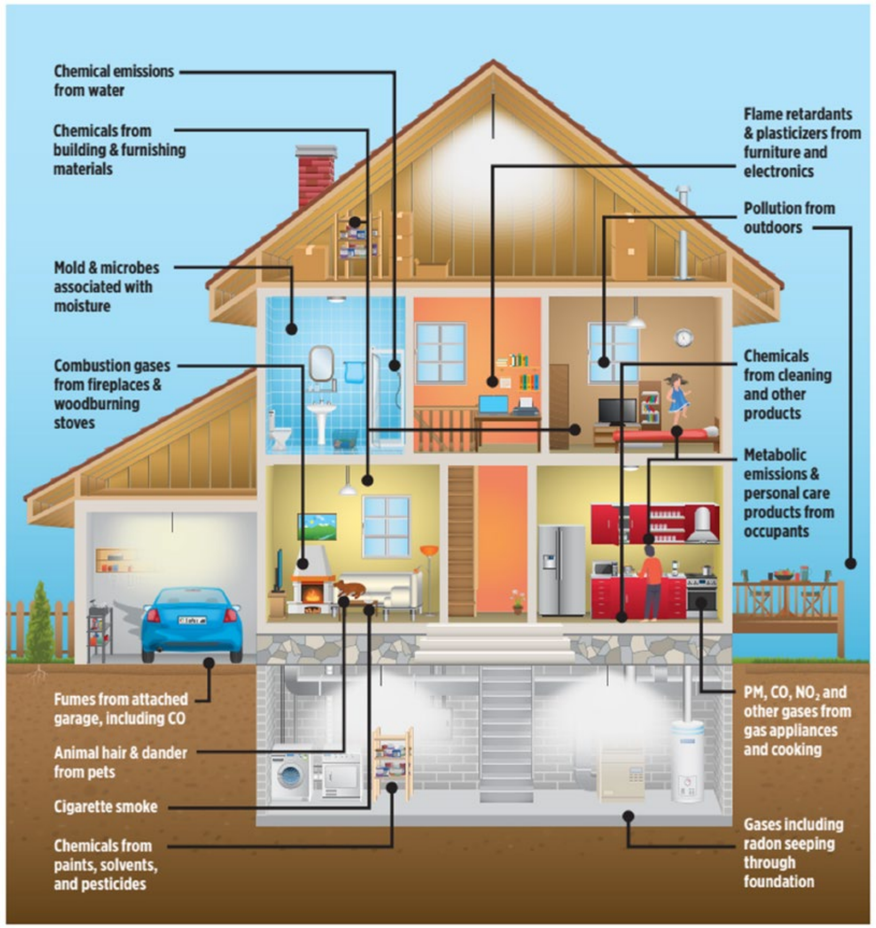
Chemical Transformations and their Impacts

A perspective from the National Academies Consensus Report

Delphine K. Farmer

Department of Chemistry,

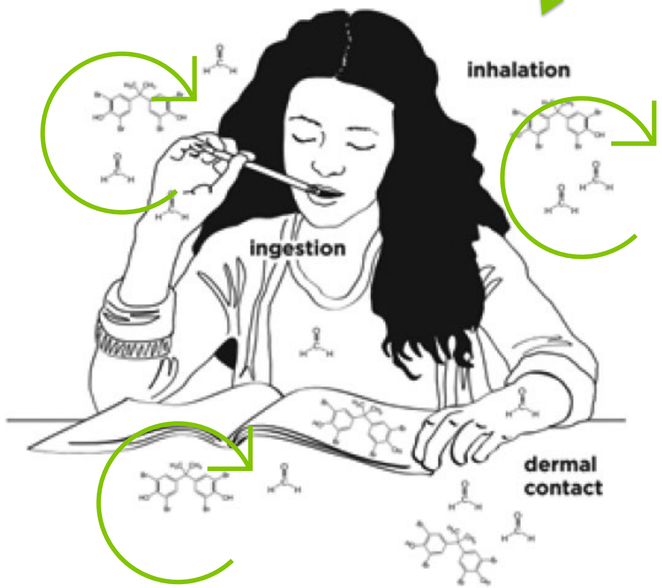
Colorado State University

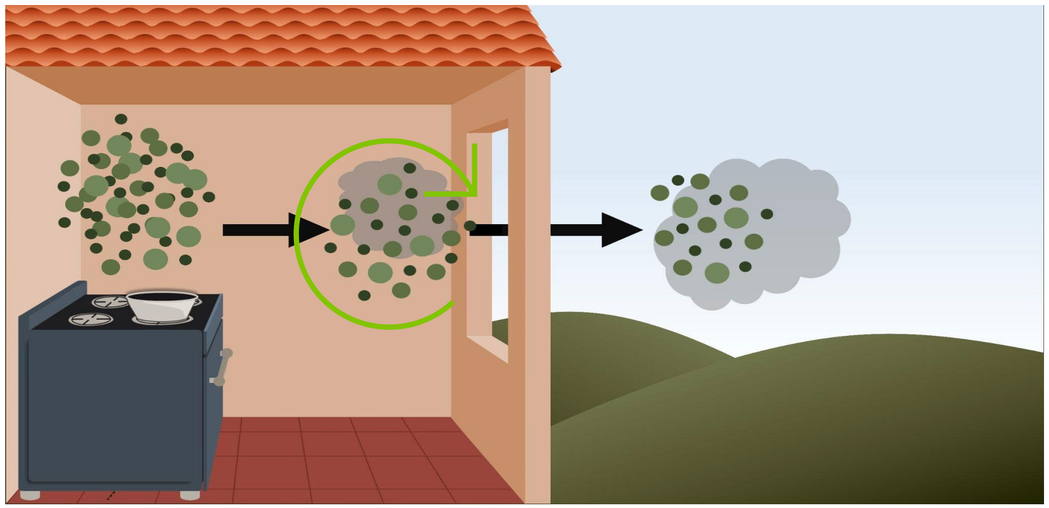


"Indoor chemistry matters". National Academy of Sciences, Engineering and Medicine. Consensus report. 2022

Photos from Colorado State University

Indoor air is chemically complex, which enables many reactions and impacts how we think about health and outdoor air quality



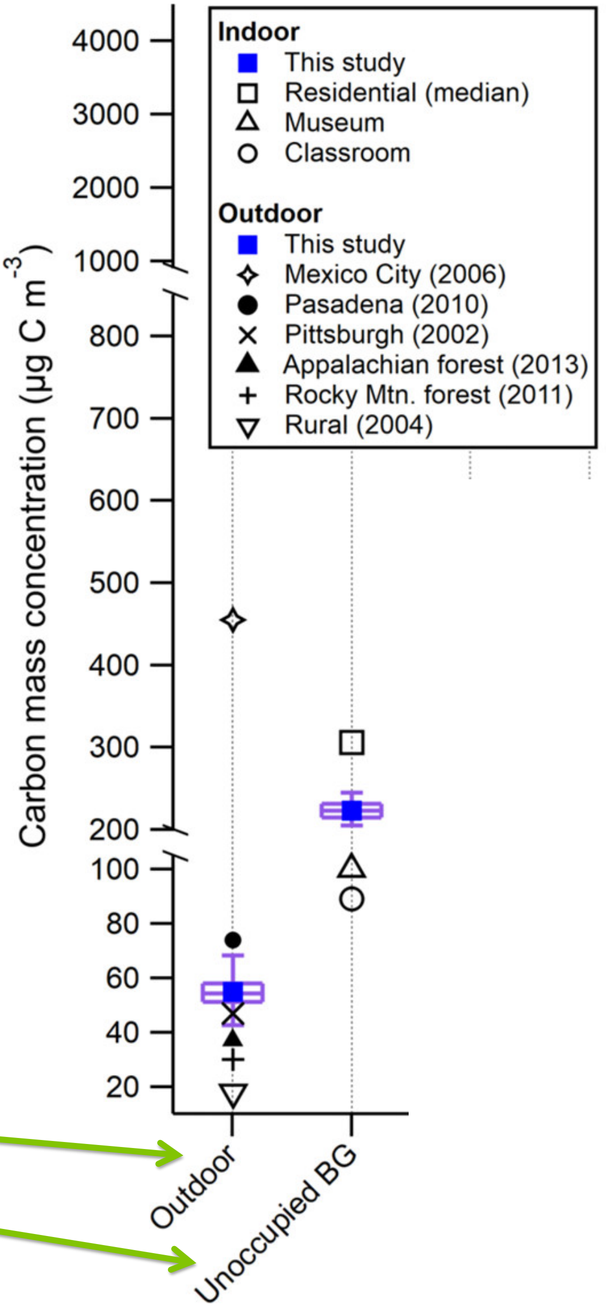


"Indoor chemistry matters". National Academy of Sciences, Engineering and Medicine. Consensus report. 2022

[Pothier et al. Env Sci:Proc Imp. 2023]

Indoor air has much more reactive organic carbon than outdoor air

- Homes are strong sources of reactive organic C
- Unoccupied, the HOMEChem house emitted ~0.7 g reactive organic C/day, or ~2 gC m^{-2} yr^{-1} (about ½ of orange grove!)



HOMEChem

[Mattila et al. Env Sci Tech. 2021]

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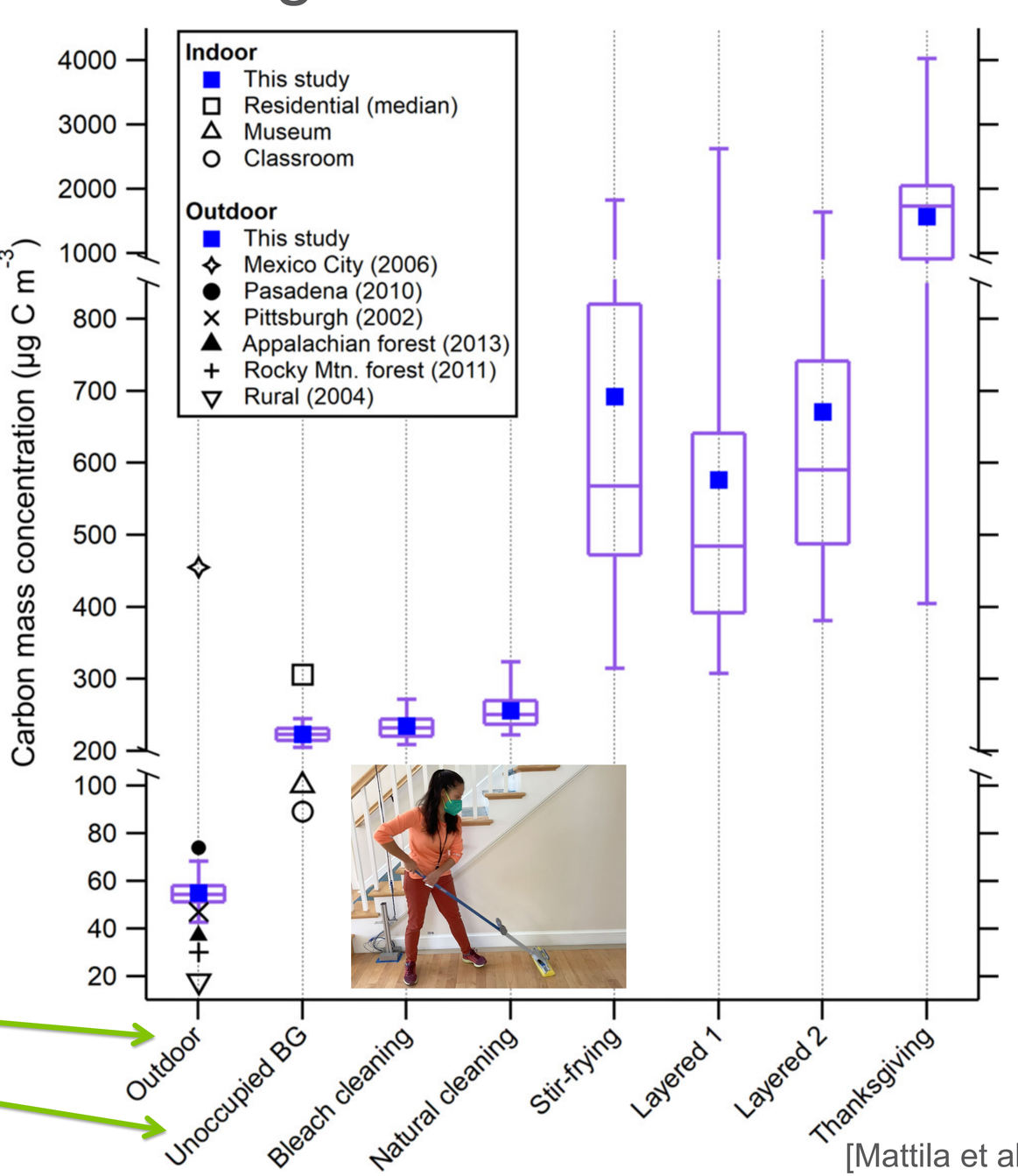

