

Recent research on the health effects of indoor chemistry

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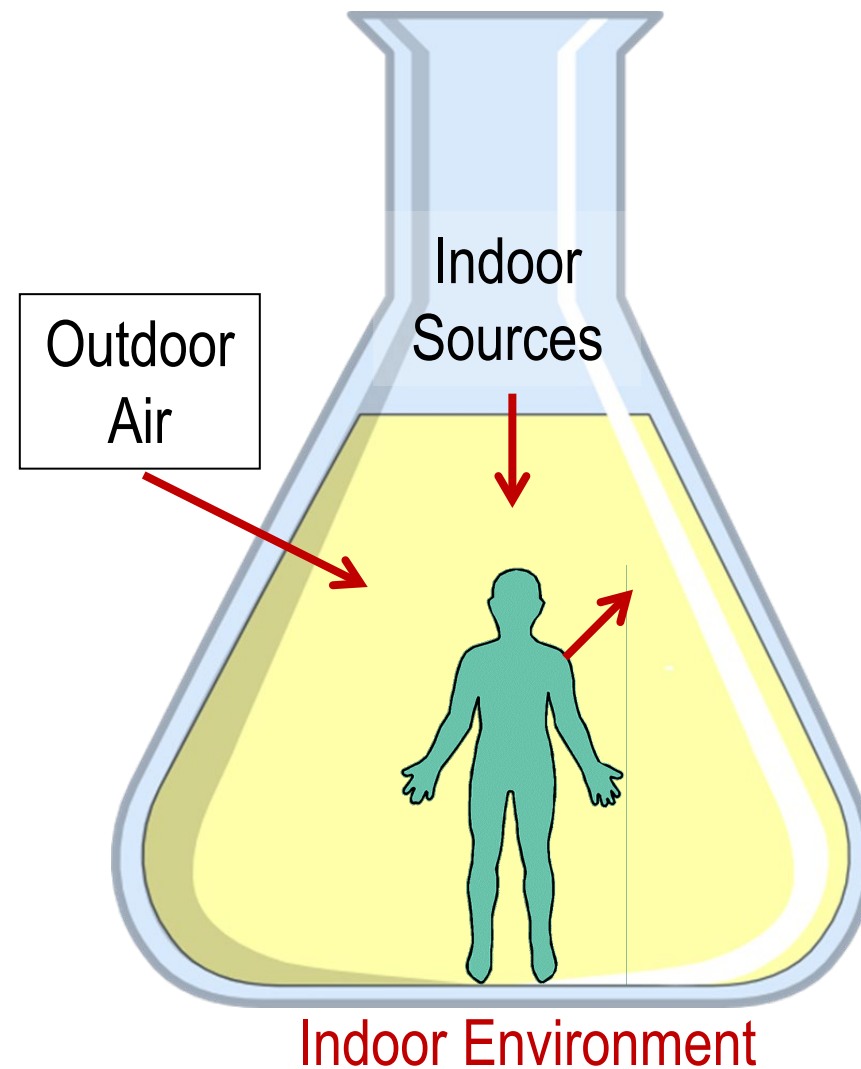
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What is indoor chemistry?

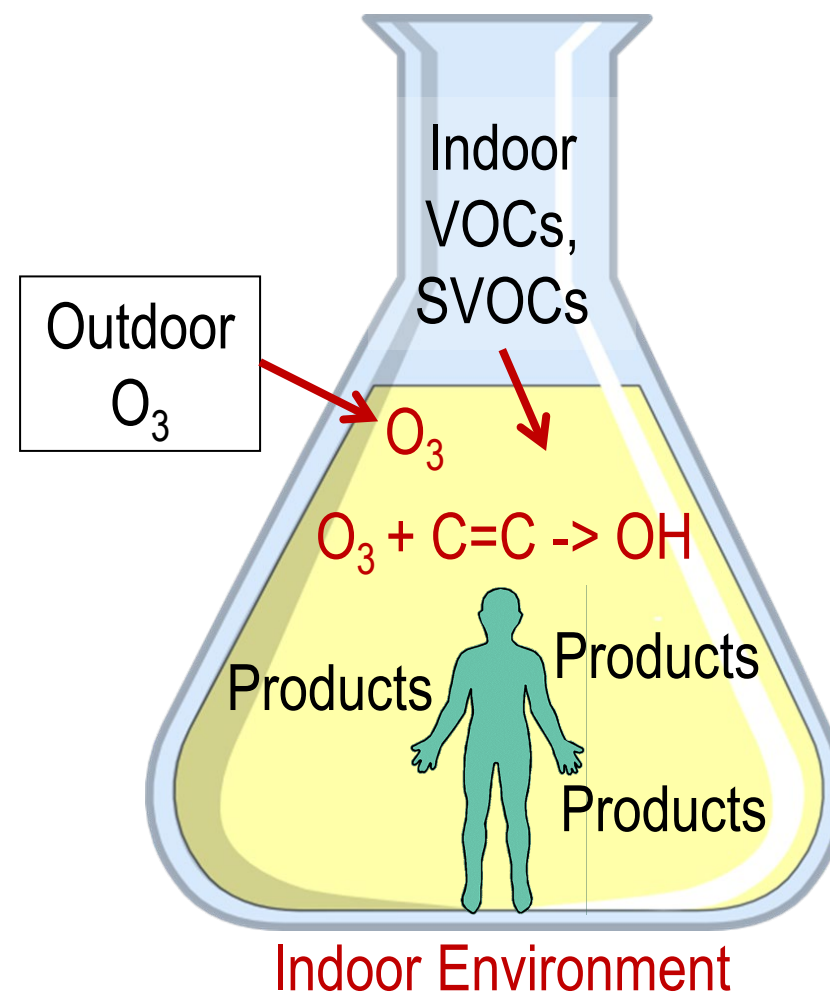
Indoor chemistry:

Chemical transformations that occur in indoor air (both gas- and particle-phase) and on indoor surfaces, as well as the associated transport and partitioning phenomena.



