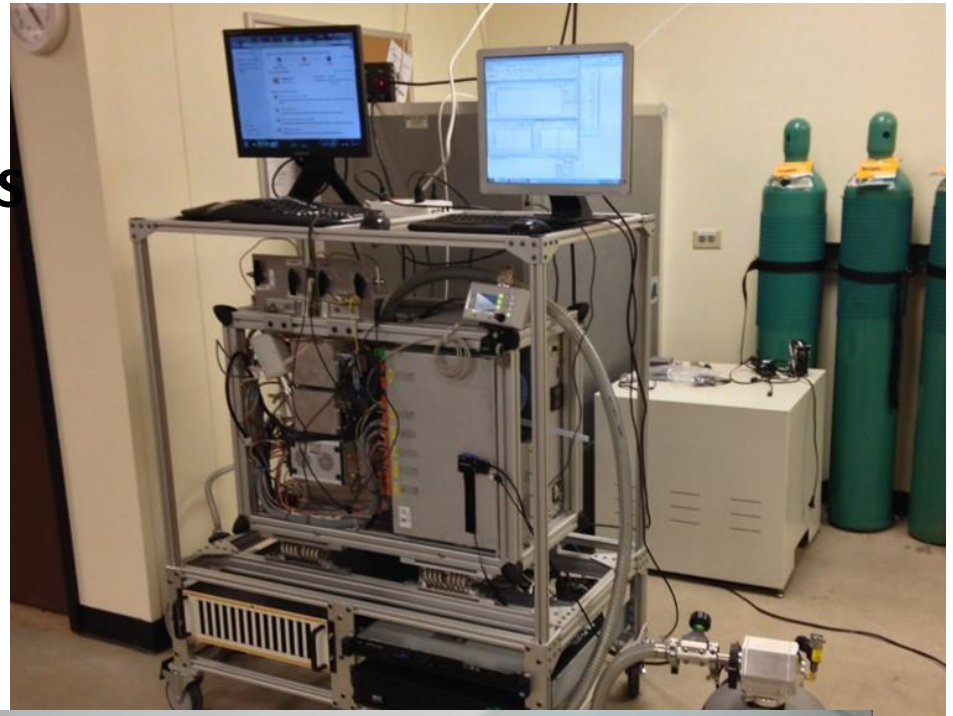
An adult woman heard on the news to clean all recently purchased groceries before consuming them. She filled a sink with a mixture of 10% bleach solution, vinegar, and hot water, and soaked her produce. While cleaning her other groceries, she noted a noxious smell described as “chlorine” in her kitchen. She developed difficulty breathing, coughing, and wheezing, and called 911. She was transported to the emergency department (ED) via ambulance and was noted to have mild hypoxemia and end-expiratory wheezing. She improved with oxygen and bronchodilators. Her chest radiograph was unremarkable, and she was discharged after a few hours of observation.

[Chang et al. MMWR Morb Mortal Wkly Rep 2020;69:496–498]

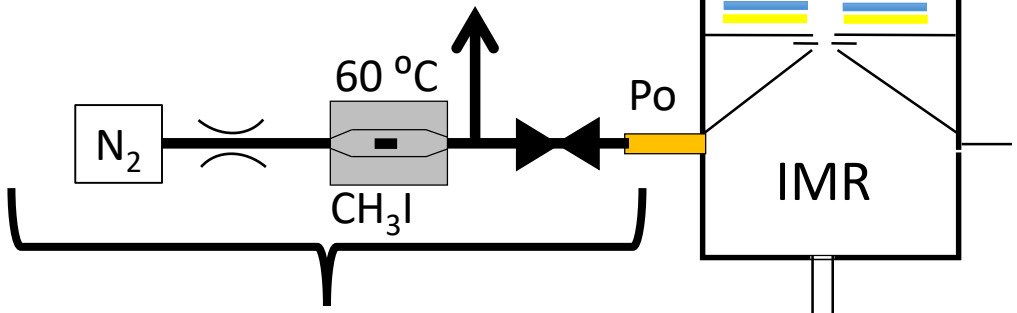
Our fancy instruments: Chemical Ionization Mass Spectrometry



Time of Flight MS



Segmented quadrupoles



Iodide

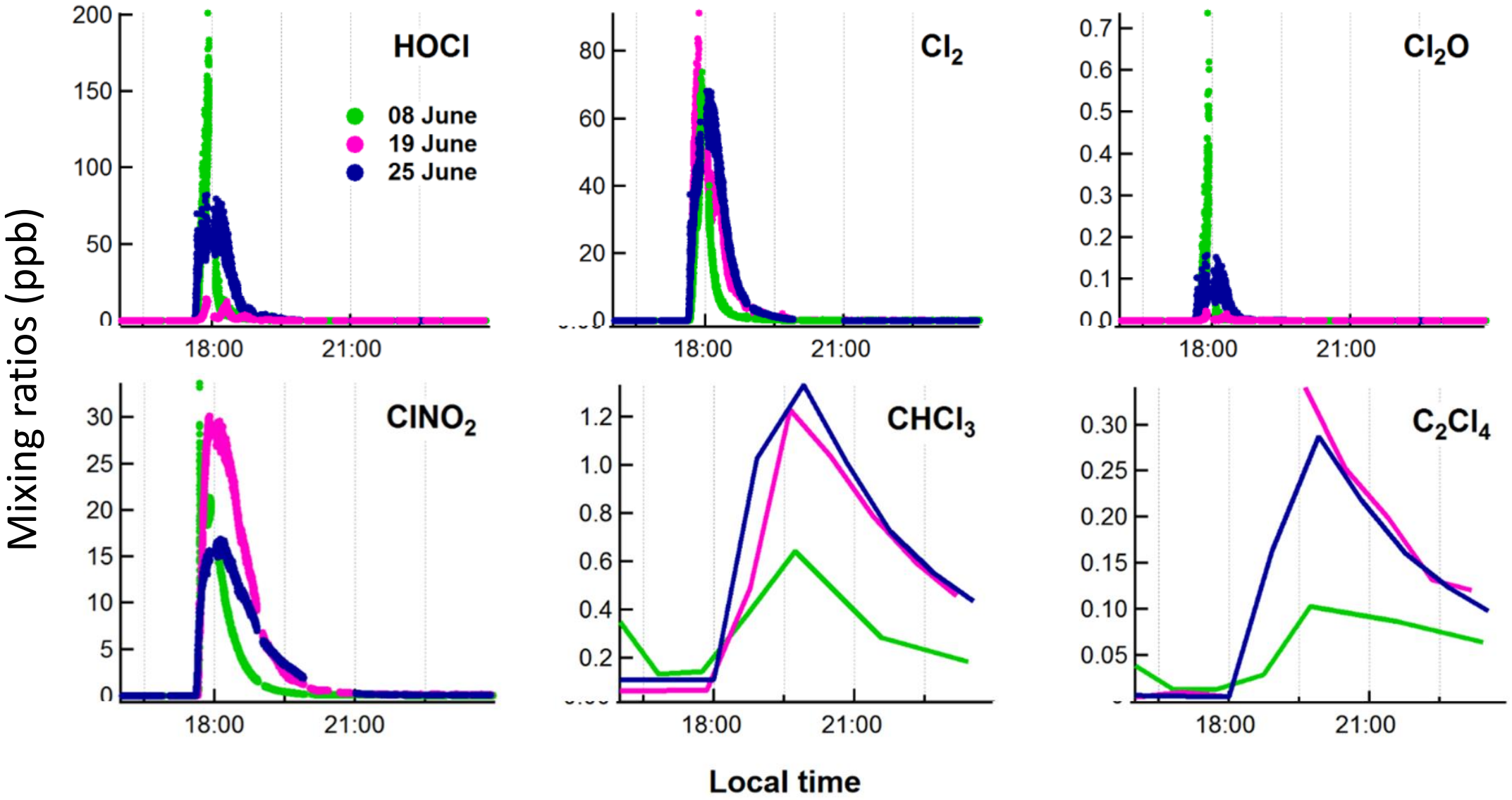
$I^- + HA \rightarrow [I \cdot HA]^-$

$I[H_2O]^- + HA \rightarrow [I \cdot HA]^- + H_2O$

Gas-phase Inlet

[Brophy & Farmer. 2015. *Atmos Meas Tech. 8:*2945]