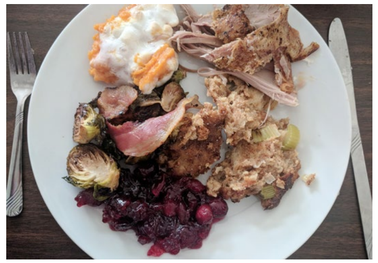

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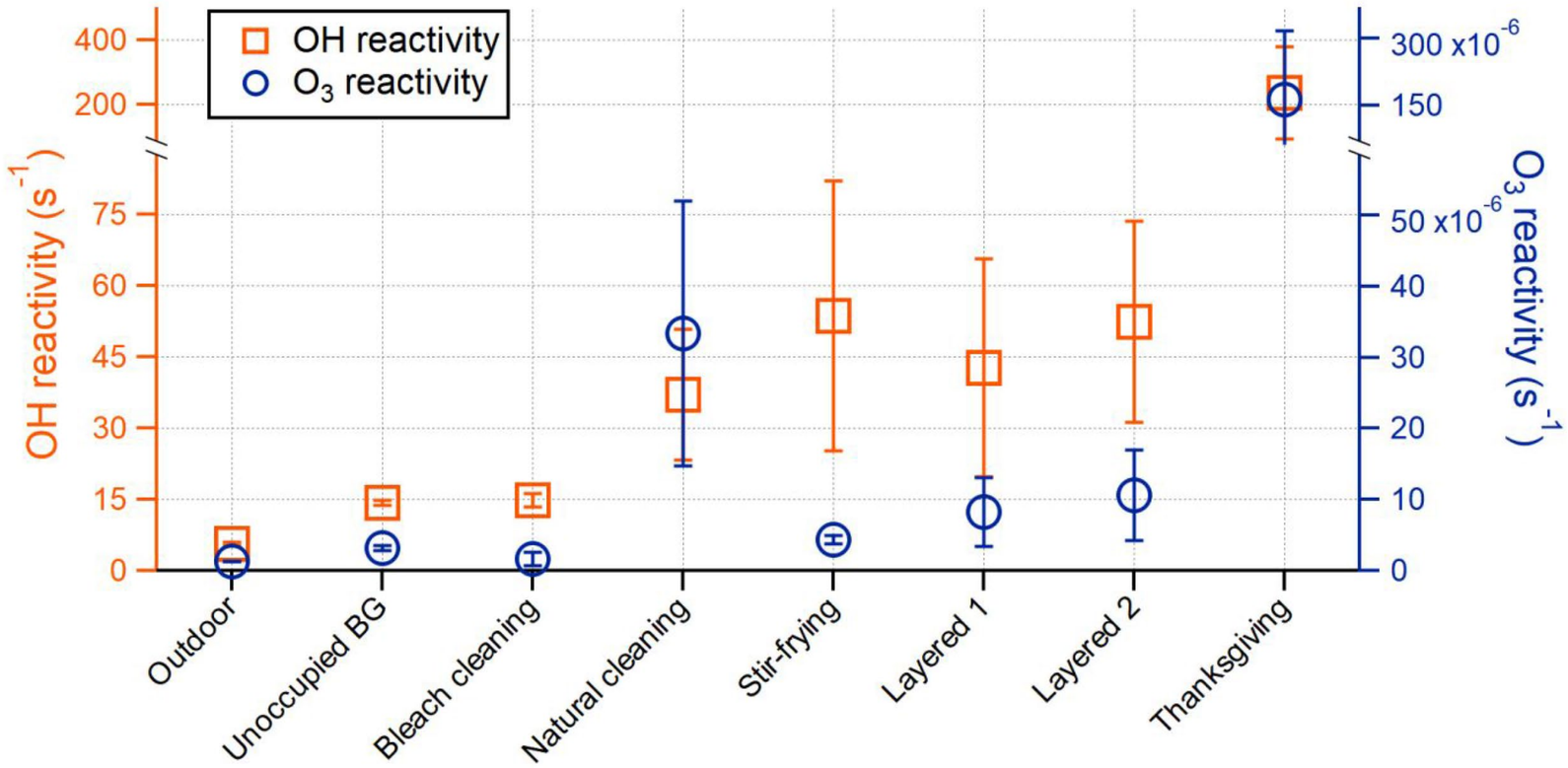
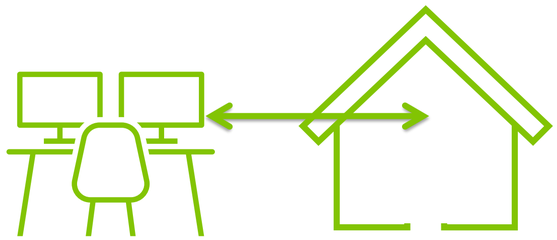


- All this organic C is very, very reactive!
- Potential for chemical reactions and secondary organic aerosol (SOA) formation at any given time
  - Likely substantial effects once outdoors – or if we bring oxidants or reaction initiators indoors

[Mattila et al. Env Sci Tech. 2021]

Many reactions are possible – and have been demonstrated to occur – indoors

Partitioning



Phase partitioning is the *movement of molecules across air, liquid and solid phases* (including building materials and indoor aerosols) as the chemical system moves towards equilibrium.

Far higher surface area-to-volume ratio indoors than outdoors

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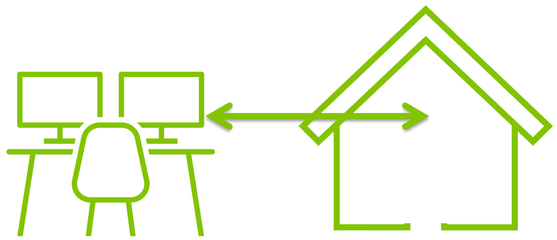
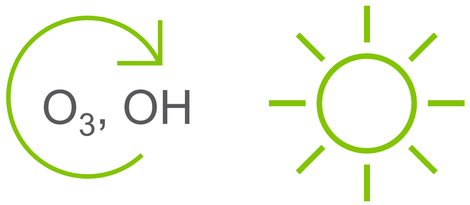
Partitioning



Airborne Chemical Reactions



<u>Oxidation</u>

- O_3 is a well-established oxidant
- HOCl, $OH\cdot$ and $NO_3\cdot$ are of emerging interest

<u>Photolysis</u>

- Sunlight vs artificial light
- Spatial gradients due to attenuation

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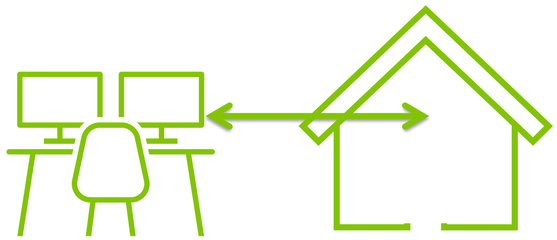

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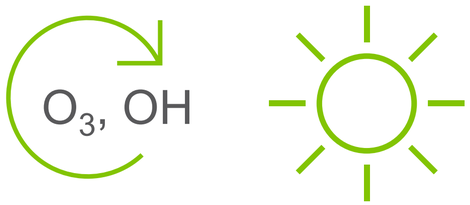
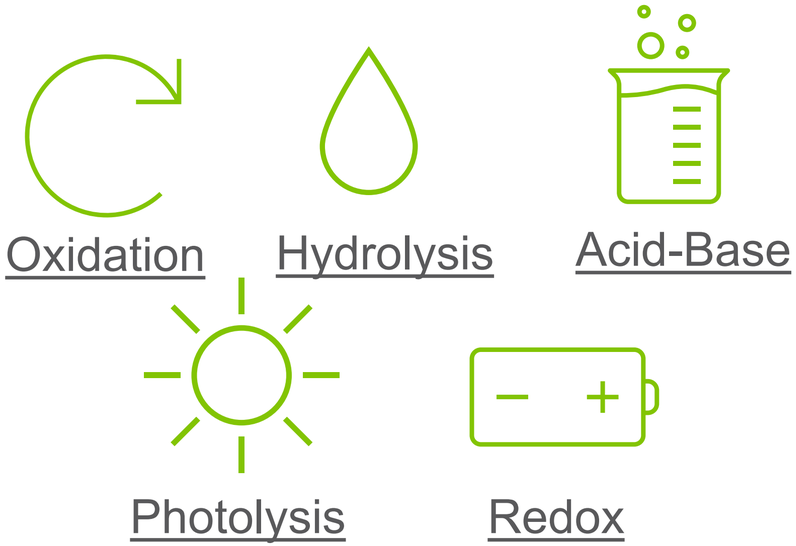


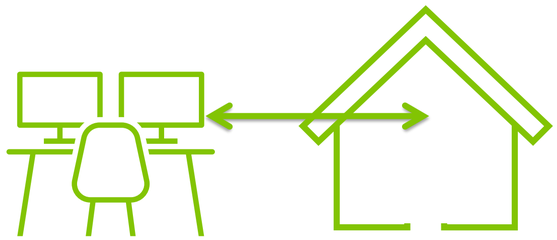
Surface-involved Chemical Reactions



Multiphase chemistry occurs across interconnected gas, solid and liquid phases and thus encompasses a large range of potential reactions occurring on multiple timescales

A few examples highlight why these transformations matter

Partitioning



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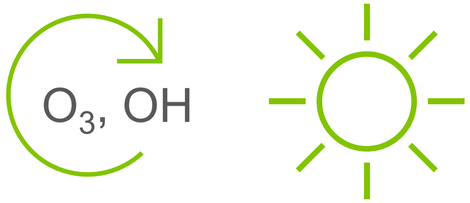