Focus of this presentation: oxidation reactions

- Given our limited time, we will focus on one type of indoor chemistry: **oxidation reactions**
- Ozone (O_3) tends to be the driver of indoor oxidation, supported by the hydroxyl radical (OH)
- Other oxidants (e.g., the nitrate radical, chlorine containing species, hydrogen peroxide) have impacts that are more episodic

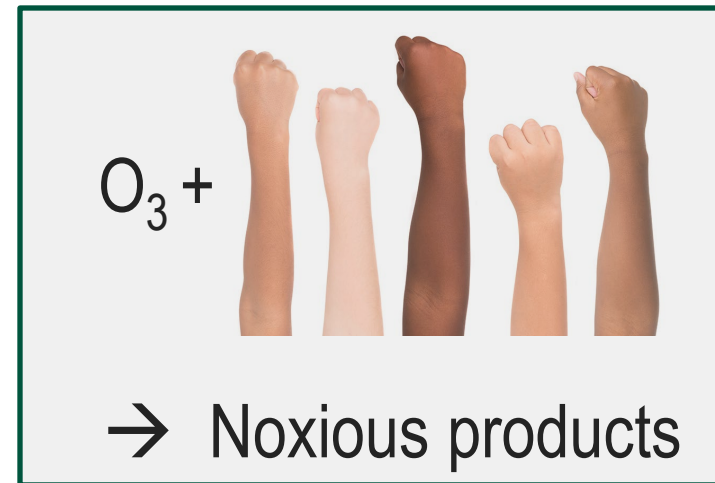
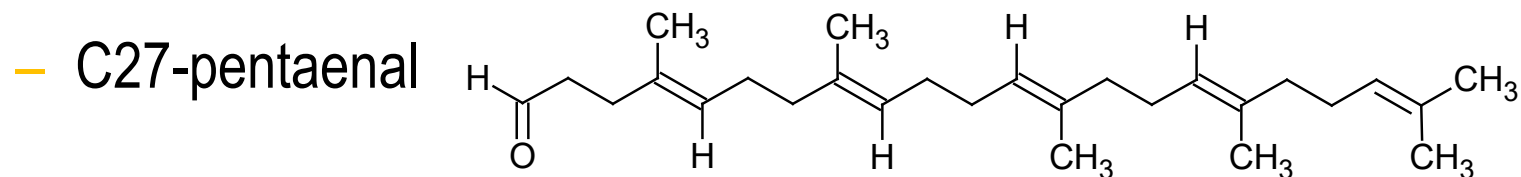
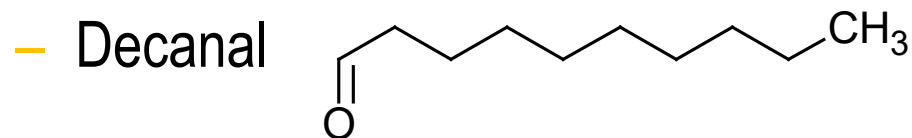
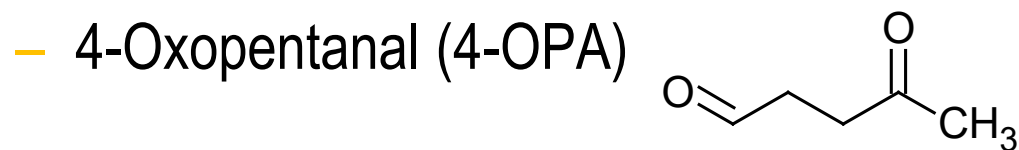


Why do we care?

- The net concentration of organic compounds in indoor air is roughly an order of magnitude larger than in outdoor air
- More than 90% of the organic compounds in indoor air have been emitted indoors
- Organic compounds of indoor origin tend to have low oxygen-to-carbon ratios (O/C)
- Indoor air contains oxidants (e.g., O_3 and $OH\cdot$)
- Oxidation increases the O/C ratio of the compounds that have been emitted indoors
- This increases their water solubility, decreases their volatility, and increases the time they spend in the lungs
- Crudely speaking, oxidation of indoor VOCs tends to increase the adverse health effects associated with the indoor VOC mix

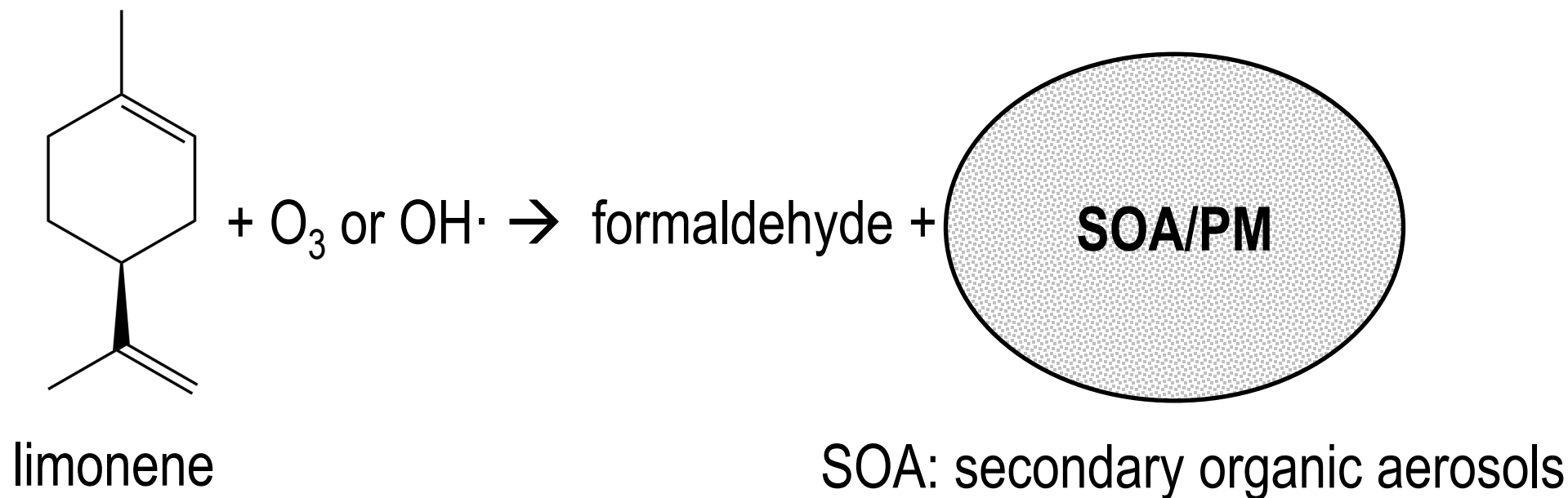
Why do we care? (surface chemistry example)