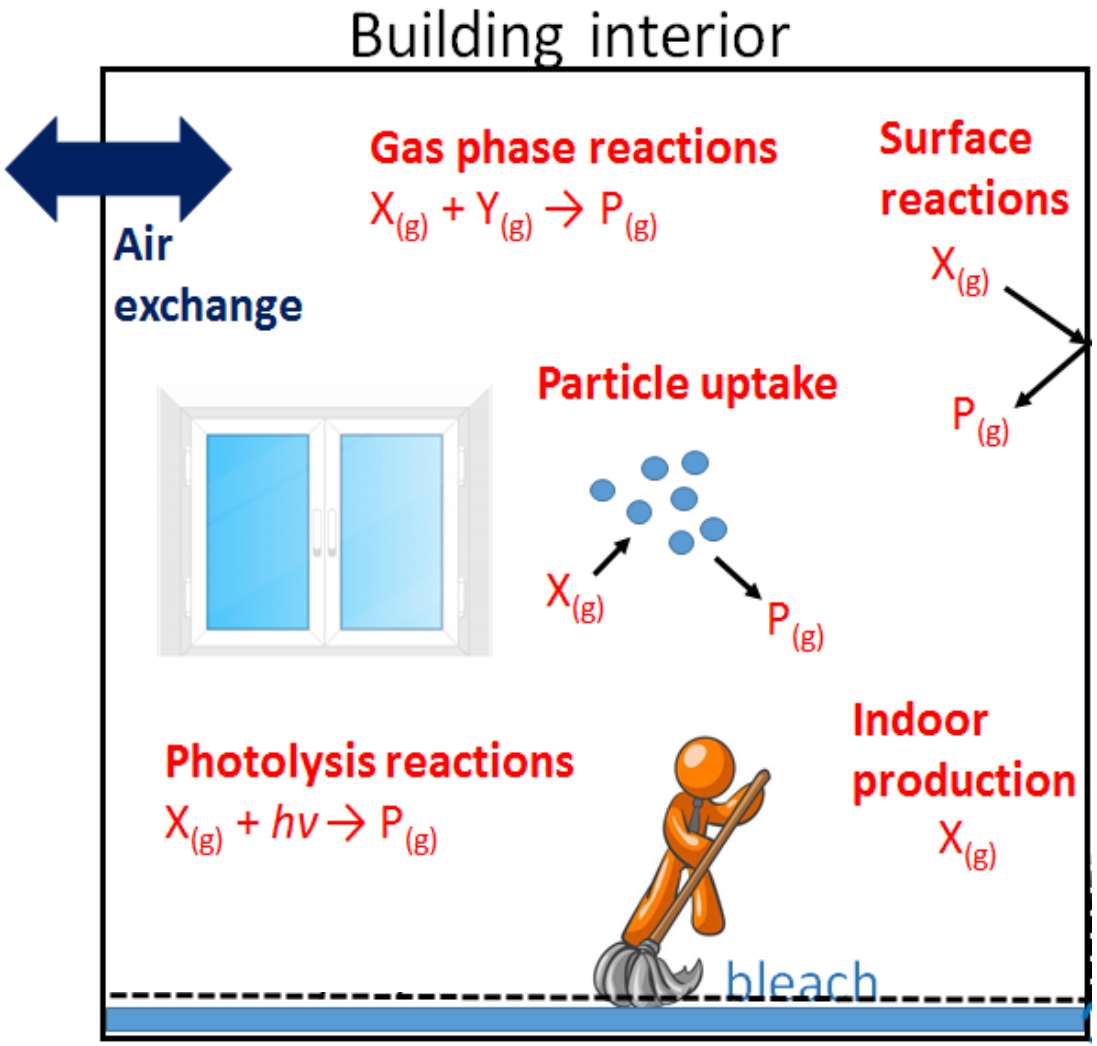
Mopping with bleach induces primary and secondary chemistry



- Bleach is a source of halocarbons and inorganic chlorinated compounds

[Mattila, Lakey et al. 2020. Env Sci Tech]

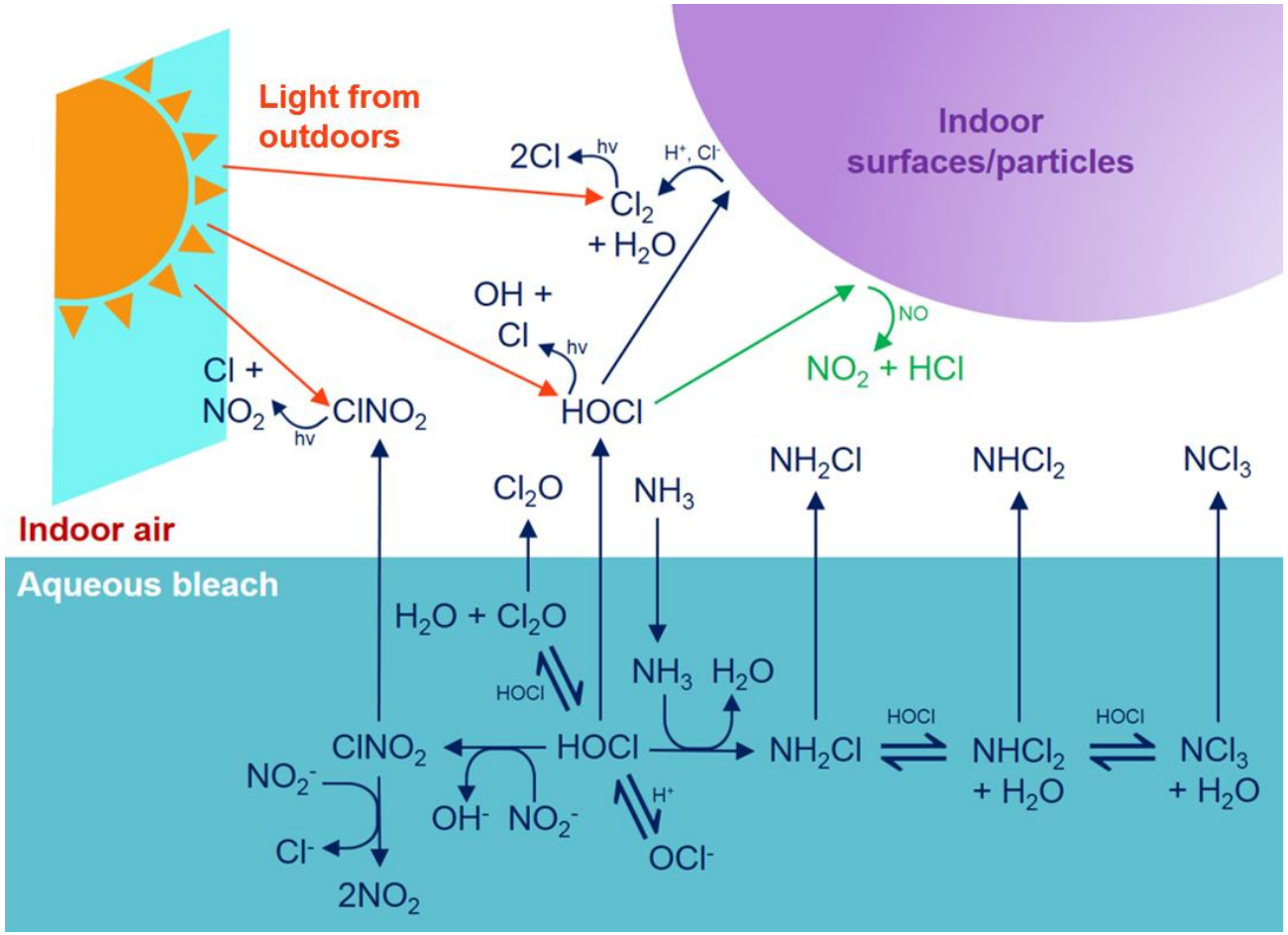
We use a mathematical model of indoor chemistry