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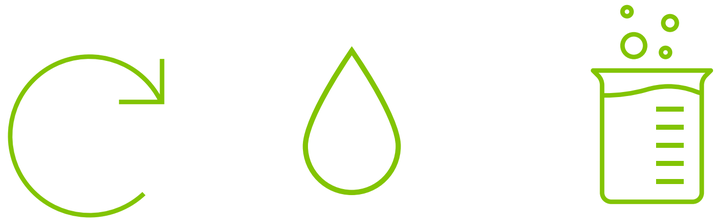
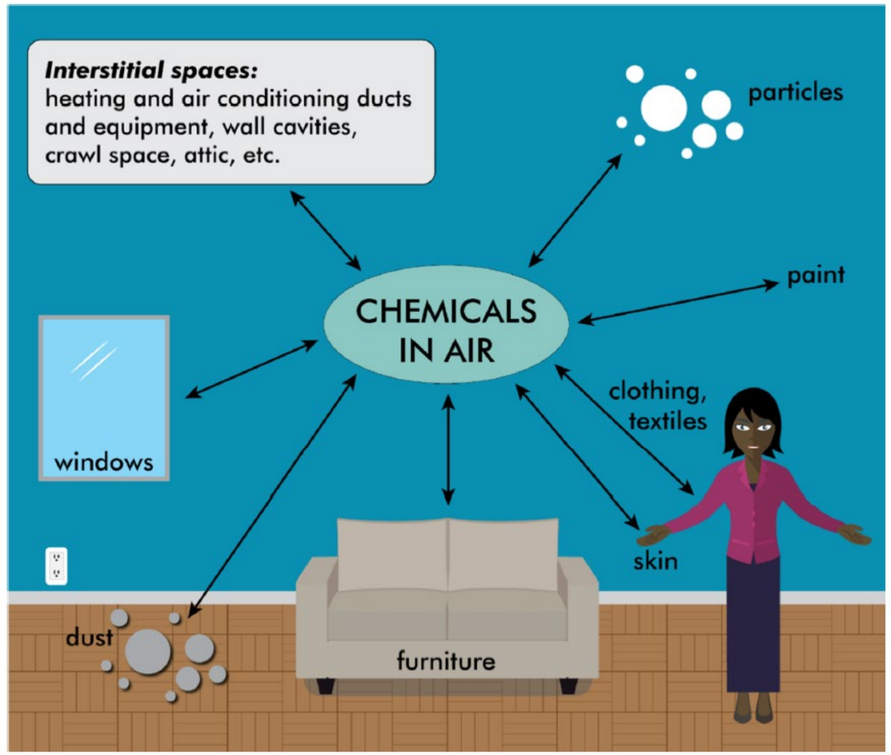
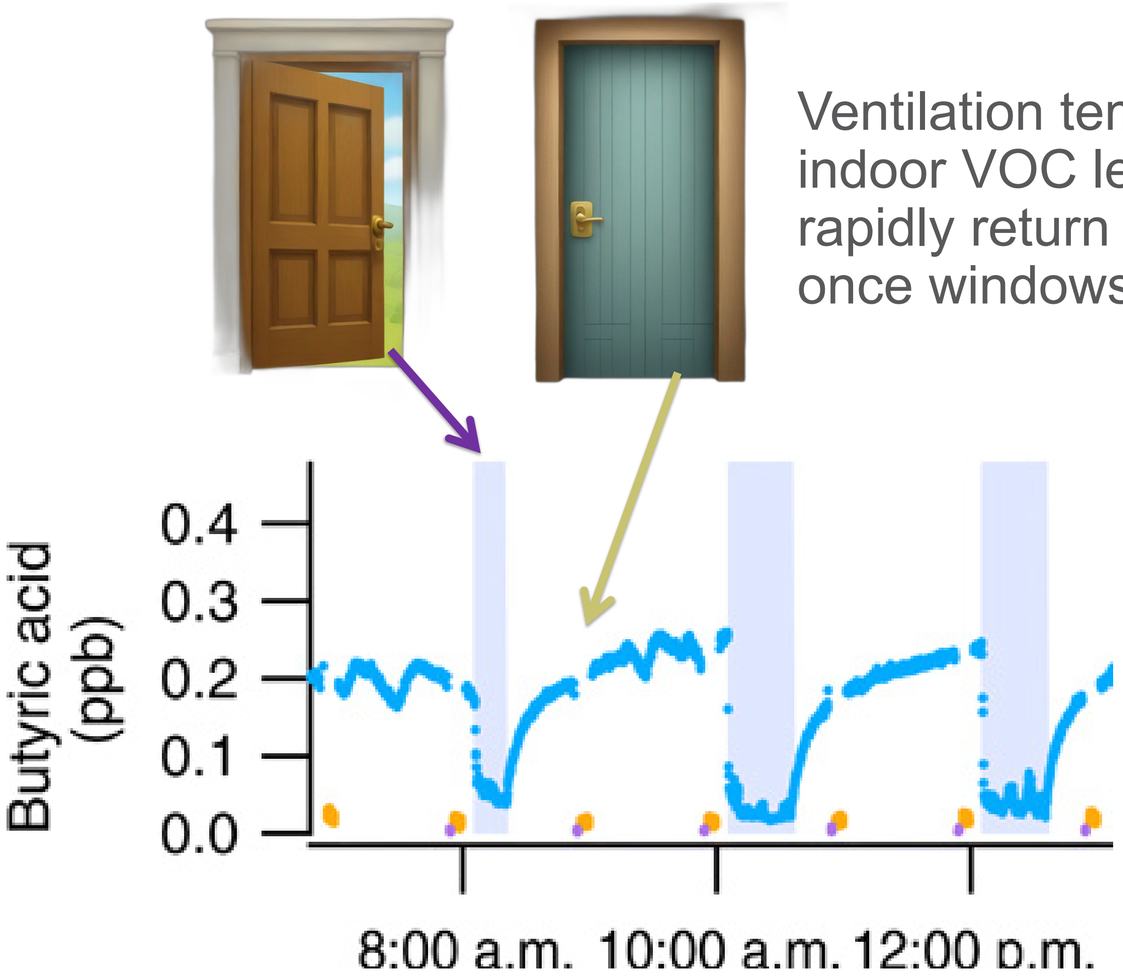


I. Phase partitioning from indoor surface reservoirs drives high indoor levels of many compounds



NASEM 2022 report, modified from Weschler and Nazaroff (2008)

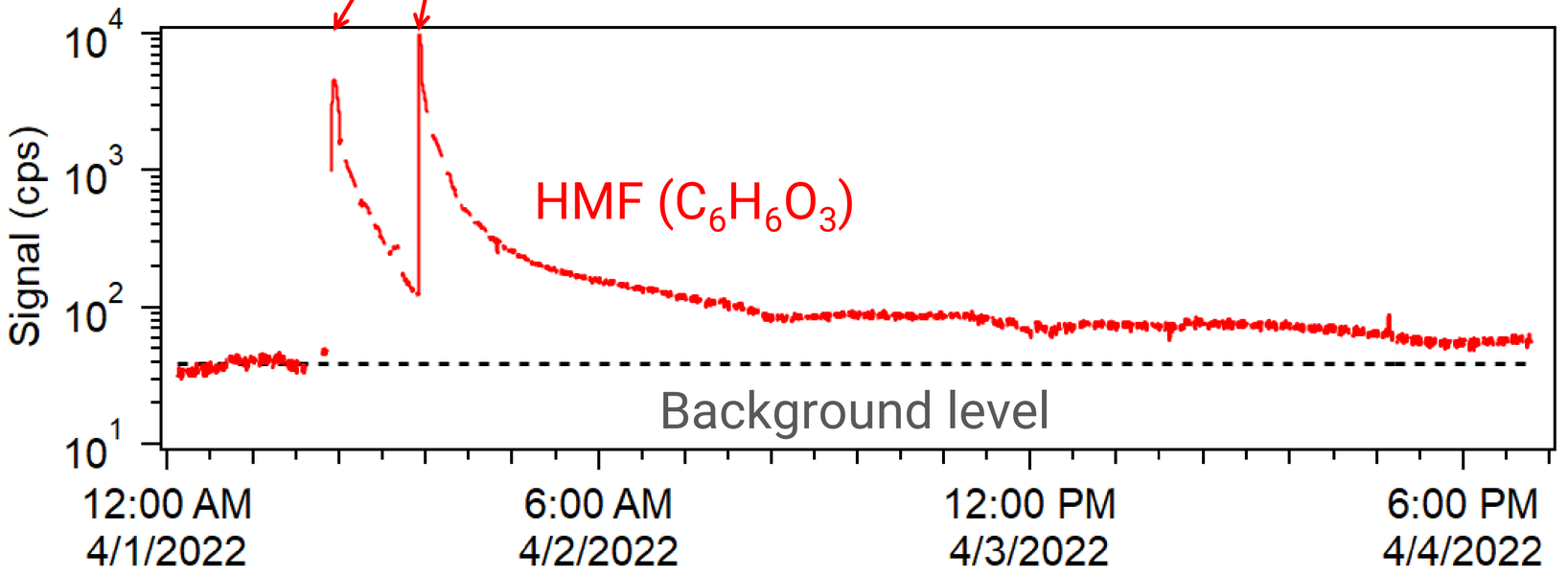


Ventilation temporarily reduces indoor VOC levels, but they rapidly return to previous levels once windows are closed

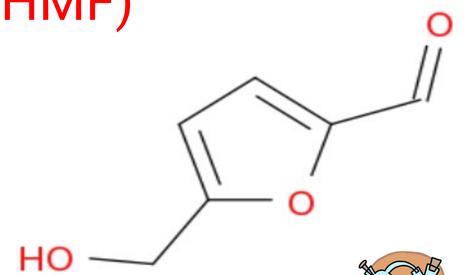
[Wang et al. Sci Adv. 2020]

Dynamic partitioning enables wildfire smoke VOCs to persist indoors

- We added wildfire smoke proxy to house
- Air levels never returned to background after smoke addition, even after days due to surface reservoirs



Hydroxymethylfurfural (HMF)



[Li et al. Sci Adv. 2023]