Beneficial chemicals in human skin oil can react with O_3 to produce a mix of noxious oxidation products:



Why do we care? (gas phase chemistry example)

Limonene (pleasant scent) can react with O_3 or $\text{OH}\cdot$ to produce formaldehyde and secondary organic aerosols (both unhealthy)



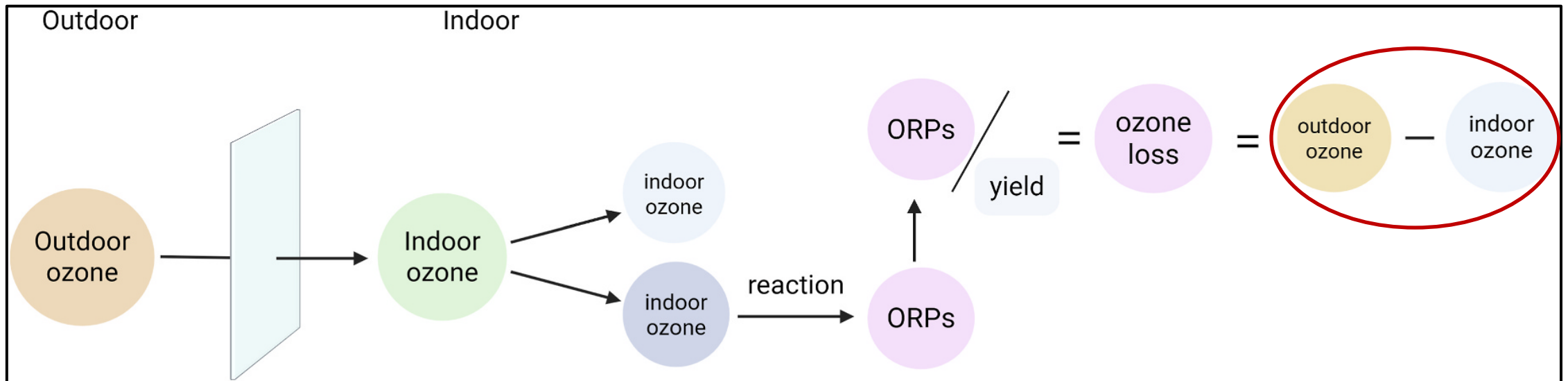
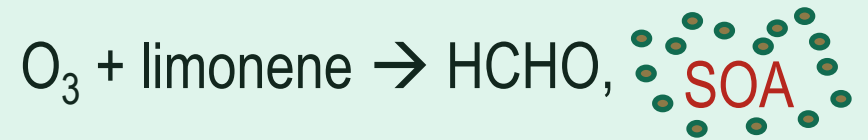
Ozone reaction products (ORPs)

A fraction of the O_3 transported indoors reacts with organics:

On surfaces



In the air



What are some oxidation products of concern?

- Stable species
 - Saturated & unsaturated aldehydes, ketones, and dicarbonyls
 - Hydrogen peroxide, organic peroxides including organic hydroperoxides (e.g., α -hydroxyhydroperoxides) and secondary ozonides (thermally stable, but react quickly with water)
 - Organic nitrates and peroxyacyl nitrate-type species (PAN)
 - Nitrosamines
 - Secondary organic aerosols (SOA)
- Short-lived, highly reactive species
 - Stabilized Criegee intermediates (carbonyl oxides)
 - Hydroxyl radicals ($\text{OH}\cdot$), hydroperoxy radicals ($\text{HO}_2\cdot$), alkylperoxy radicals ($\text{RO}_2\cdot$), nitrate radicals ($\text{NO}_3\cdot$)/dinitrogen pentoxide (N_2O_5)

Exploratory analysis: influence of ORPs on health biomarkers?

Aim: to examine the independent health biomarker effects of personal exposure to **ozone** compared to personal exposure to **ozone reaction products (ORPs)**

- Define **O₃ loss** as $([O_3]_{\text{outdoor}} - [O_3]_{\text{indoor}})$
- **[ORPs]_{indoor}** proportional to **O₃ loss**
- Use **O₃ loss** to assess exposure to **ORPs**

This analysis uses data from the two previously published studies:

- 1) 89 healthy adults living at a factory campus in Changsha
- 2) 43 children with asthma living in residences in Shanghai

Adverse effects of exposure to O₃ or ORPs – Adults' study

Biomarker	O ₃	ORPs
EBC NN: lung inflammation		adverse
EBC MDA: lung oxidative stress		
FeNO: lung inflammation		adverse
Urinary 8-OHdG: oxidative stress		adverse
20-HETE: vasoconstriction		adverse
P-selectin: risk for thrombosis	adverse	adverse
VWF: blood clotting	adverse	
Diastolic BP		adverse
Systolic BP		adverse
AI: arterial stiffness		
PWV: arterial stiffness		