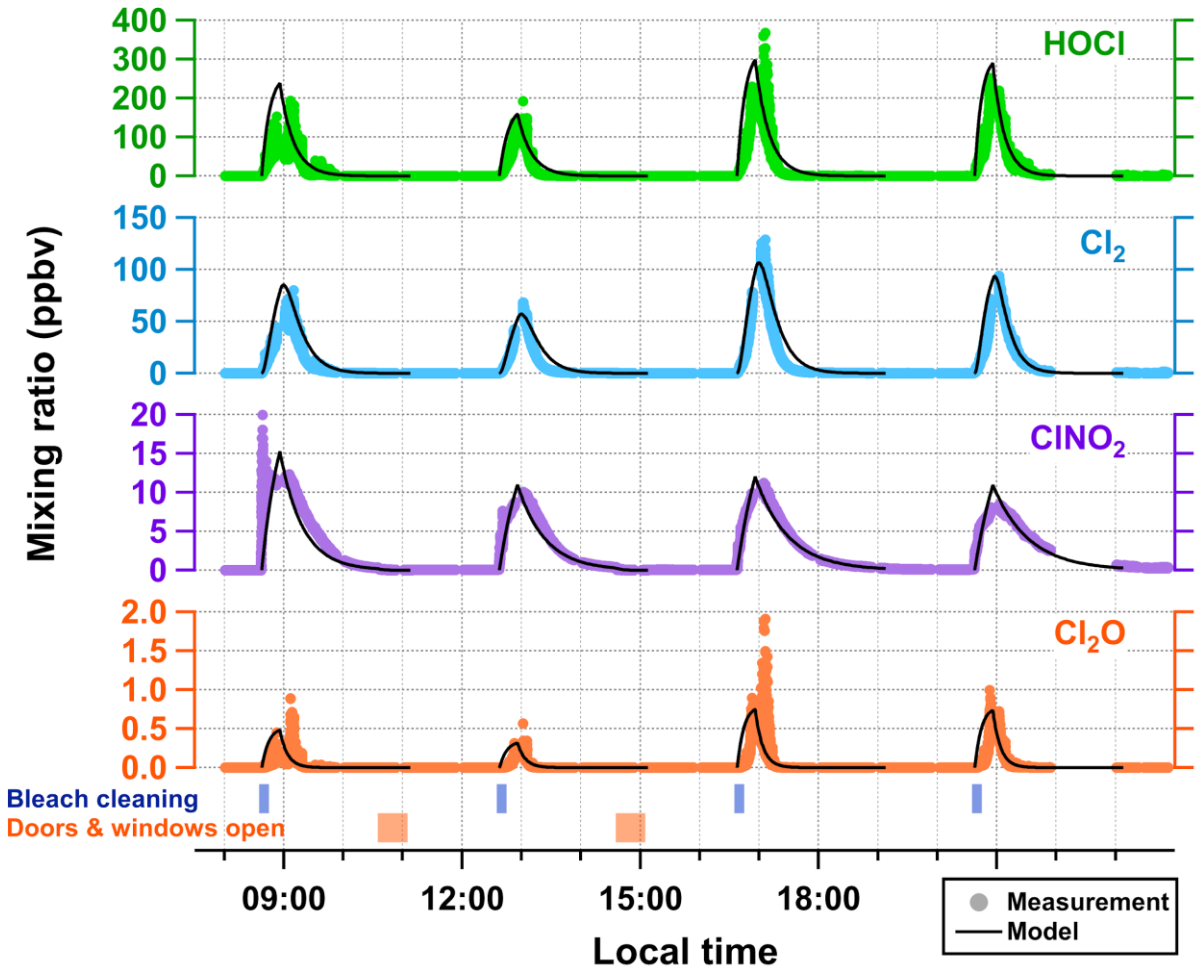


- Considers variety of multiphase chemical reactions
- Uses known reaction rates
- Constrains outputs to measured observations
- Explicit heterogeneous chemistry only modeled on *particle* surfaces (limitation)
  - Adding total interior surface area may affect outputs

[Mattila, Lakey et al. 2020. Env Sci Tech]