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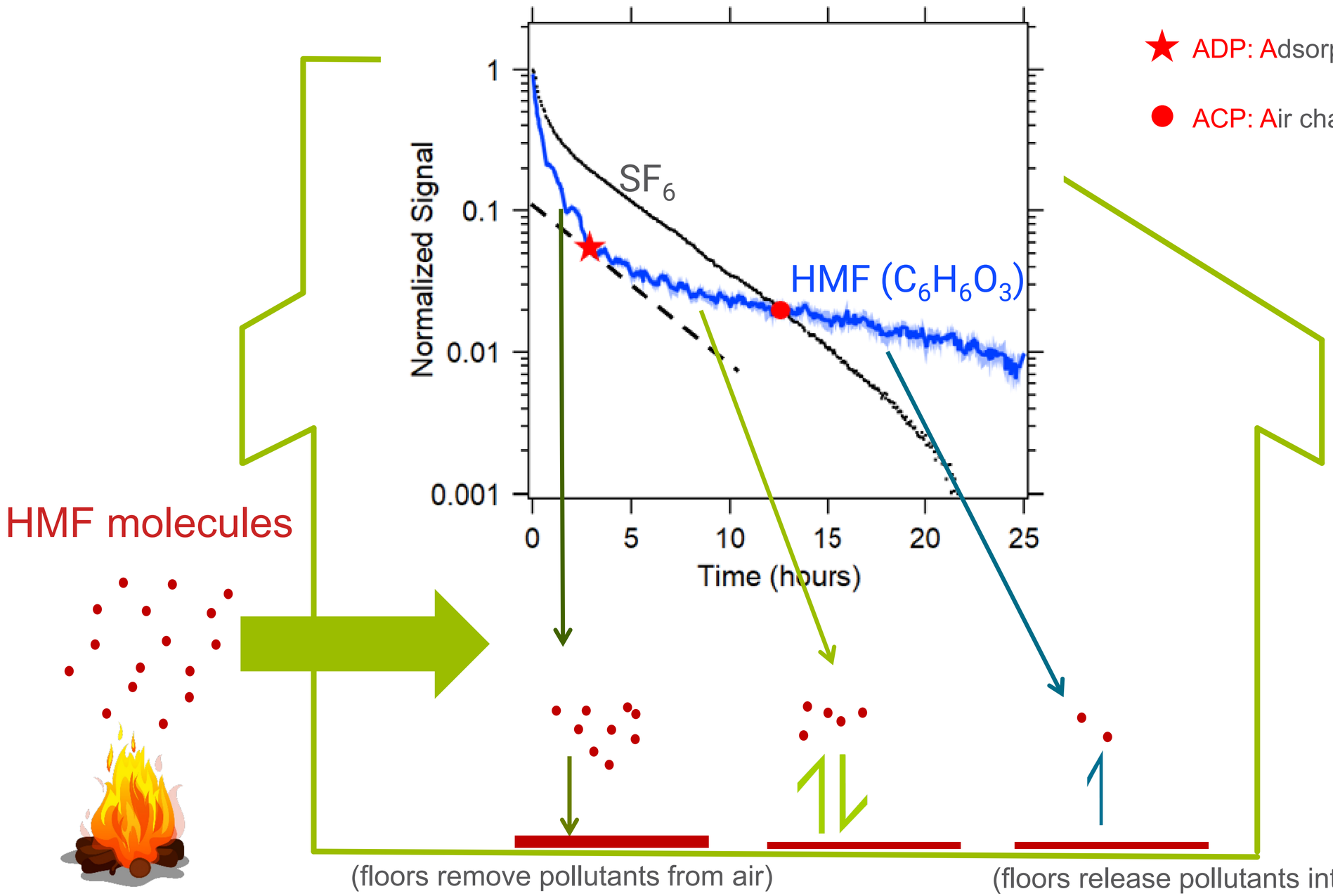
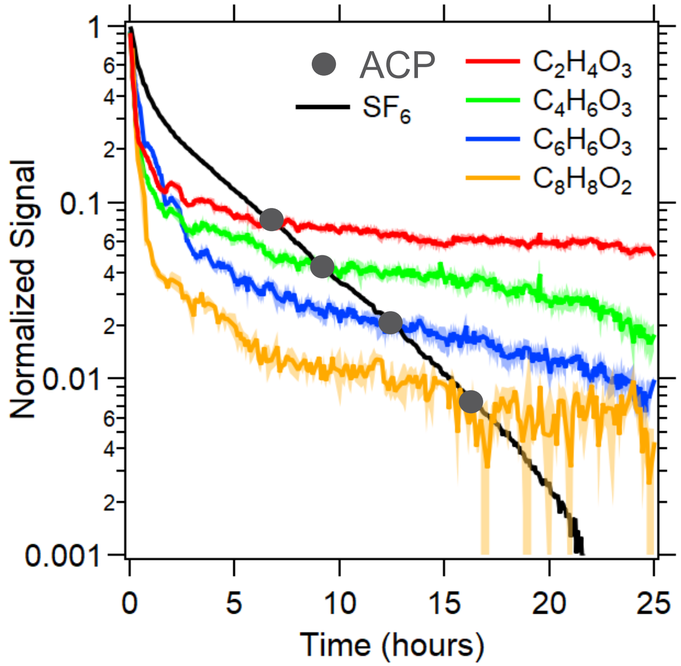
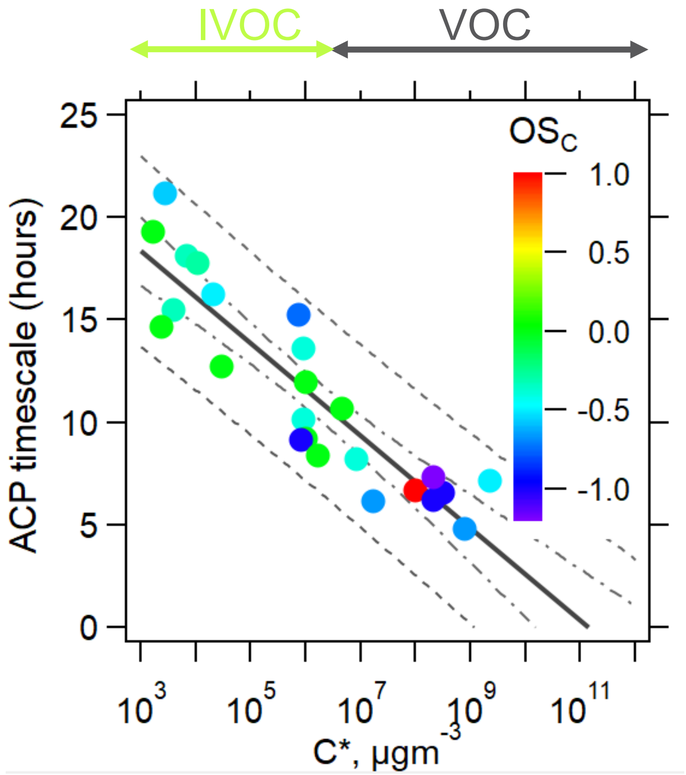
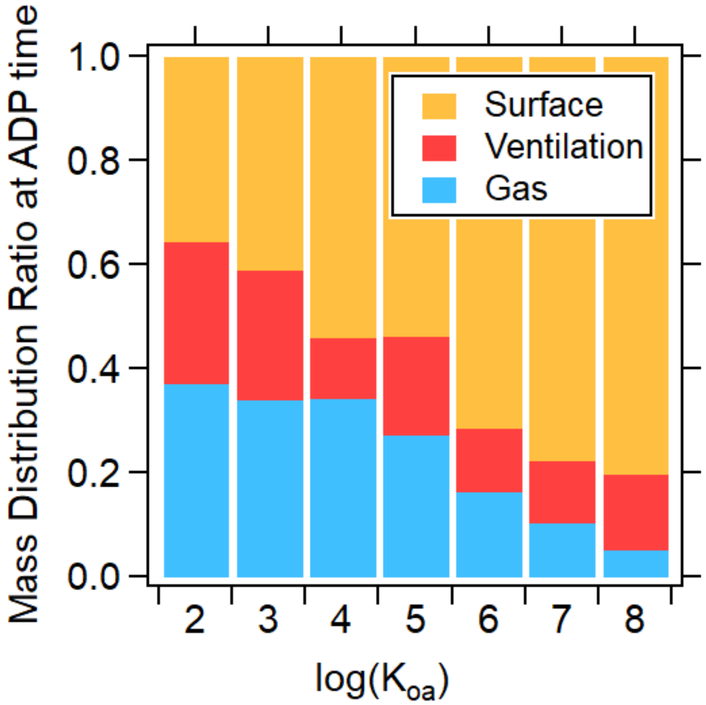


[Li et al. Sci Adv. 2023]

Chemical structure controls partitioning behavior, which gives us a tool to predict fate





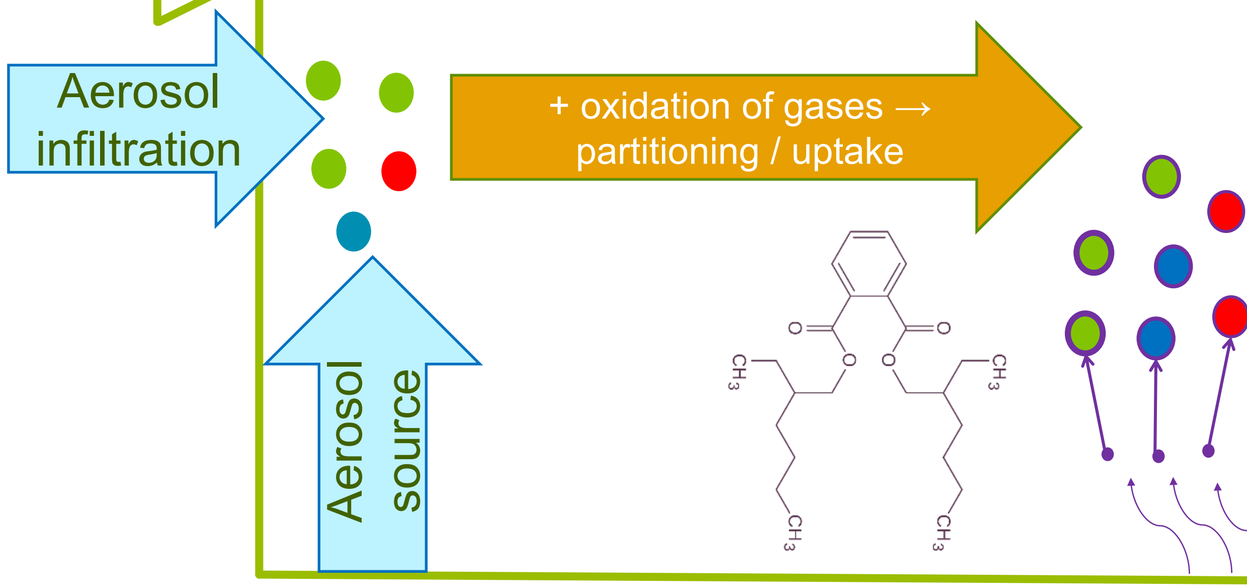


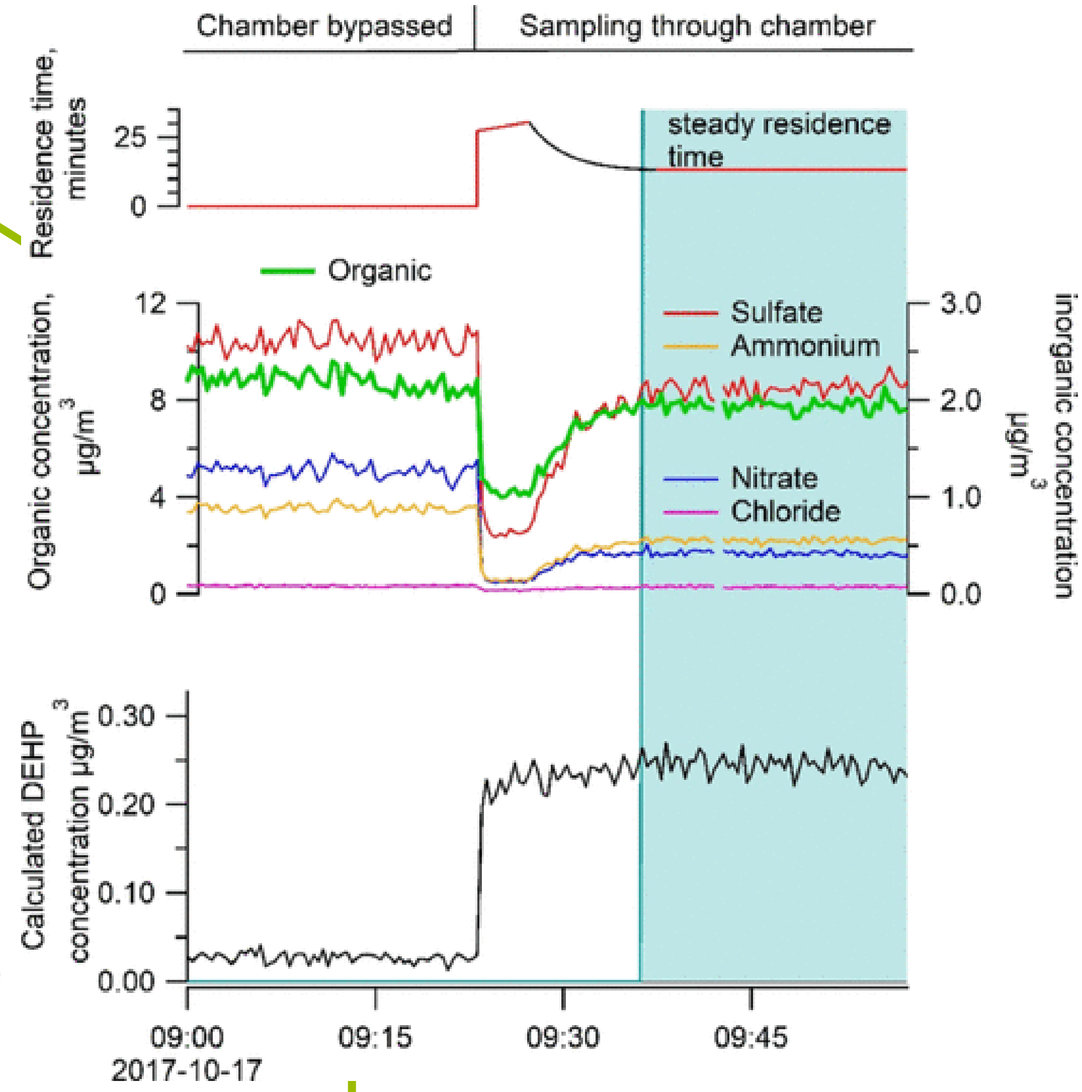
ACP: Air change rate Crossing Point
C*: Saturation concentration
K_{oa}: octanol–air partition coefficient

[Li et al. Sci Adv. 2023]

Partitioning to aerosols enables transport – and new exposure pathways – for low-volatility compounds (e.g., phthalates)