He ... Zhang, Am J Res Crit Care Medicine, 207, 1243, 2023

Conclusions – Healthy Adults' study

- **Exposure to ORPs** was associated (adversely) with **7** biomarkers of deep lung and cardiovascular effects, after controlling for exposure to ozone and $\text{PM}_{2.5}$
- **Exposure to O_3** was associated (adversely) with **2** biomarkers of cardiovascular effects, after controlling for exposure to ORPs and $\text{PM}_{2.5}$



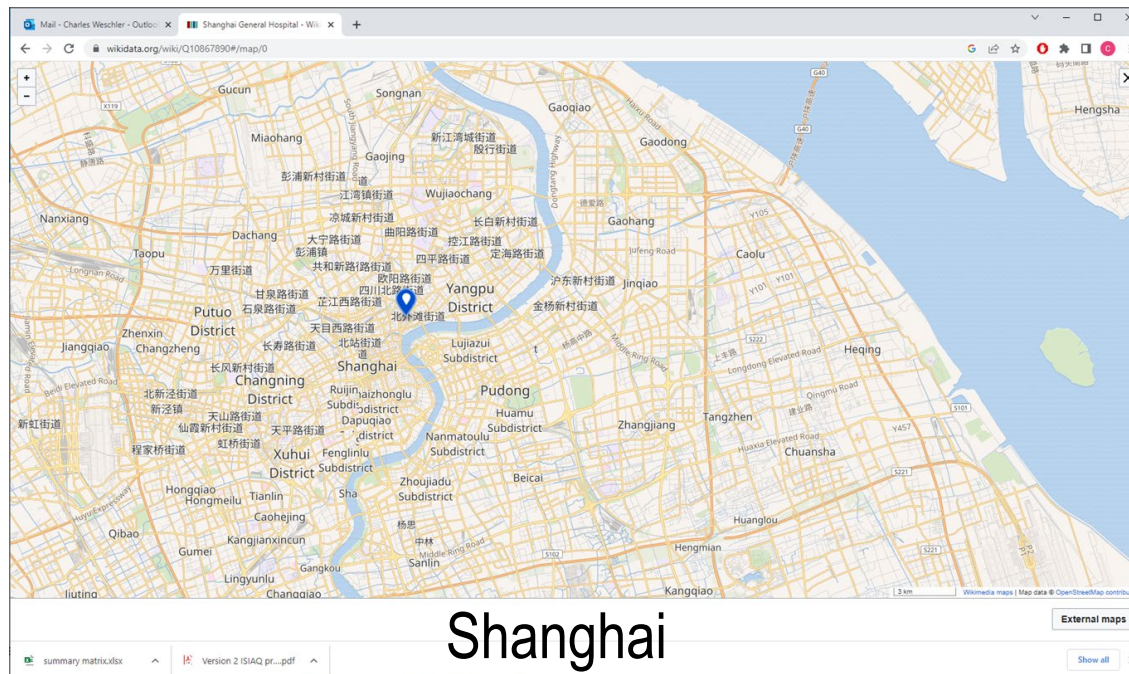
89 healthy adults,
(22–52 yr old)
Broad Town Campus,
Changsha

Adverse effects of exposure to O₃ or ORPs – Children's study

Biomarker	O ₃	ORPs
Nasal MDA: upper respiratory tract oxidative stress	adverse	
FeNO: airway inflammation		adverse
Z ₅ : airway impedance		adverse
X ₅ : airway reactance		adverse
Fres: airway reactance		adverse
FEV ₁ /FVC: airflow obstruction risk		adverse

Conclusions – Asthmatic Children's study

- **Exposure to ORPs** was associated (adversely) with **5** biomarkers of deep lung and cardiovascular effects, after controlling for exposure to ozone and $PM_{2.5}$
- **Exposure to O_3** was associated (adversely) with **1** biomarker of upper airway oxidative stress, after controlling for exposure to ORPs and $PM_{2.5}$

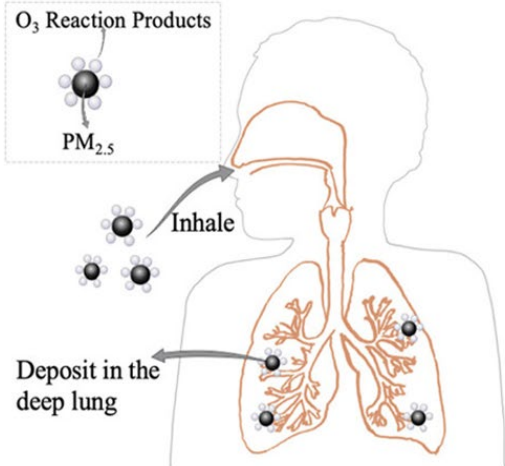


43 children with asthma
(5–13 yr old)
Homes in the vicinity of
Shanghai General Hospital

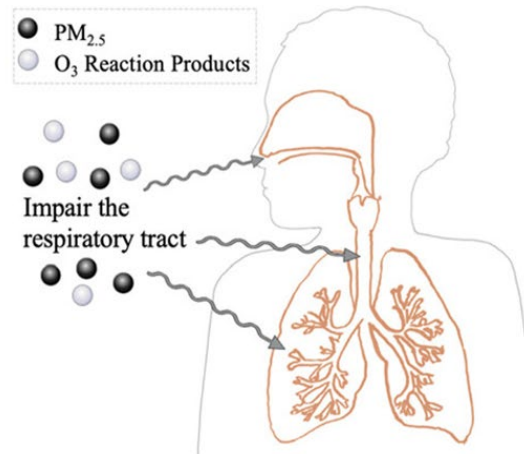
Recent papers supporting the preliminary findings of He et al. 2023