Multiphase chemistry controls gas-phase chemistry during bleach cleaning

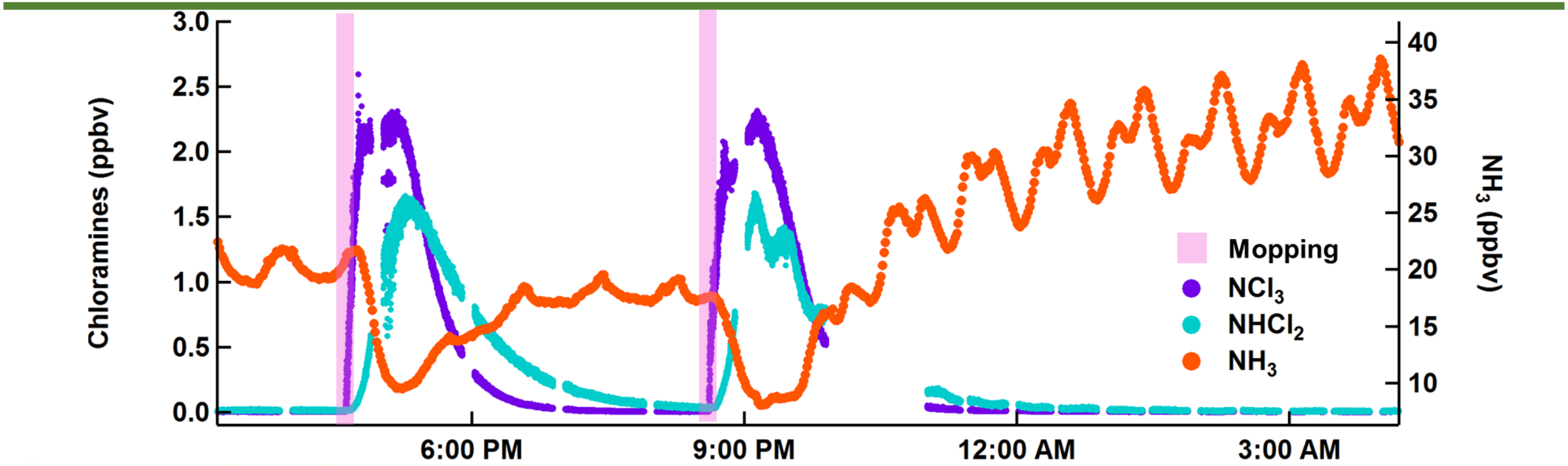


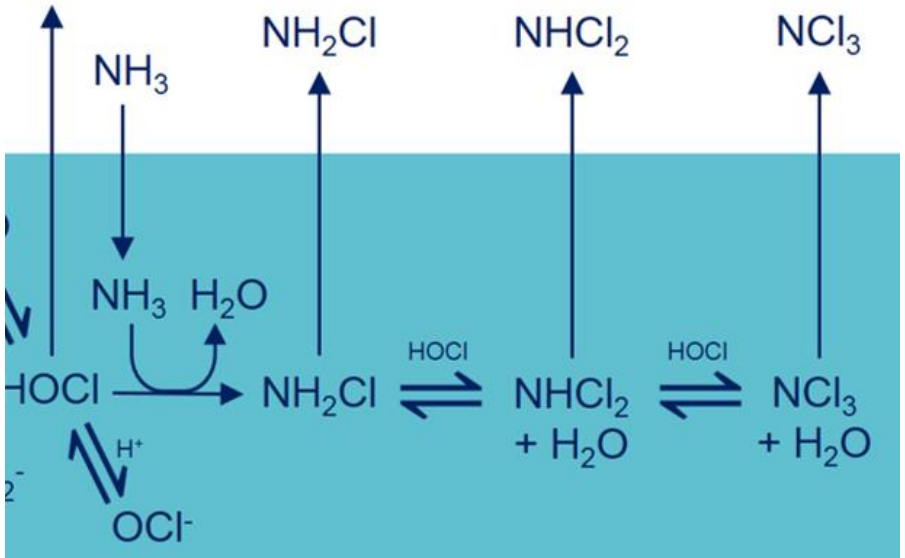


- Aqueous phase formation and emission of $ClNO_2$, chloramine species
- Surfaces in a house (walls, floors, cabinets…) play an important role!

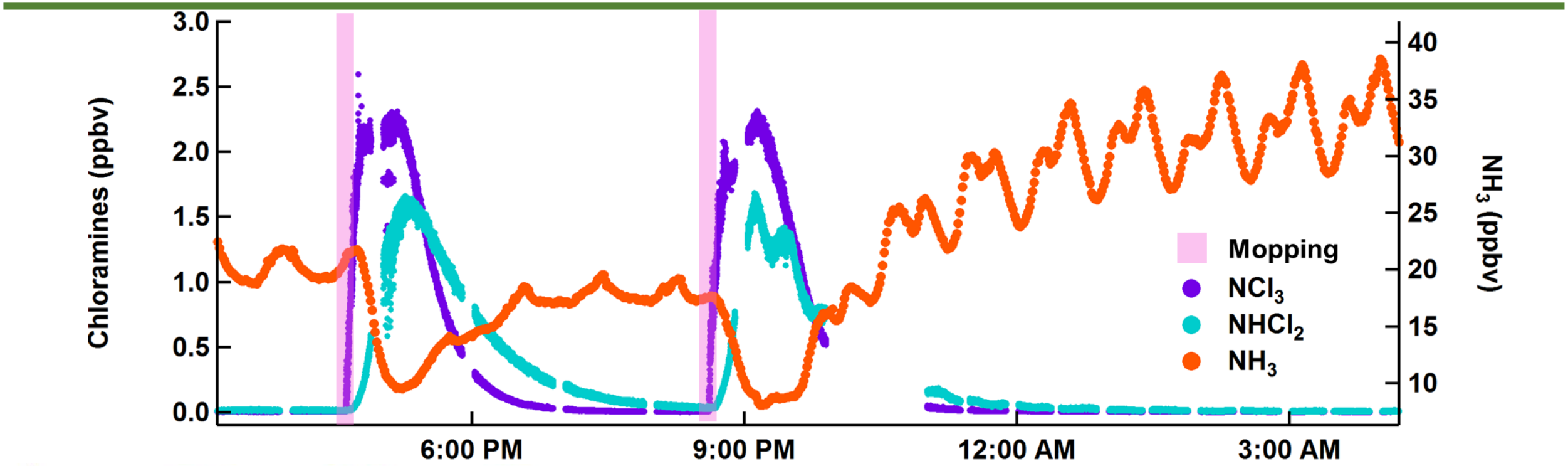
[Mattila, Lakey et al. 2020. Env Sci Tech]