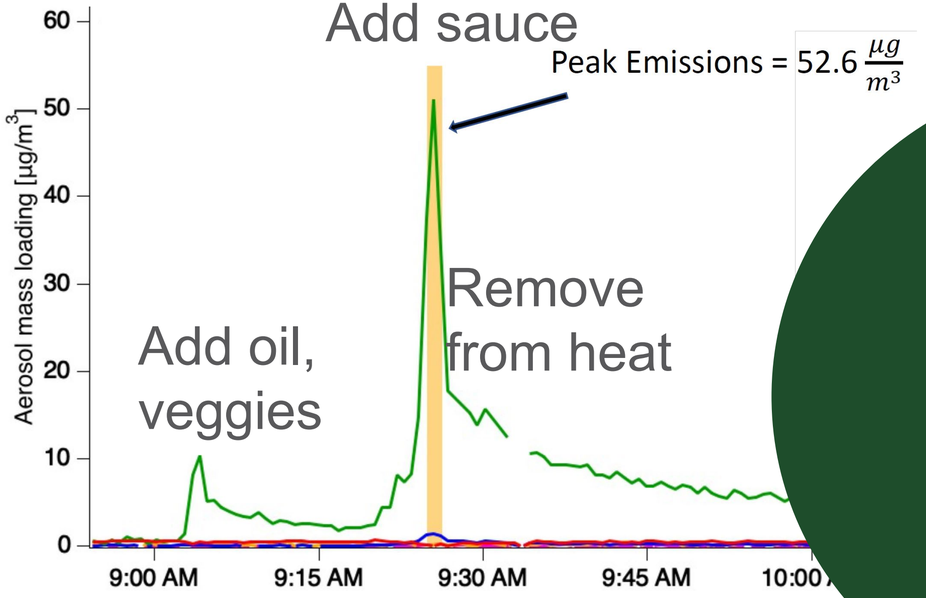
- Low volatility phthalate esters from flooring can be taken up on aerosol
- DEHP condenses more efficiently on ‘fresh’ organic aerosol than oxidized organic aerosol or sulfate

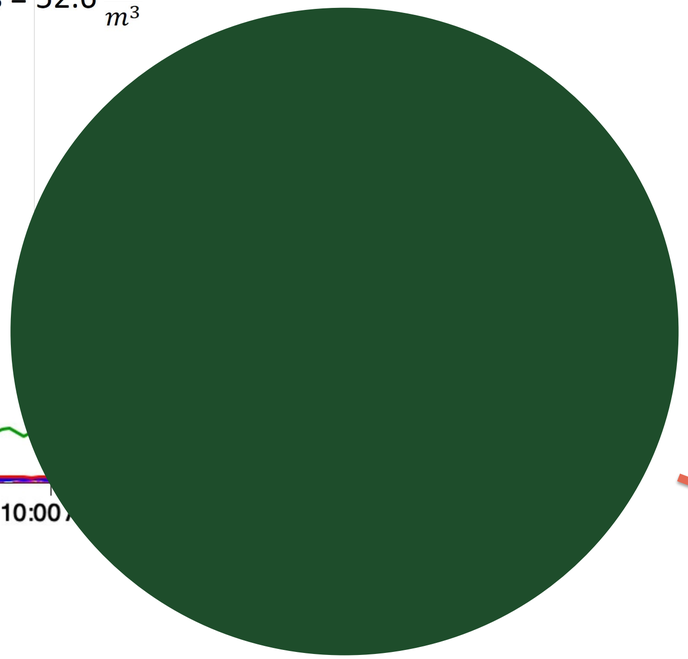




[Eriksson et al. Env Sci Tech. 2020]

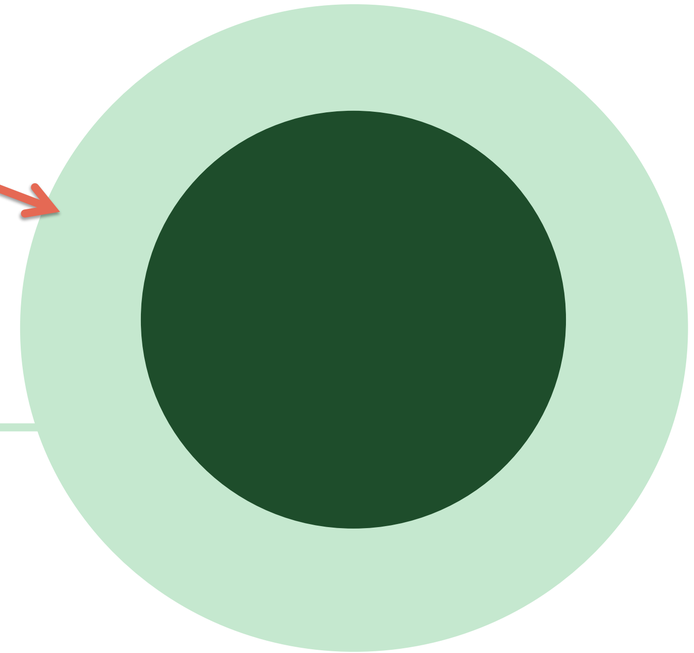
Cooking aerosol-air partitioning occurs, and may impact both indoor and outdoor exposure





- Cooking aerosol is dominantly organic
- Cooking organic aerosol undergoes dilution-driven evaporation
- **Volatilized components contribute to *outdoor O_3 and SOA formation***

Move outdoors



30-60% mass evaporates and can participate in atmospheric chemistry

[Pothier et al. Env Sci:Proc Imp. 2023]

Partitioning

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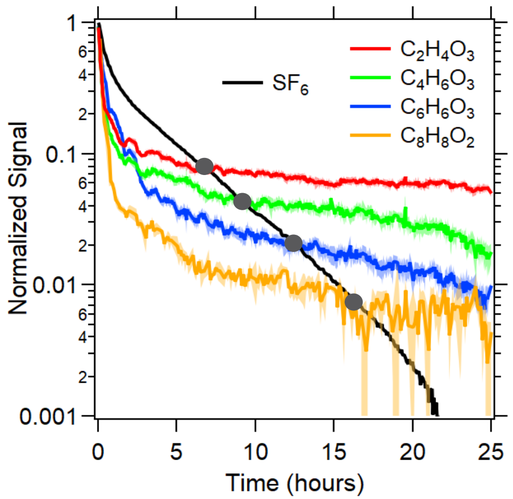
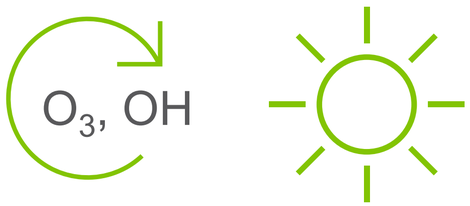
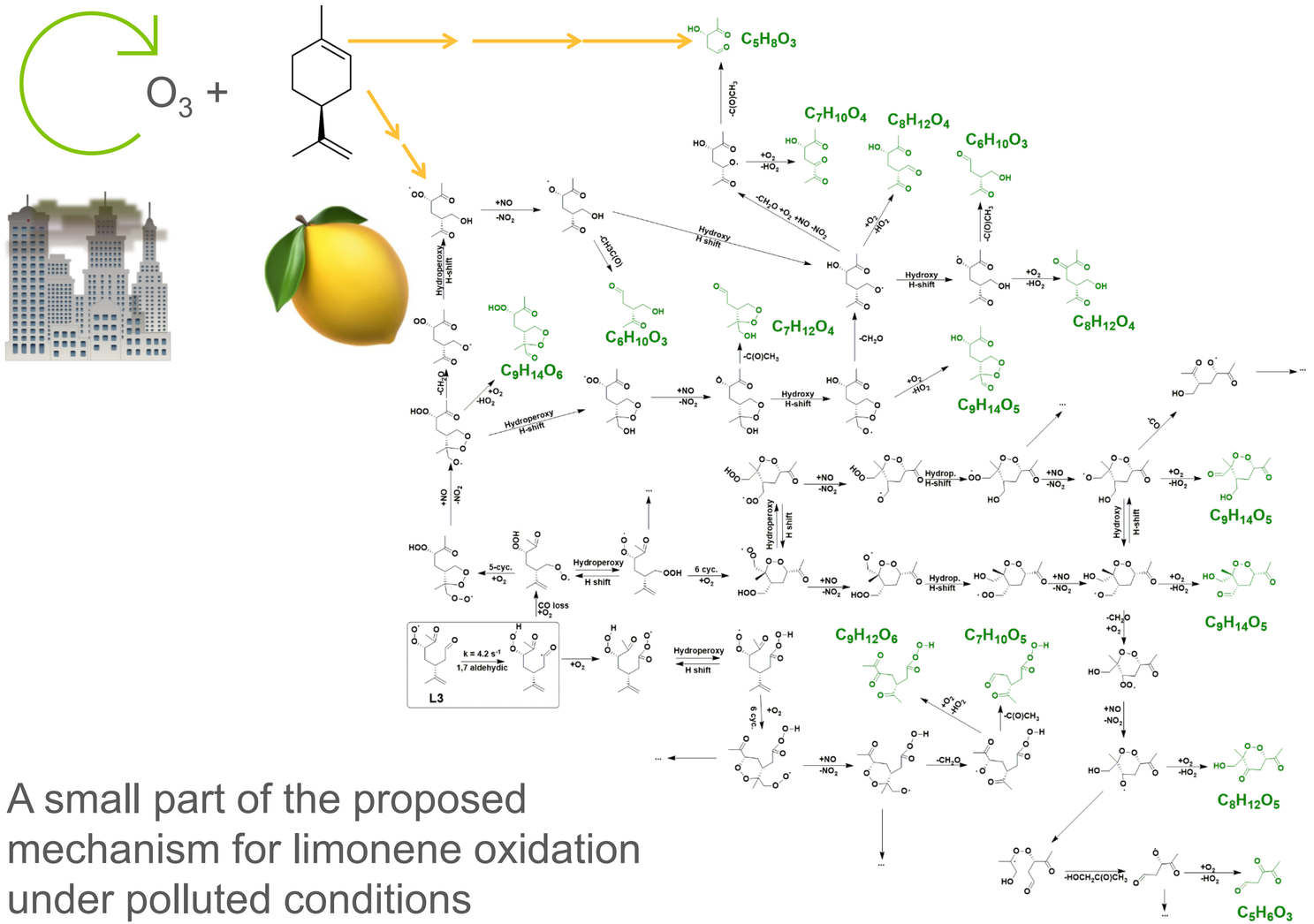


Li et al. Science Advances. 2023]

Airborne Chemical Reactions



II. Gas-phase chemistry can create new chemical products that have health, outdoor air quality, or climate impacts

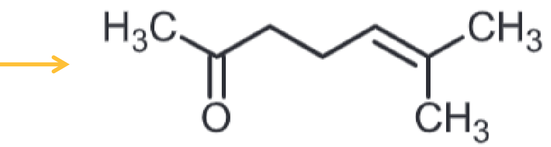


A small part of the proposed mechanism for limonene oxidation under polluted conditions
[Chen et al. J Phys Chem A. 2021]

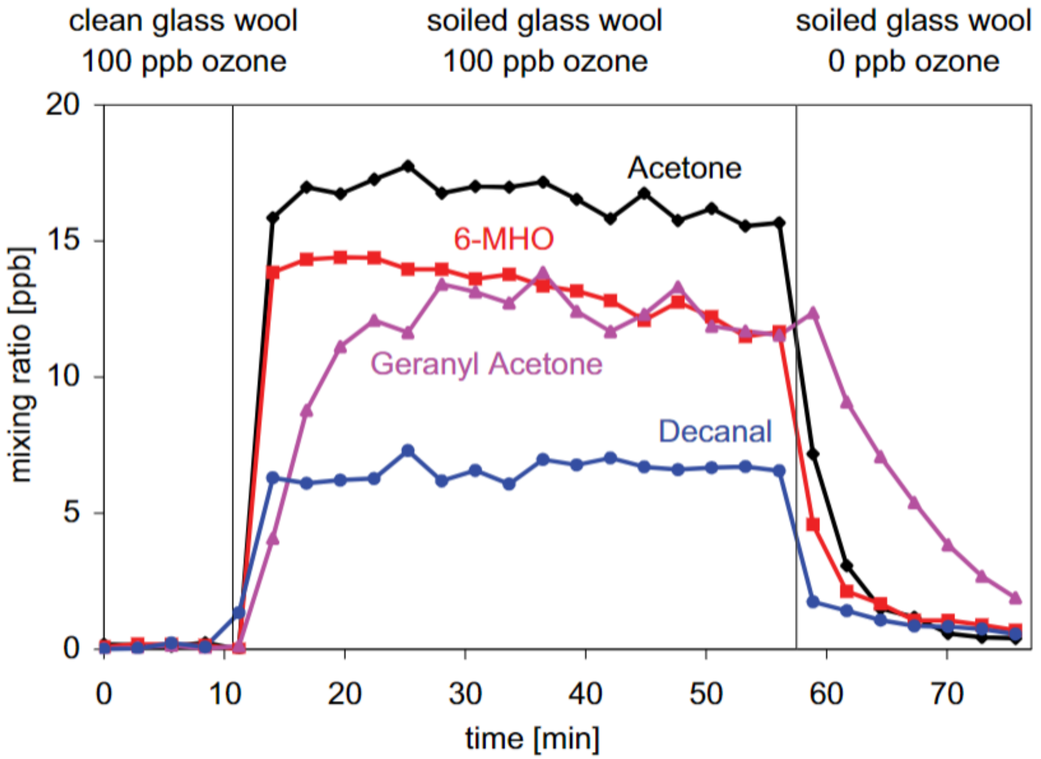
- Secondary Organic Aerosol / $PM_{2.5}$
  - Health effects of PM2.5 well established
  - Short-lived climate forcer
- Toxic by-products (including HCHO)
- Generate more oxidants (OH)