He ... Zhang, Synergistic effects of ORP and $PM_{2.5}$ on Respiratory Pathophysiology in Children with Asthma, *Environ Sci & Technol Air*, 1, 908, 2024

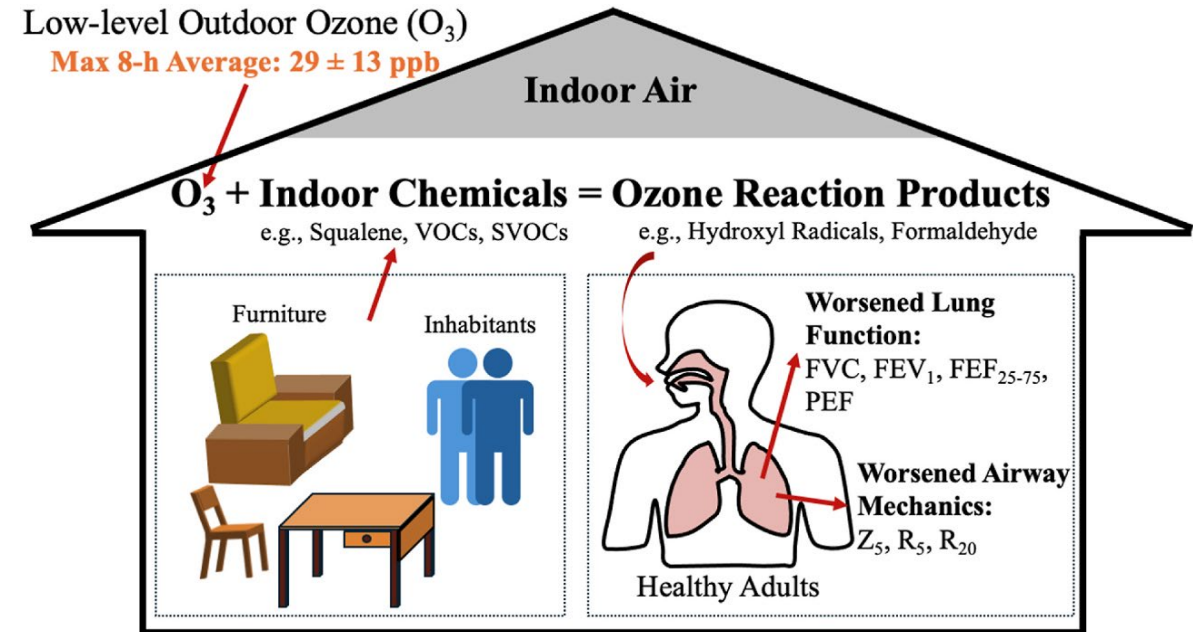
Mechanism 1: O_3 reaction products are carried by $PM_{2.5}$ to reach and deposit in the deep lung.



Mechanism 2: $PM_{2.5}$ predisposes the respiratory tract to be more susceptible to O_3 reaction products and vice versa.



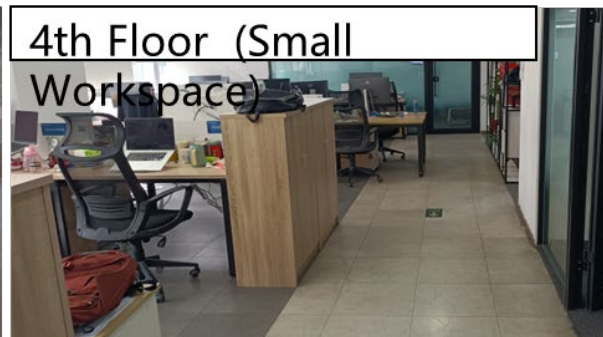
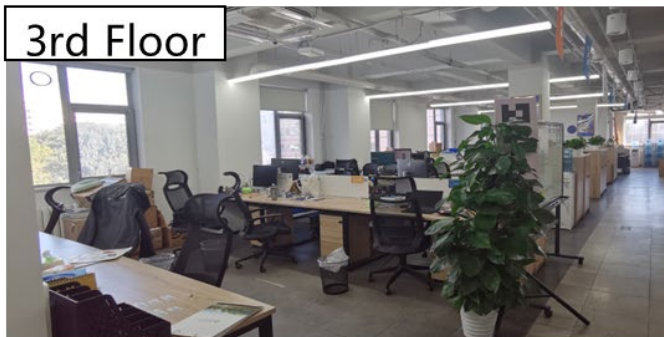
Synergistic effects of O_3 reaction products and $PM_{2.5}$ on respiratory health



He ... Zhang, Indoor ozone reaction products: Contributors to the respiratory health effects associated with low-level outdoor ozone, *Atmos Environ*, 340, 120920, 2025

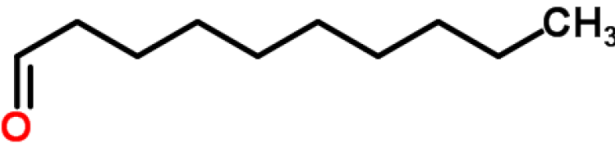
Ozone reaction products and negative emotions

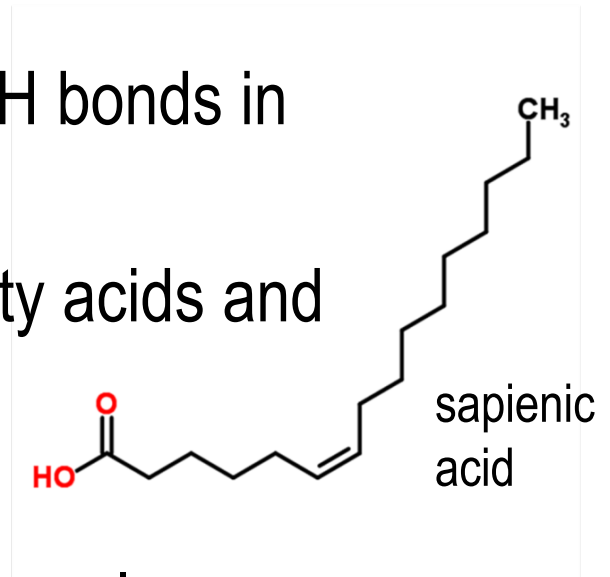
- Ozone reaction products associated with negative emotions among office workers during repeated evaluations (surveys and biomarkers) over 21 workdays in September and October of 2022