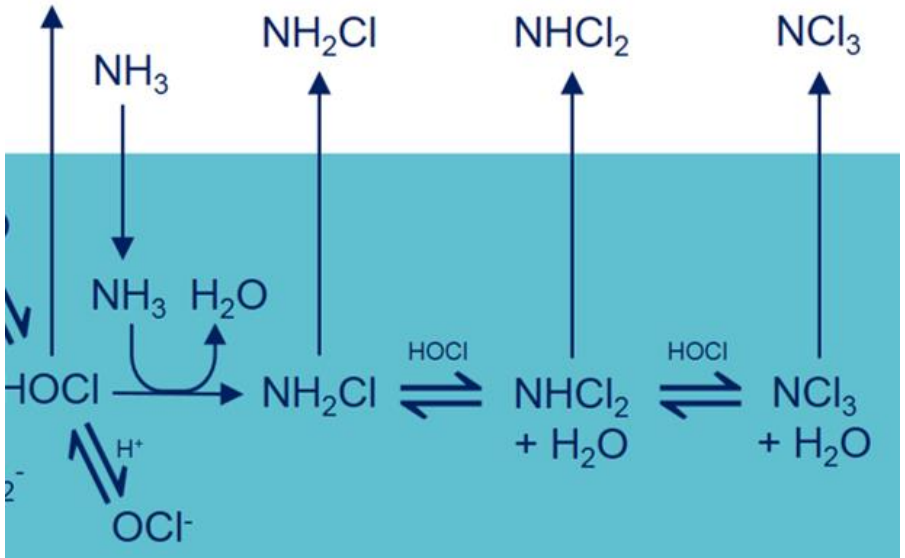
Multiphase chemistry impacts reduced N





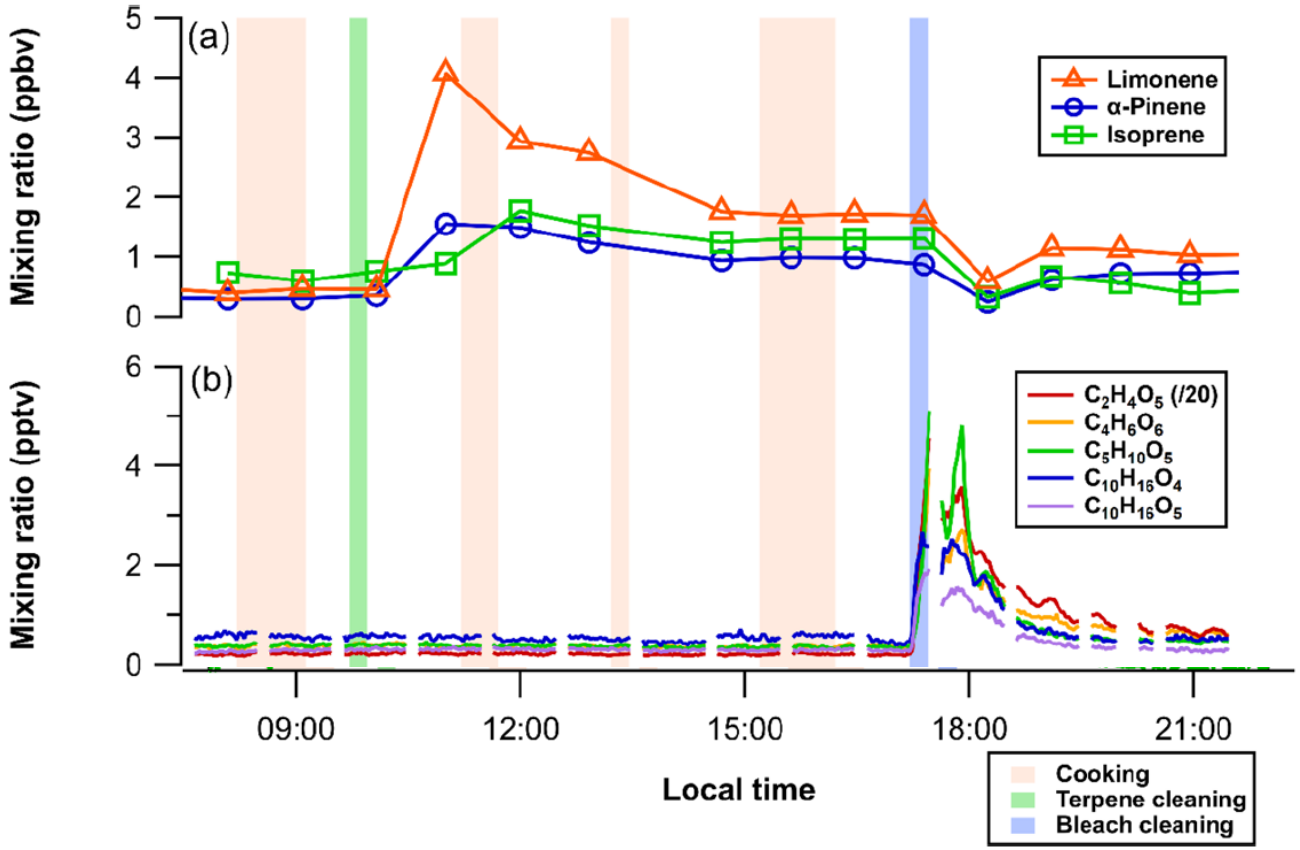
Multiphase chemistry impacts reduced N





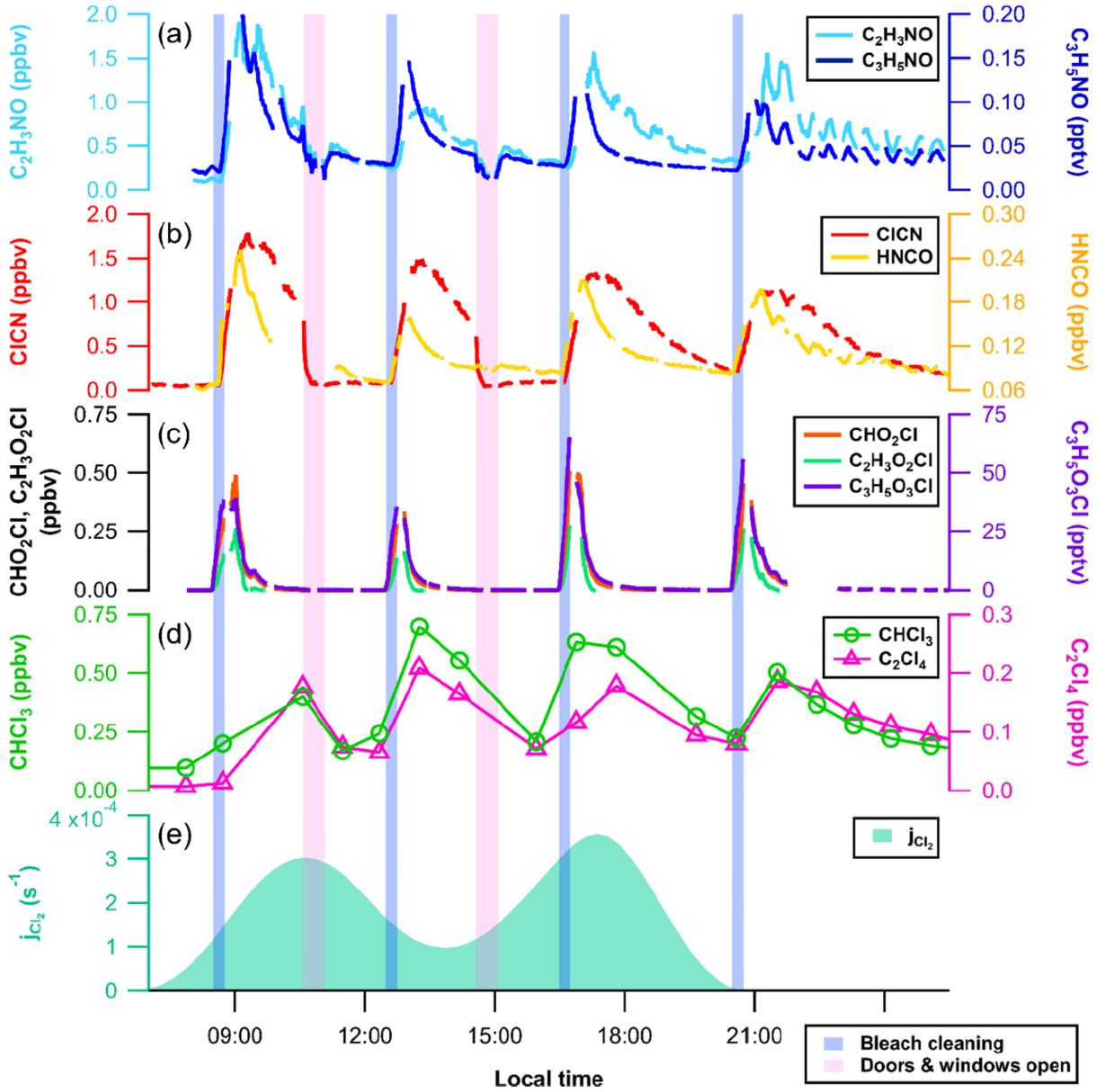
- NCl_3 and $NHCl_2$ have health effects at these levels
- Ambient NH_3 drops by ~10 ppb, takes hours to re-establish gas-surface equilibria
- Multiphase chemistry can control indoor N species

Some VOCs decrease after bleach additions → chemistry!



[Mattila et al. 2020. Env Sci Tech Lett]

Organics + bleach → Chlorinated organic molecules!