Ozonolysis products observed indoors despite low [O_3]

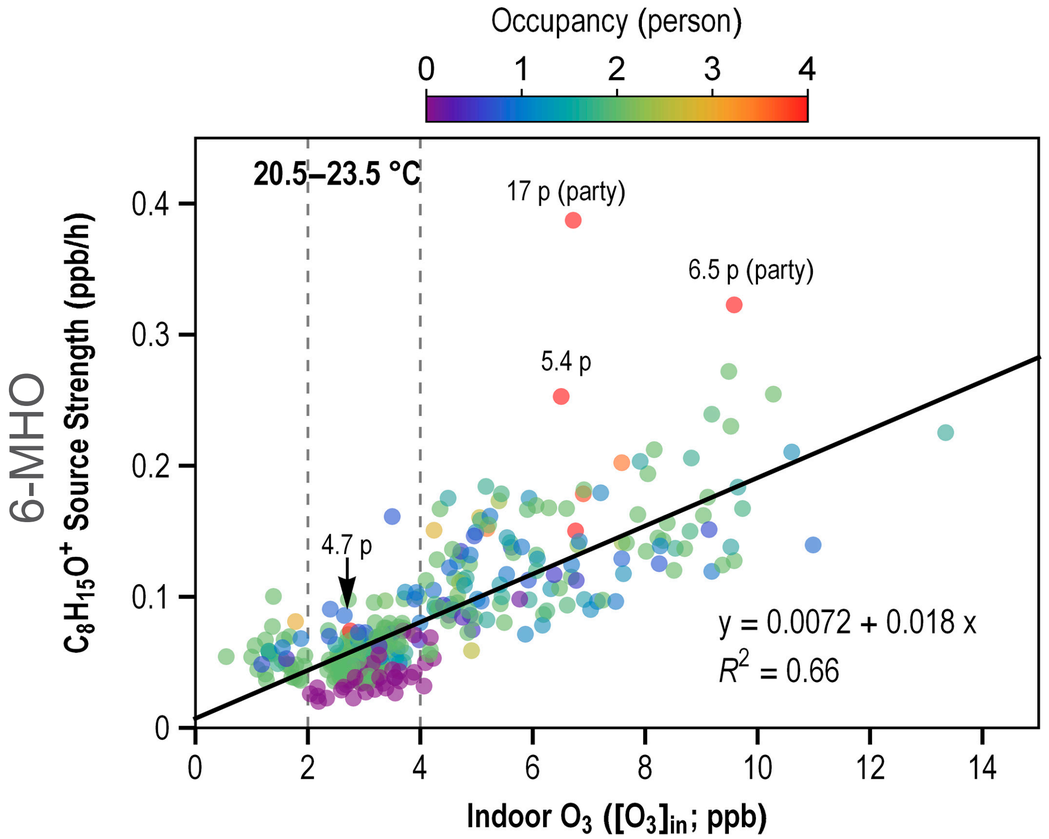
O_3 + skin lipids



6-methyl-5-hepten-2-one (6-MHO)



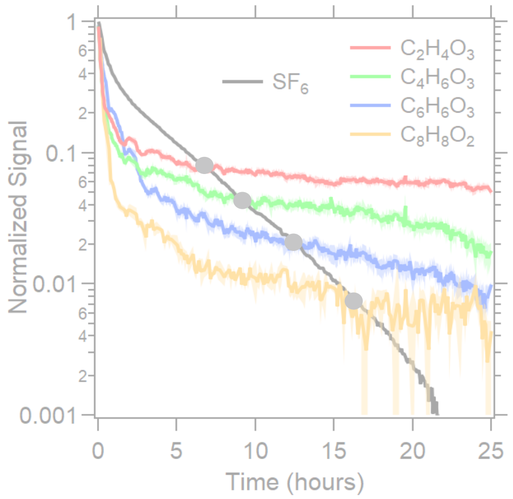
[Wisthaler and Weschler. PNAS. 2010]



[Liu et al. PNAS. 2021]

Partitioning

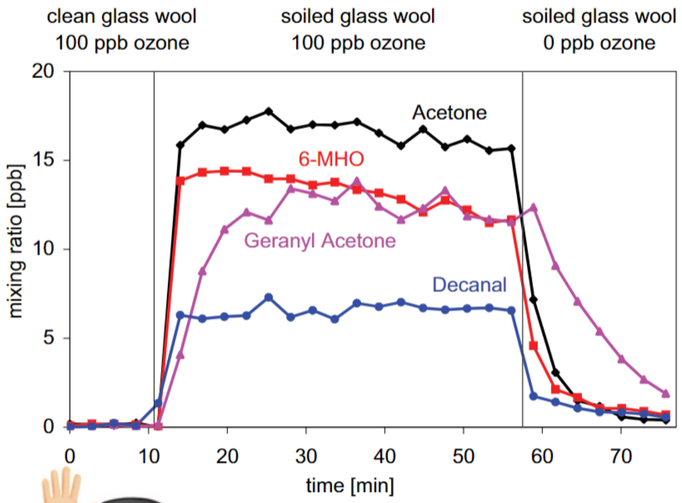
determines indoor concentrations of many compounds, enables diffferent exposure pathways (smoke, phthalates), and impacts outdoor air (cooking)



Li et al. Science Advances. 2023]

Airborne Chemical Reactions

occur rapidly and are ubiquitous despite seemingly low [O_3], can generate toxic byproducts



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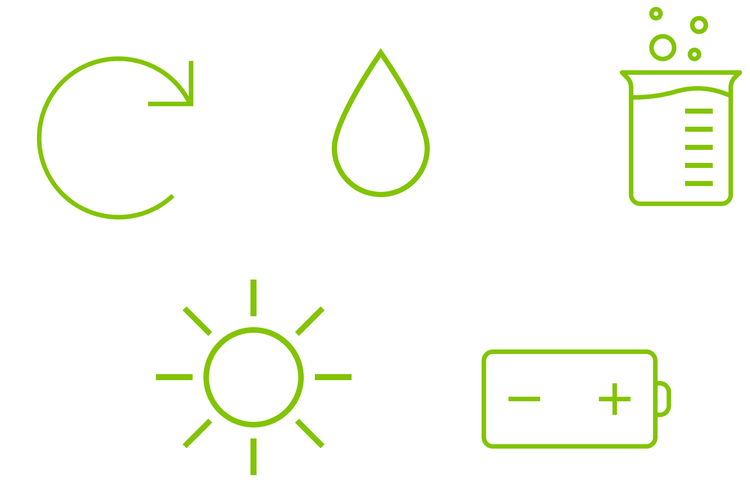
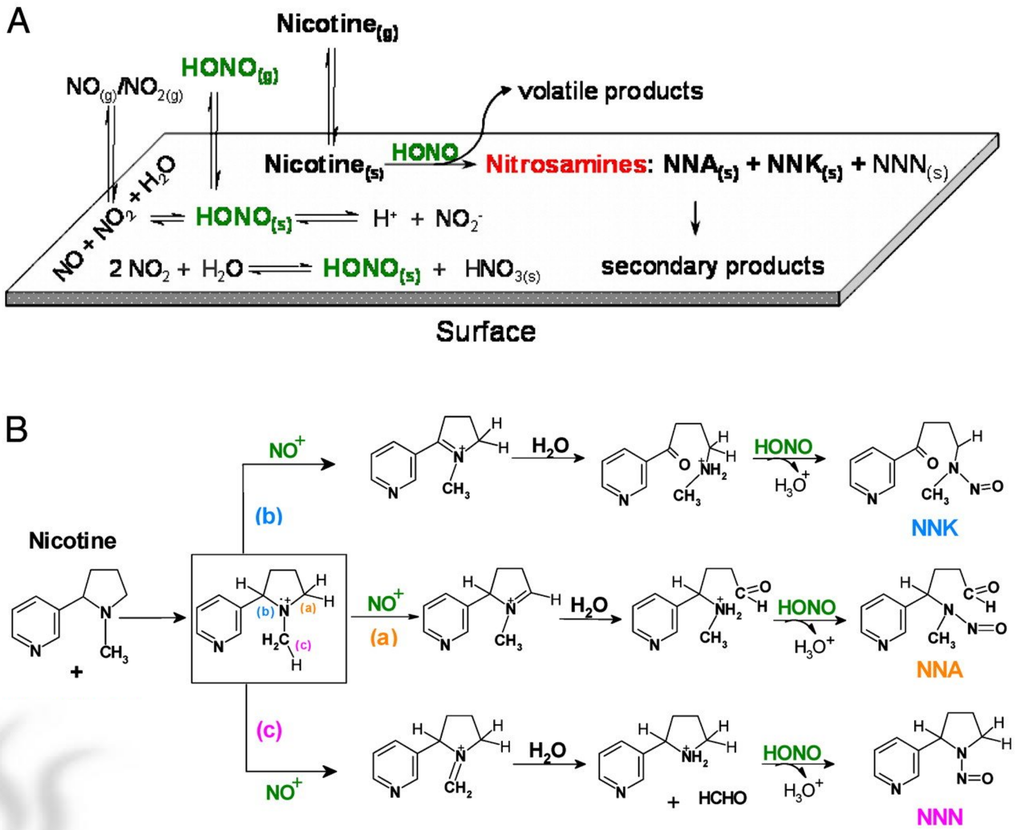