- Continuous monitoring of VOCs by PTR-MS; outdoor & indoor ozone by UV instruments
- 141 participants: 2 times/day completed survey to evaluate emotional state
- 52 participants: repeated collection of relevant biomarkers

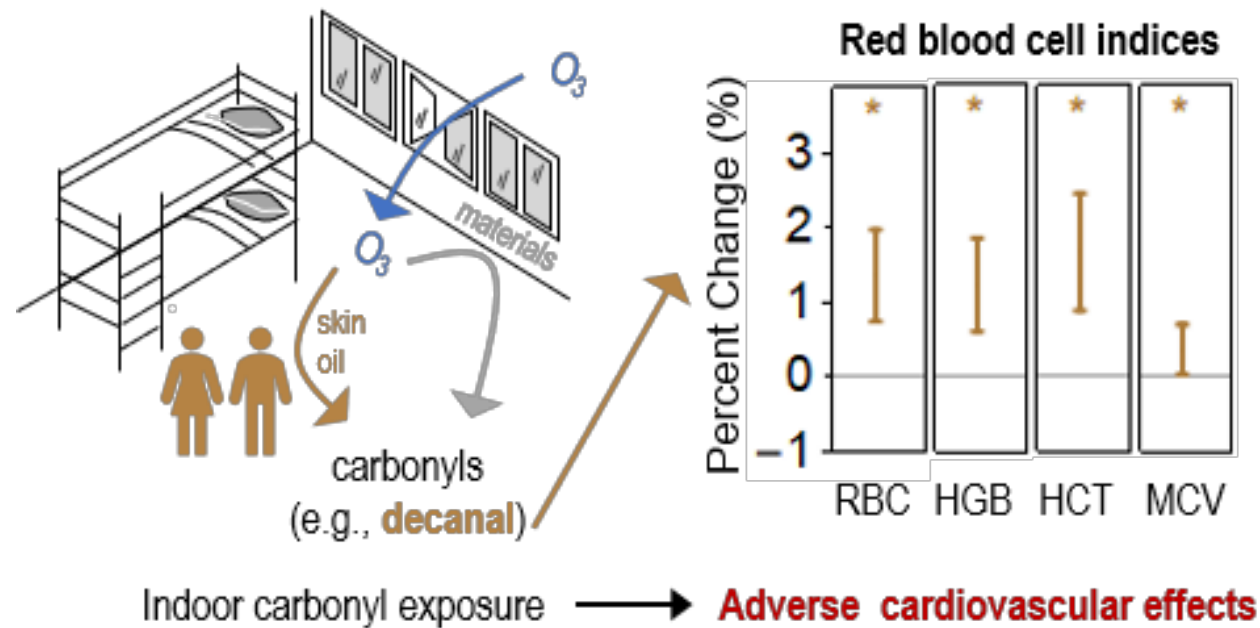
Decanal is indicative of O₃/skin oil chemistry

- Decanal: 
- Decanal is a major product when O₃ reacts with CH=CH bonds in ω -10 acyl groups (i.e., CH₃(CH₂)₈CH=CH-)
- About 1/3 of the double bonds in skin oil come from fatty acids and triglycerides with ω -10 acyl groups
- Very few other compounds found indoors contain ω -10 acyl groups
- Decanal does not itself react with ozone
- Decanal well-suited for estimating the *ozone reaction products* derived from O₃/skin oil chemistry



Decanal and cardiovascular biomarkers

- Indoor exposure to aldehydes, especially decanal, associated with changes in cardiovascular biomarkers among healthy young adults in Tibet

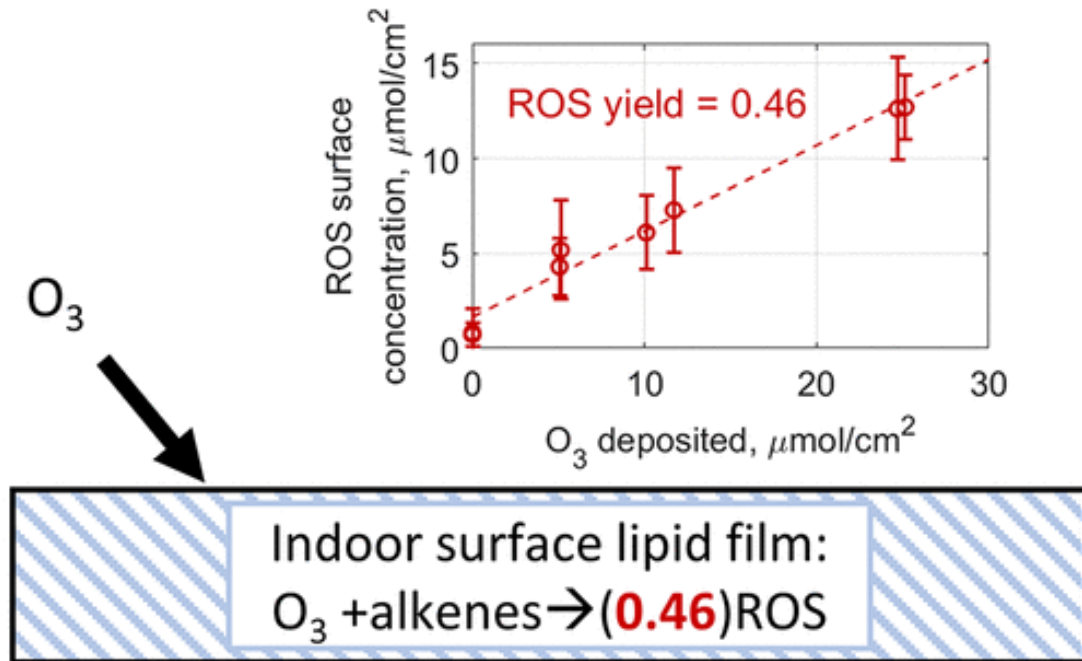


Ruohong Qiao... Yingjun Liu, Indoor exposure to ozone-derived carbonyls: association with indicators of blood and cardiovascular physiology among healthy young adults, submitted, 2025