Methyl and Ethyl isocyanate

Cyanogen chloride and Isocyanic acid

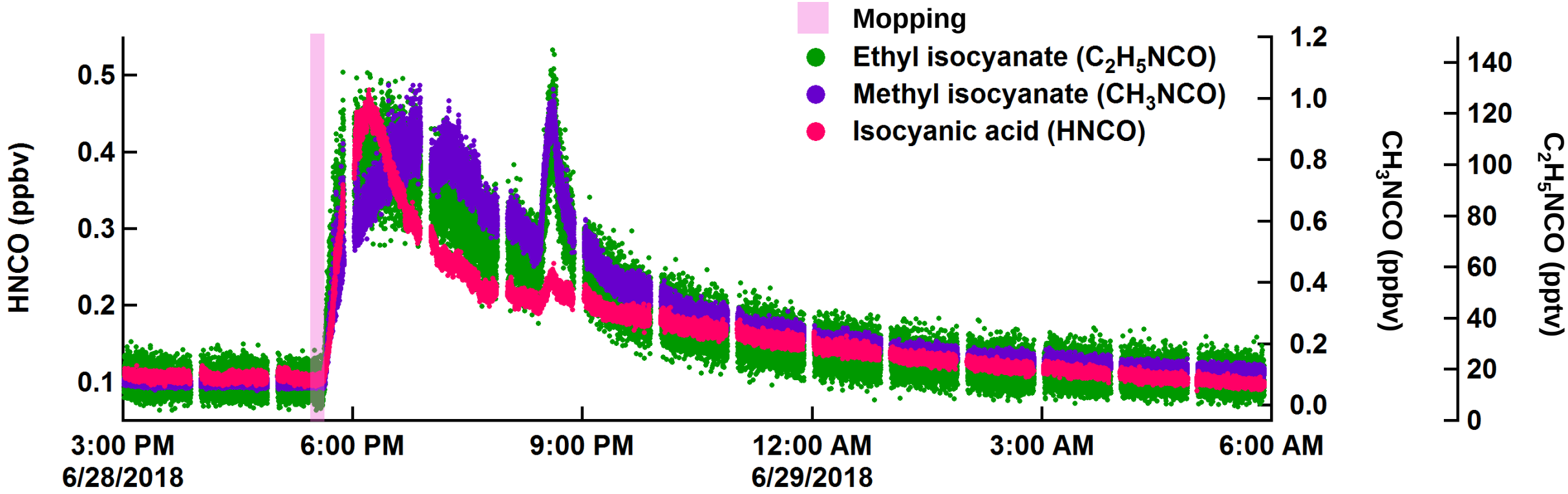
Chlorocarboxylic acids

Halocarbons

Products didn't change with light

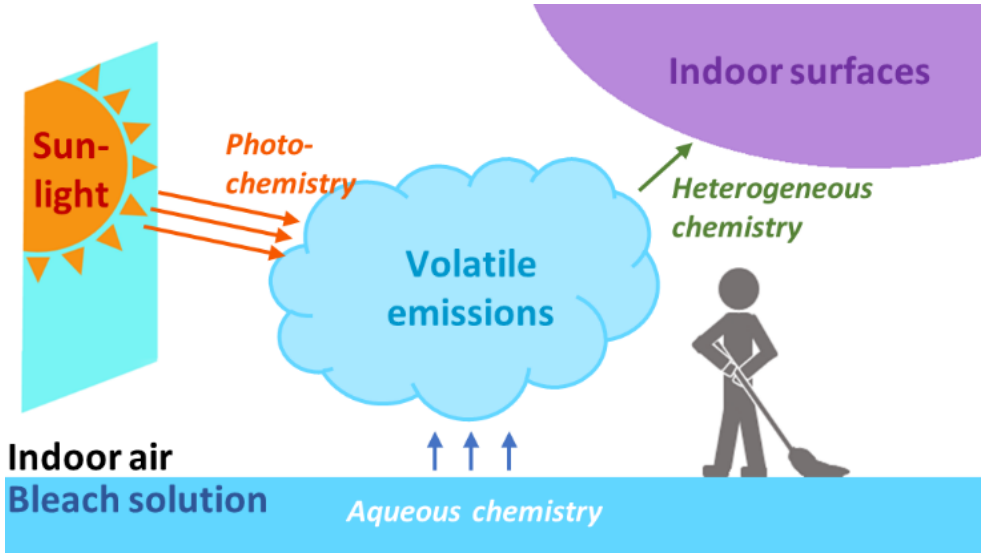
[Mattila et al. 2020. Env Sci Tech Lett]

Gas-phase isocyanates from oxidation of reduced org N?



- Isocyanic acid (HNCO) exposure > 1 ppb linked to human health issues
- Methyl isocyanate: 20 ppb (OSHA PEL)
- Substantial isocyanate formation after mopping

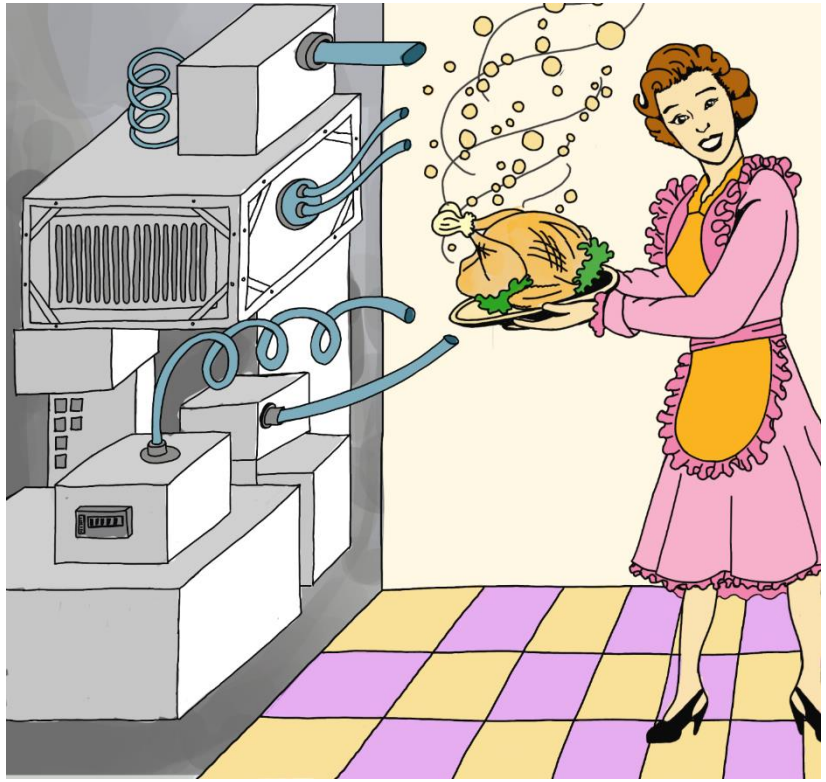
Are there chemical transformations indoors?