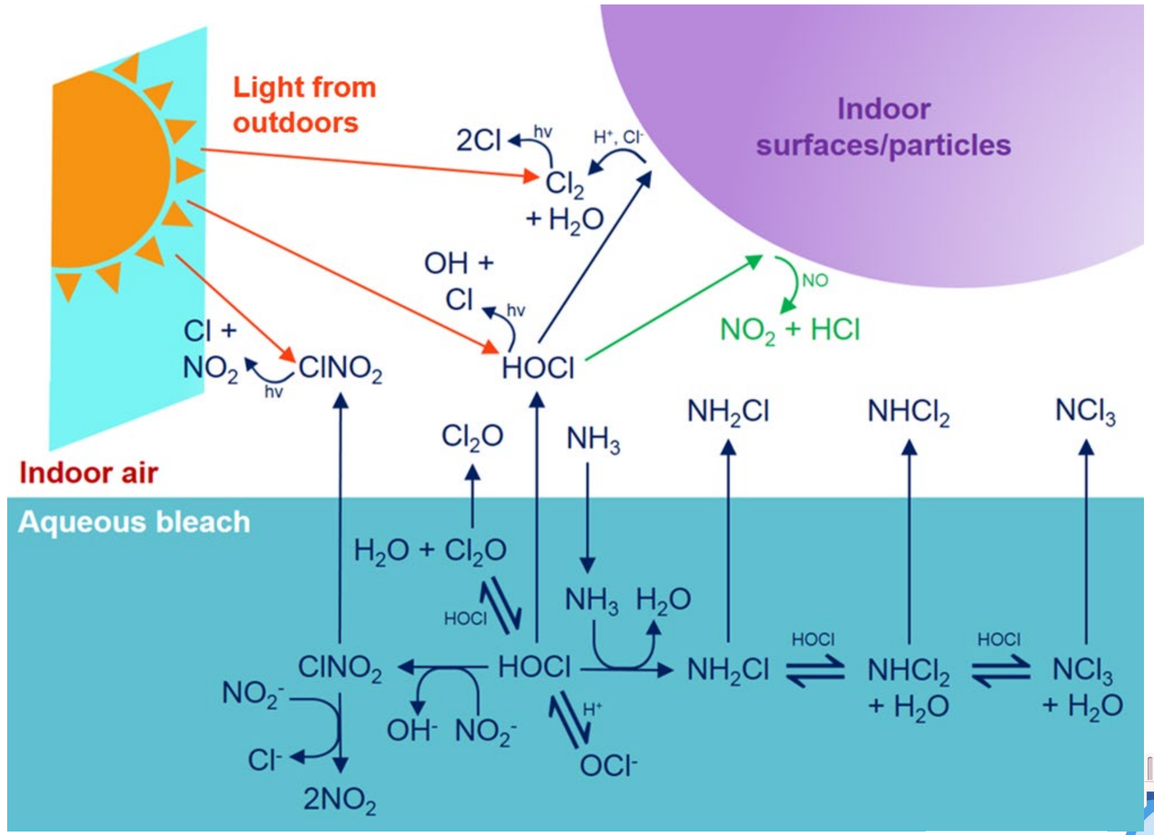
III. Surface chemistry can mediate human exposure in unexplored ways and on temporal scales that are distinct from outdoor air

Nicotine undergoes chemical reactions on indoor surfaces and produces toxic products



[Sleiman et al. PNAS. 2010]

Commercial bleach solutions initiate multiphase reactions that form chloramines and other secondary air toxics



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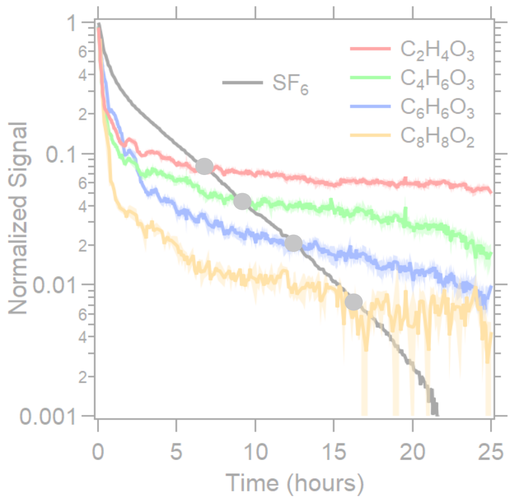

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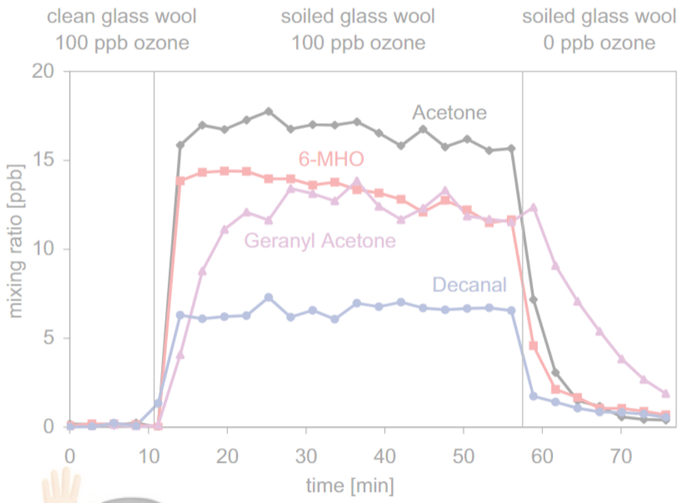

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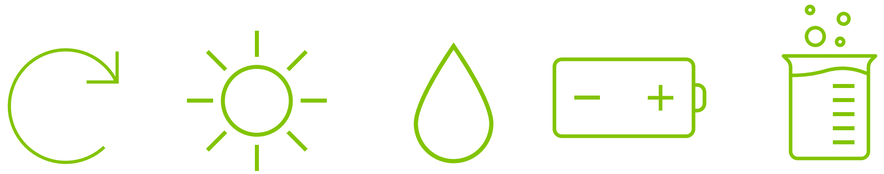
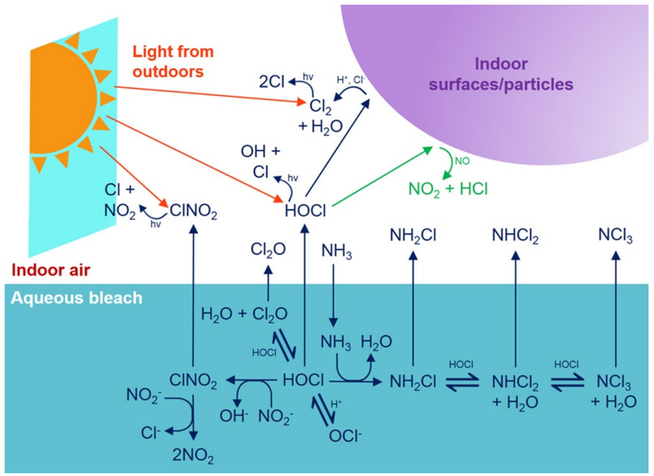
Surface-involved Chemical Reactions

Large surface area-to-volume ratio means that multiphase processes can drive health-relevant chemistry (cigarettes, cleaning)





Mattila et al. ES&T. 2020]

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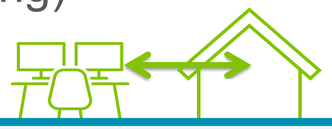

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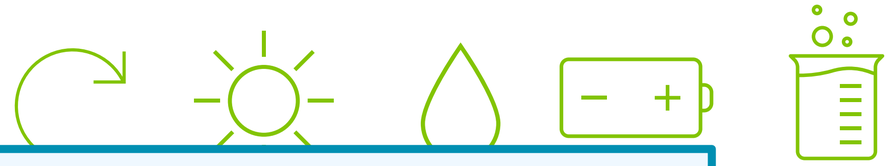
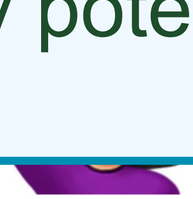
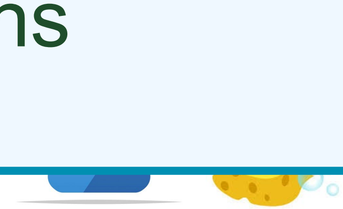
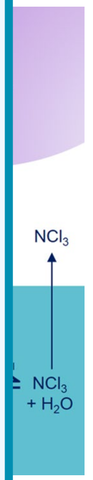


These partitioning, gas, and surface processes are not independent.

Indoor air is a chemically complex multiphase system with many potential transformations



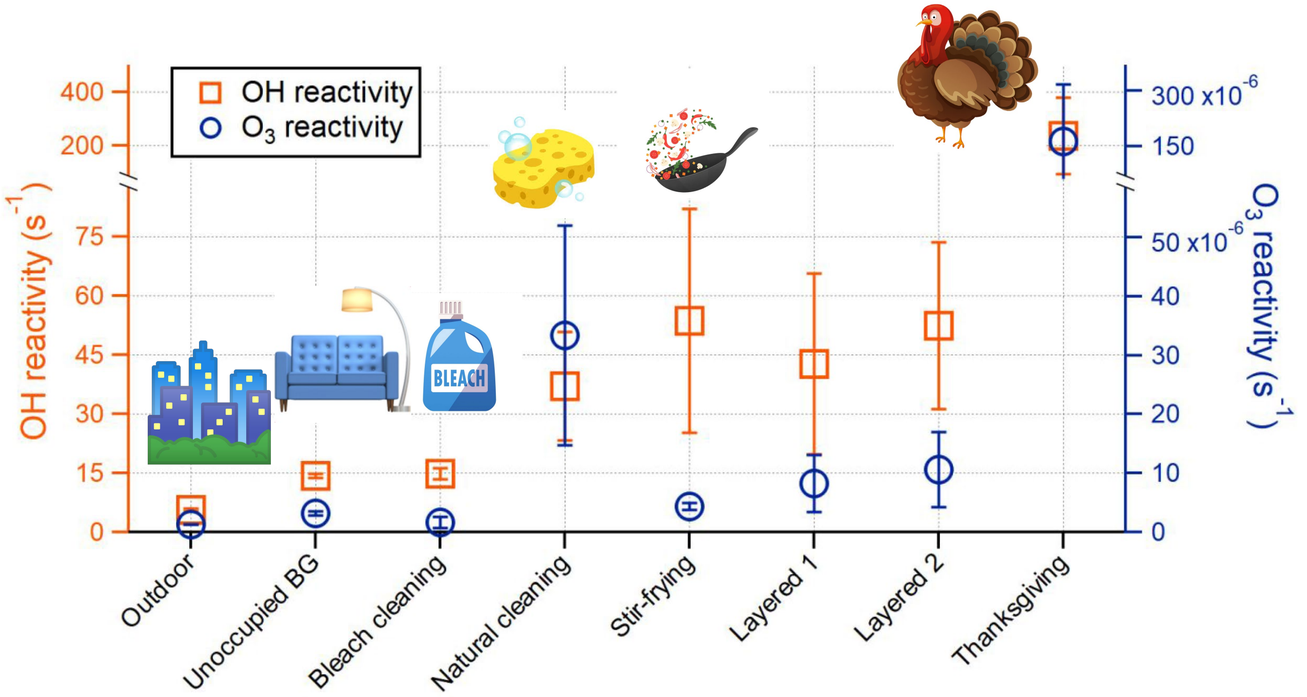


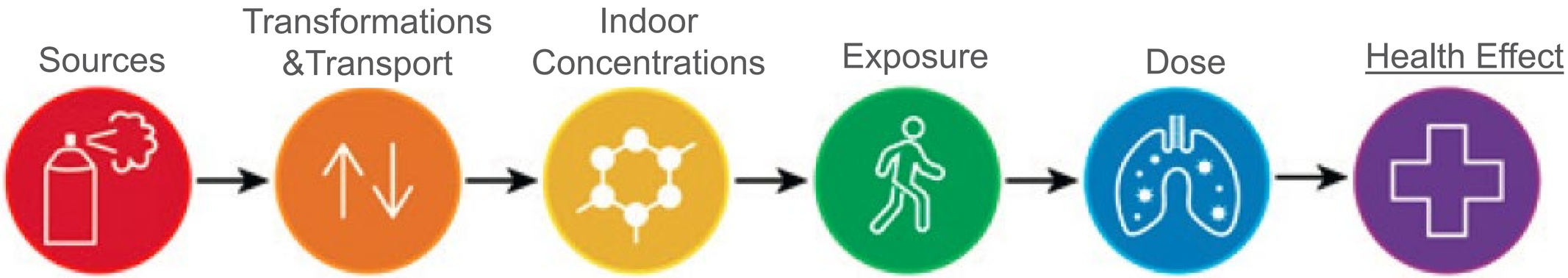


Liu et al. PNAS. 2021]

S&T. 2020]

The built environment contains a lot of reactive potential, which is fuel for oxidants, light, and multiphase reactions.