Production of reactive organic species (ROS)

ROS: hydrogen peroxide (HOOH), organic peroxides (ROOH, R_1OOR_2), and short-lived oxygen containing radicals ($RO_2\cdot$, $(R_1R_2)C\cdot O_2\cdot$)

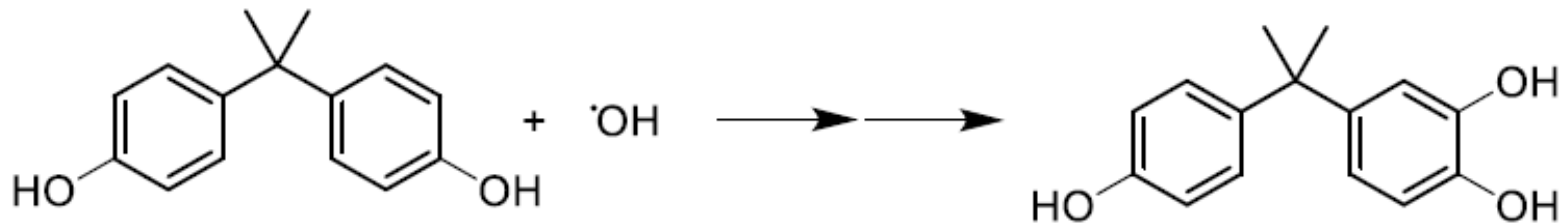
- O_3 reacts with surface lipids (mix similar to skin oil) to produce ROS with $\sim 45\%$ yield
- ROS persist on surfaces for at least a few hours
- ROS predicted to partition from surfaces to inhalable airborne PM
- Less volatile, more hydrophobic ROS (e.g., organic hydroperoxides) can remain on inhaled PM into the alveolar region



Morrison et al., *Environ Sci: Processes Impacts*, 24, 2310, 2022;
Morrison et al., *Environ Sci & Technol Letters*, 10, 528, 2023

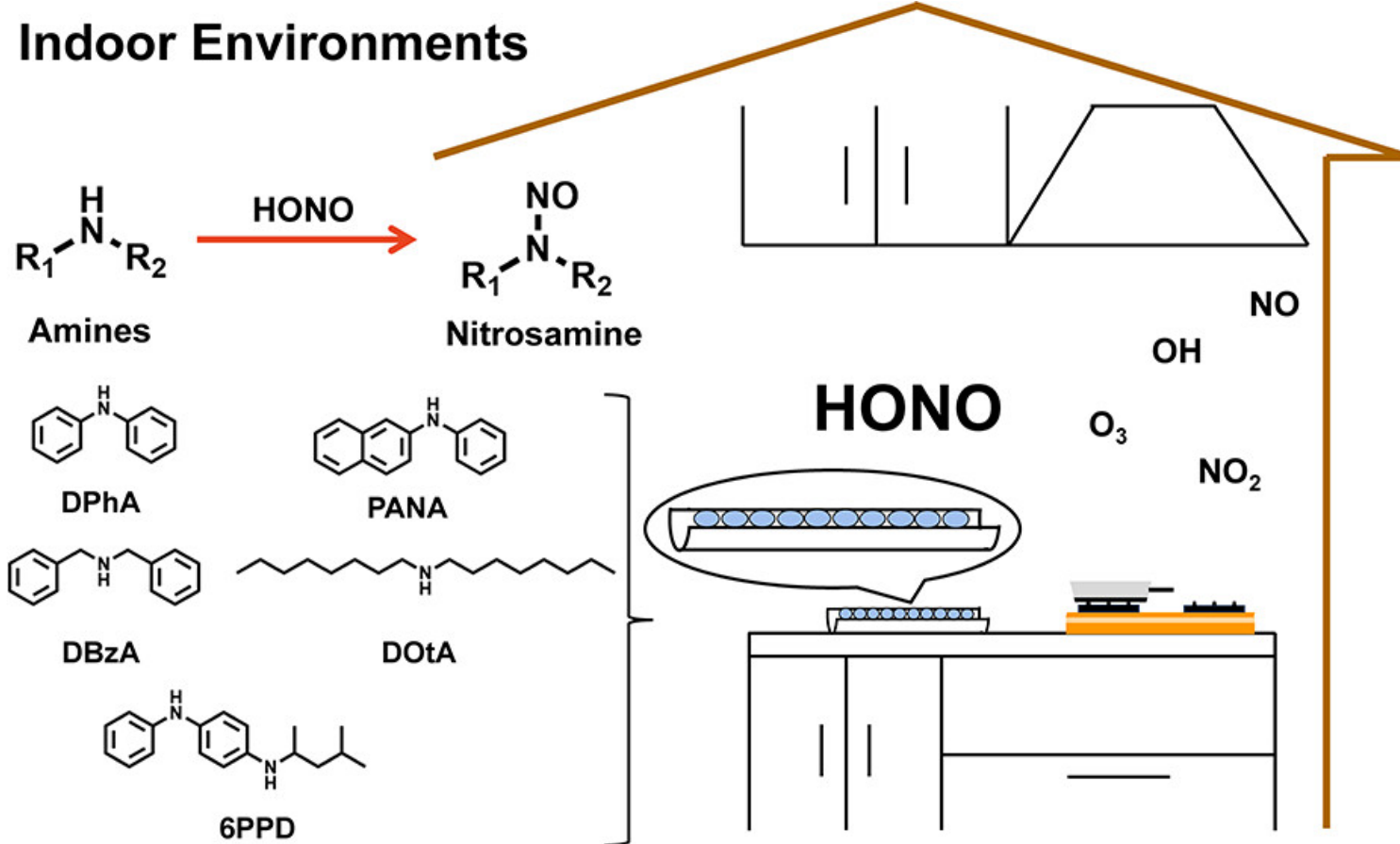
Autoxidation of unsaturated lipid films on indoor surfaces