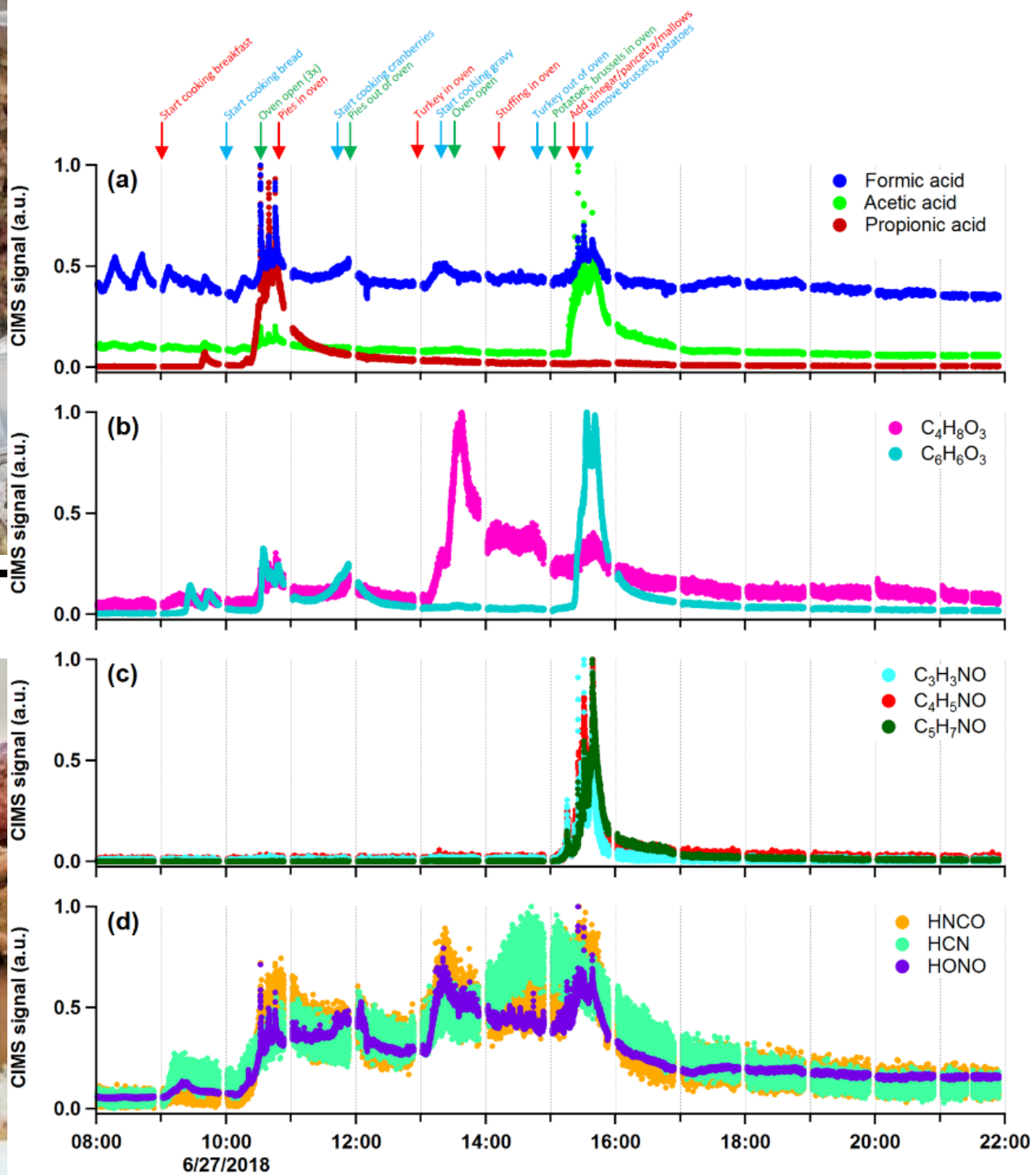


Yes - mopping chemistry!

- All the surfaces inside a house play a role
- VOCs that weren't toxic can be chemically transformed to become toxic

Thanksgiving!




Start cooking breakfast
Start cooking bread
Oven open (3x)
Pies in oven
Start cooking cranberries
Pies out of oven
Turkey in oven
Start cooking gravy
Oven open
Stuffing in oven
Turkey out of oven
Potatoes, brussels in oven
Add vinegar/pancetta/mallows
Remove brussels, potatoes
(a)
Formic acid
Acetic acid
Propionic acid
(b)
$C_4H_8O_3$
$C_6H_6O_3$
(c)
C_3H_3NO
C_4H_5NO
C_5H_7NO
(d)
HNCO
HCN
HONO
CIMS signal (a.u.)
1.0
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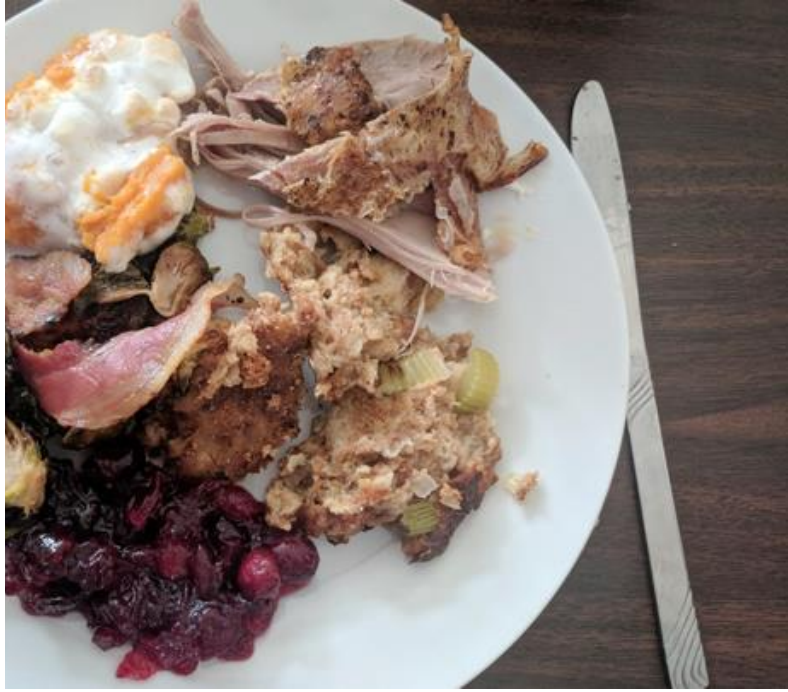
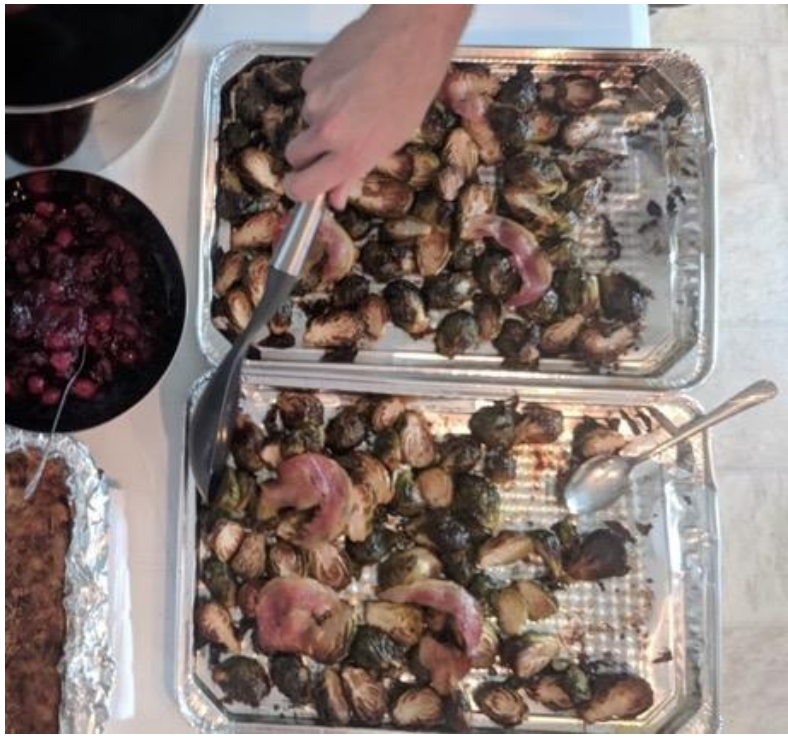
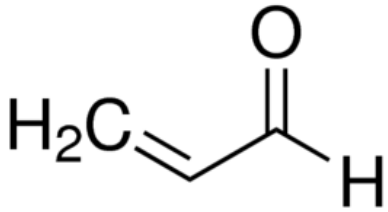