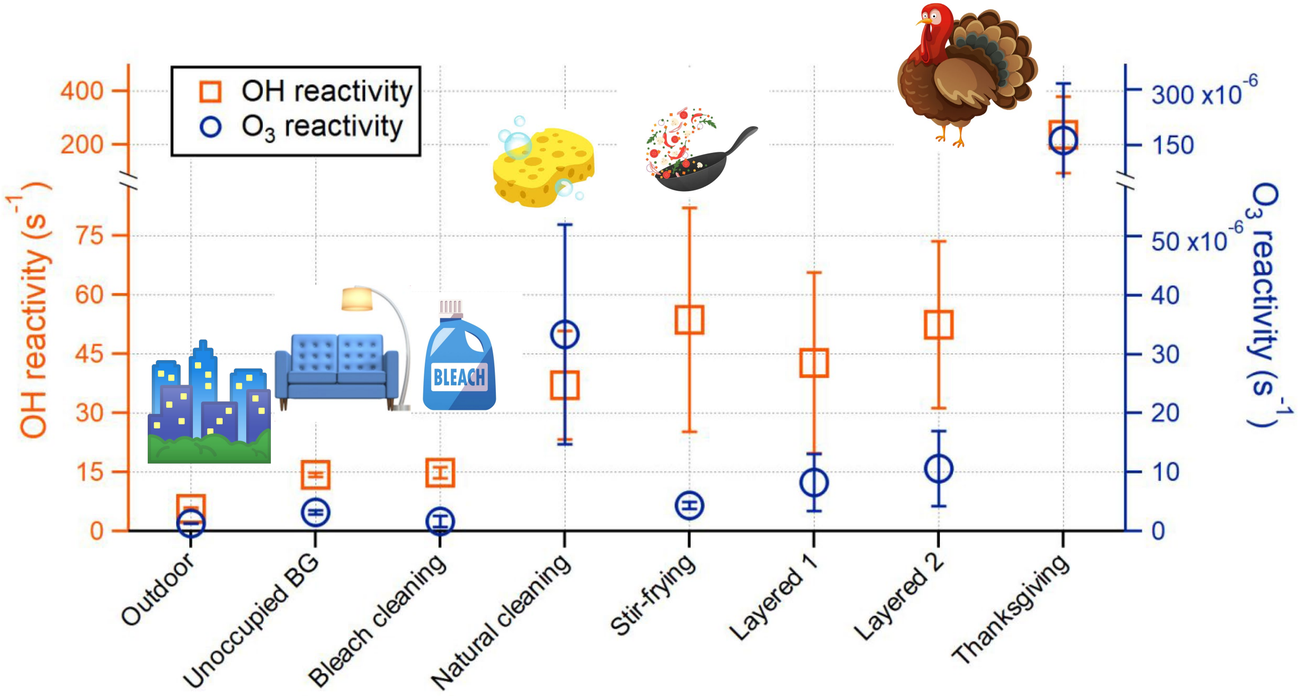


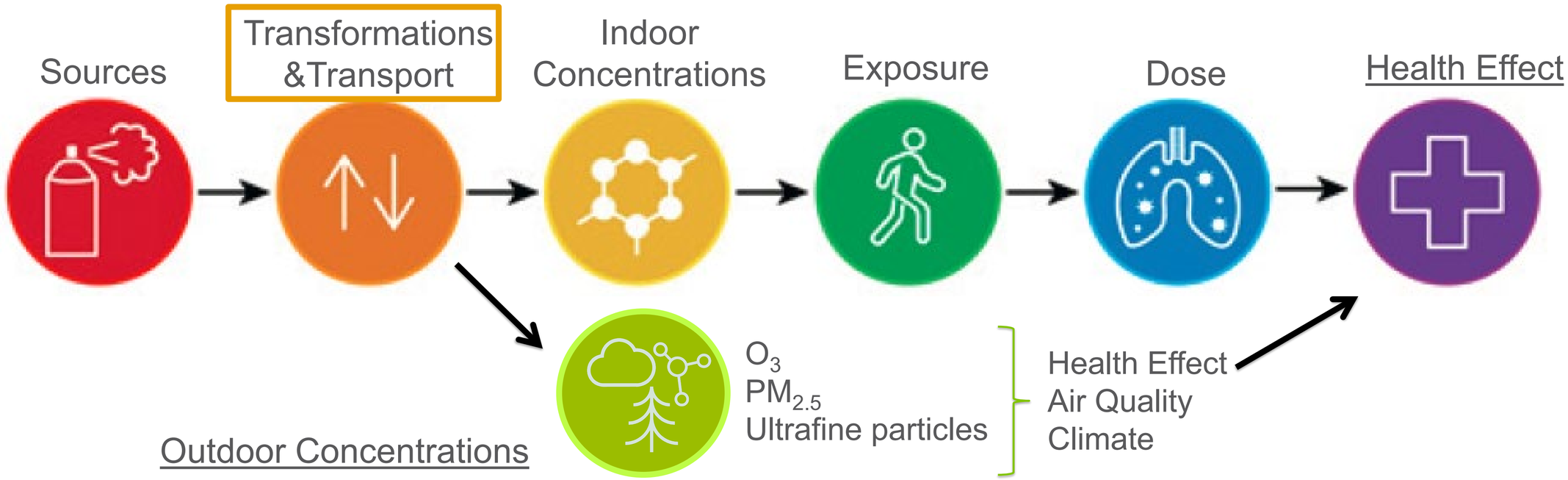


"Indoor chemistry matters". National Academy of Sciences, Engineering and Medicine. Consensus report. 2022

The built environment contains a lot of reactive potential, which is fuel for oxidants, light, and multiphase reactions.

These reactions can impact exposure and health, outdoor air quality, and potentially short-lived climate forcers (O_3, aerosols).

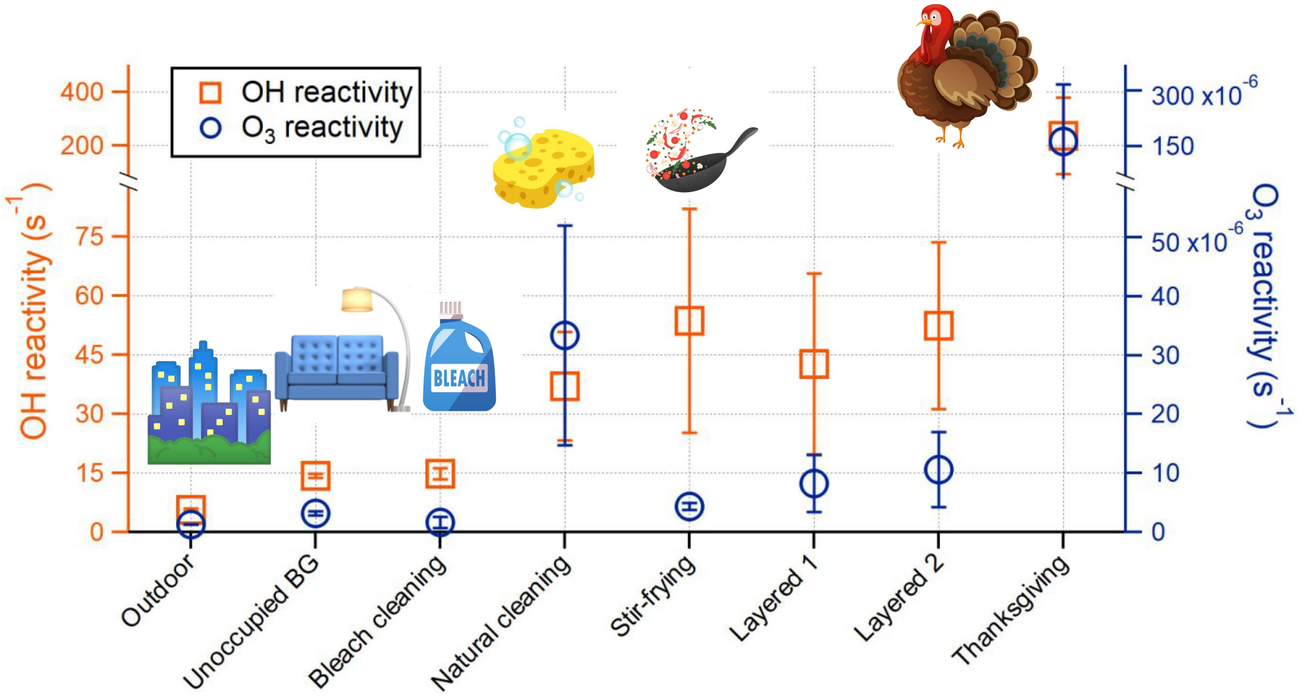


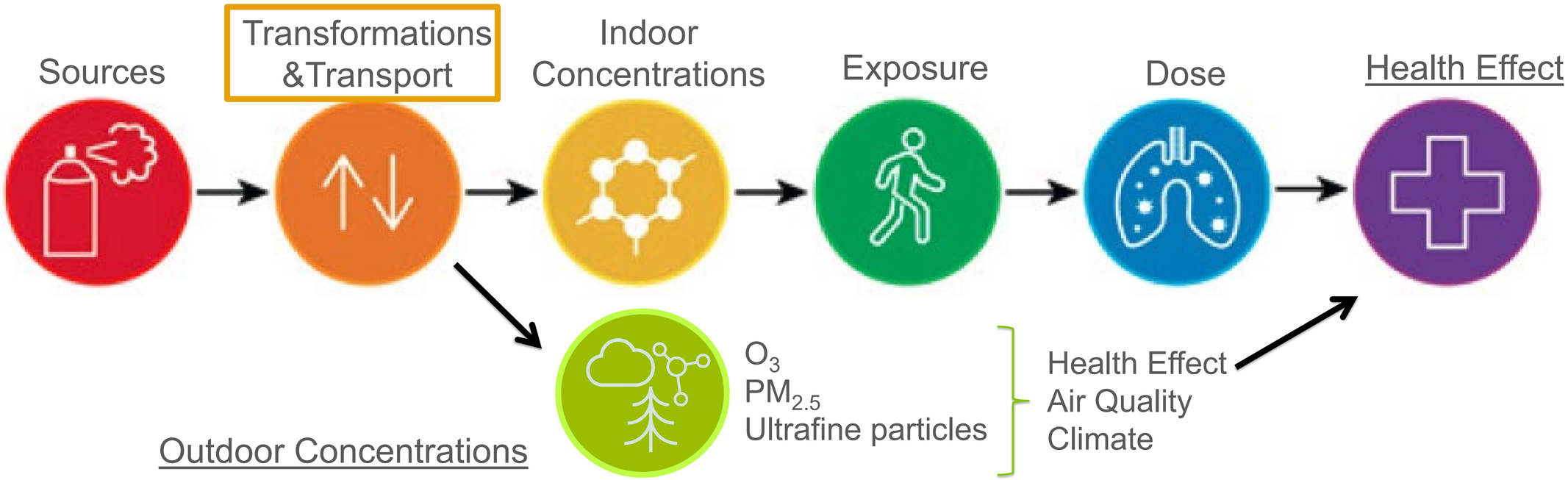


The built environment contains a lot of reactive potential, which is fuel for oxidants, light, and multiphase reactions.

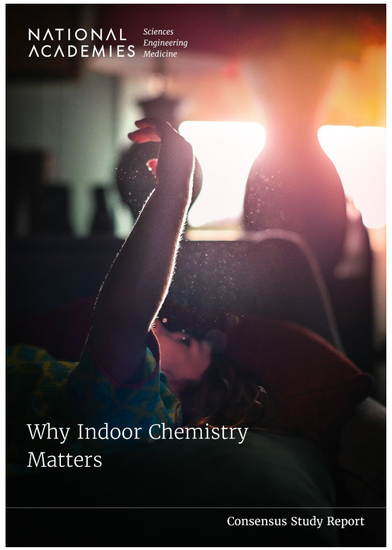
These reactions can impact exposure and health, outdoor air quality, and potentially short-lived climate forcers (O_3, aerosols).

Adding any new reactive component indoors should be done cautiously.





The NASEM report included recommendations for researchers and funders to engage across disciplines to further [our understanding] of complex indoor chemistry and its impact[s]



Three priorities include:

9. developing novel methods … to identify and quantify…wide classes of indoor chemicals, [including] secondary chemical reaction products

5. understanding indoor exposures to contaminants, including those..that undergo subsequent transformations indoors.

Sources → Transformations &Transport → Indoor Concentrations → Exposure → Dose → Health Effect

6. …identifying indoor transformations that impact outdoor air quality.

Outdoor Concentrations

O_3
$PM_{2.5}$
Ultrafine particles

Health Effect
Air Quality
Climate