- Flow reactor, elevated $[\text{OH}\cdot]$: fast autoxidation of methyl linoleate films \rightarrow *organic hydroperoxides* (ROOH)
- In dark desk drawer (~ 15 ppb O_3): ROOH formation occurs at similar rate
- Autoxidation is sustained by ROS-promoted internal radical propagation and displays minimal sensitivity to the rate of radical initiation
- Process enhances oxidation of BPA added to such lipid films

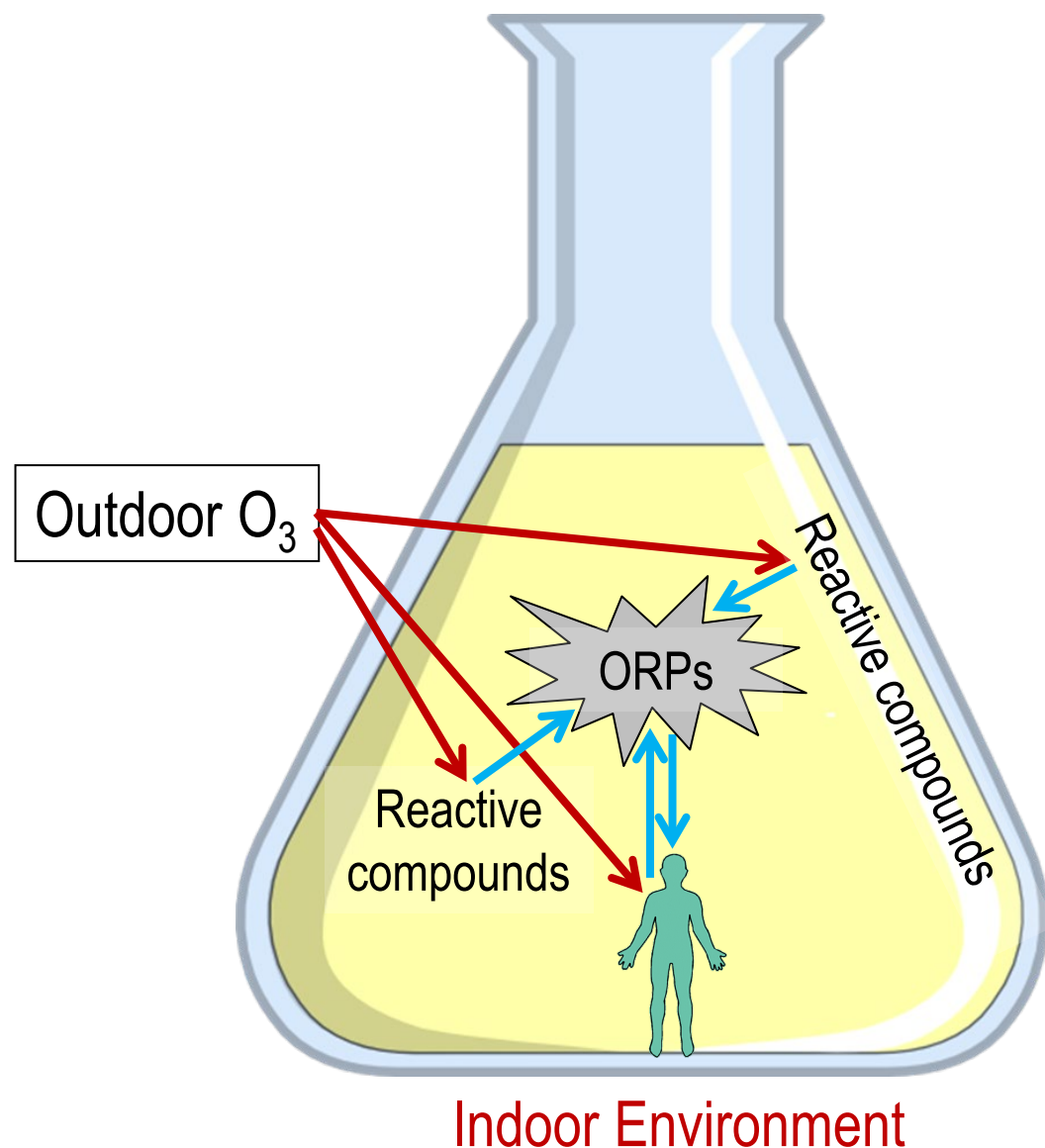


HONO + organic amines indoors → nitrosamines

- In lab experiments, HONO reacts with five different amines commonly found indoors → nitrosamines
- In a genuine indoor environment, room air exposure of 6PPD → nitroso-6PPDs and nitro-6PPDs



Summary: health effects of indoor chemistry



- “Why Indoor Chemistry Matters”
National Academies Press, 2022
- Since then, multiple studies suggest adverse health effects resulting from indoor chemistry
- More definitive studies are needed:
 - Toxicology studies
 - Chamber studies
 - Panel studies

Acknowledgements

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