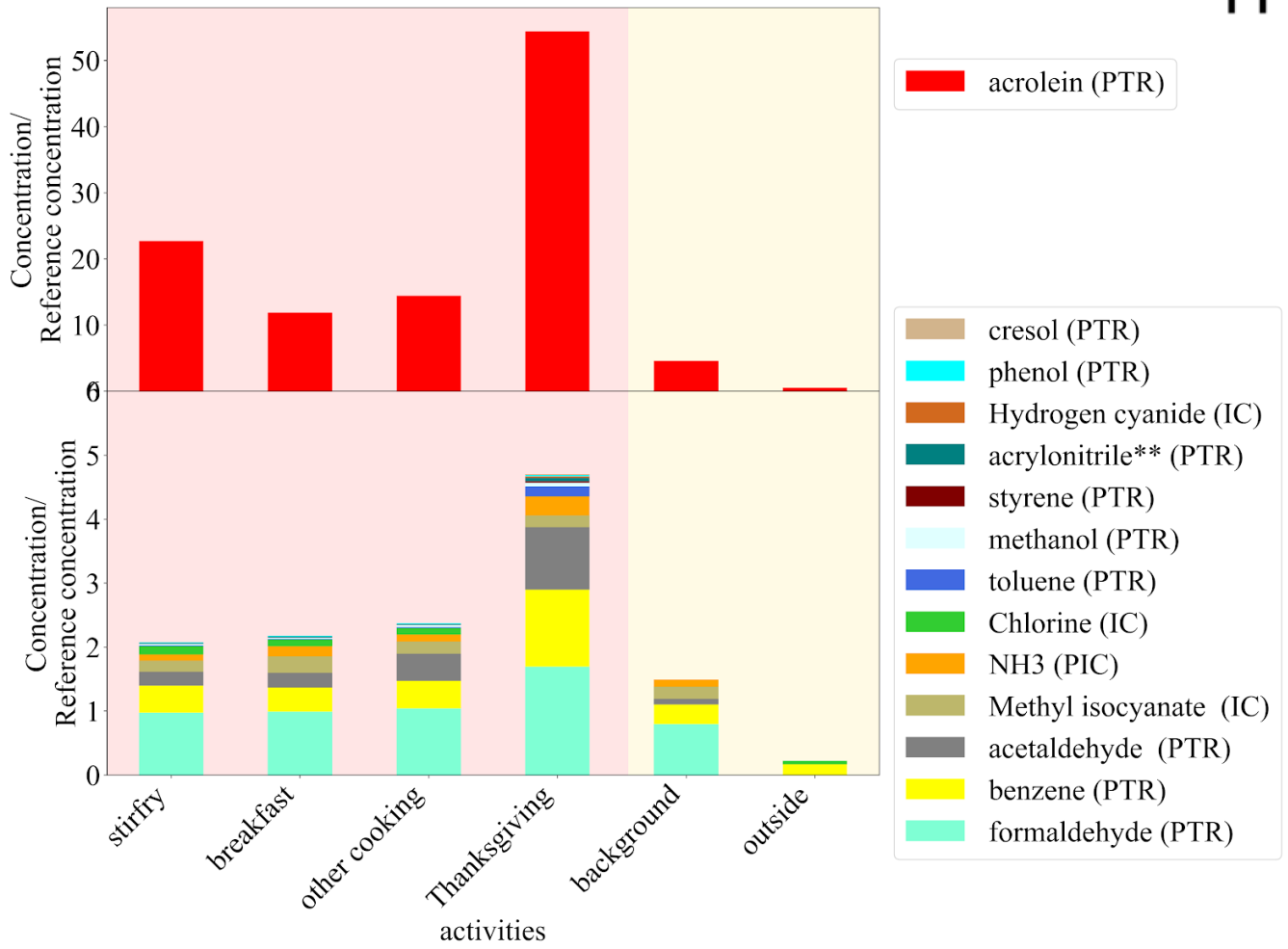


Chemical complexity complicates exposure calculations

- There are many approaches to thinking about health effects
- Traditionally household air pollution is considered chronic, driven by research in the developing world
- Arguably, repeated (daily) exposure could cause the body to respond as a chronic effect (cooking could be serious – driven by acrolein
- But… we don't cook Thanksgiving every day

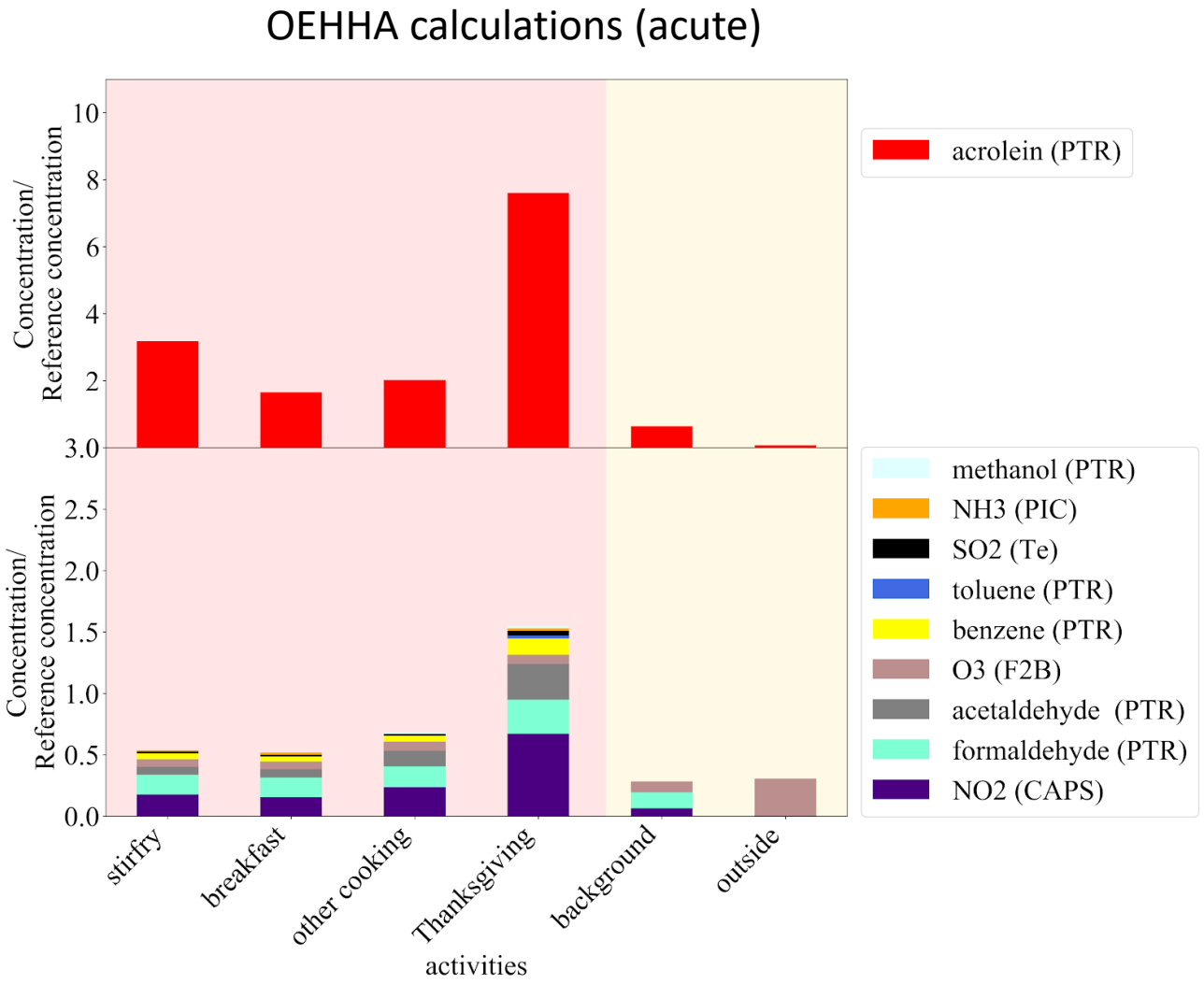


OEHHA calculations (chronic)



Chemical complexity complicates exposure calculations

- But… we don't cook Thanksgiving every day – acute exposure is less concerning – but driven by different molecules
- Acrolein + gas stove emissions (NO_2)



Summary: Your house is a chemistry experiment!

**Oops! Biomass burning is a big source of isocyanic acid and particles!*

- VOCs are high indoors even if you aren't doing anything!
- Some traditional outdoor air pollutants (ozone, particles) are lower
- Cleaning causes chemistry in air + on surfaces
- Bleach cleaning produces turns VOCs and other compounds that weren't toxic into potentially toxic isocyanates, chloramines
- Cooking produces a lot of molecules! Some may be toxic (I'm still cooking turkey for Thanksgiving)