Overview of Emerging Research and Discoveries

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NASEM Information Gathering Workshop
April 5, 2021

EOHSI
Environmental & Occupational Health Sciences Institute

ICIEE

TSINGHUA UNIVERSITY 1911

Indoor Chemistry is not a new topic

My “Indoor Chemistry” shelves – books back to 1978

Earliest modern history paper?

Int. J. Air Wat. Poll. Pergamon Press 1965 Vol. 9

INDOOR AIR POLLUTION IN ROTTERDAM HOMES

K. BIERSTEKER*, H. DE GRAAF† and CH. A. G. NASS†

(*First received* 9 *November* 1964 *and in final form* 30 *March* 1965)

Abstract—800 paired samples of indoor and outdoor smoke and SO_2 concentrations of 60 Rotterdam homes were studied in an effort to throw more light on the role that indoor air pollution may play in epidemiology. It was found that smoking increased the amount of smoke found in living rooms and the data suggest that newer houses tend to have less SO_2 in the living rooms than older houses. On the average living rooms contained approximately 80 per cent of the smoke and 20 per cent of the SO_2 measured simultaneously outdoors during 24 hr periods. The probability of having more SO_2 in the living room than outdoors is estimated at less than 2 per cent of the days by the authors, but the finding of constant high SO_2 in one living room in this small sample may mean, in the view of the authors, that faulty chimneys and heaters may play a bigger role in air pollution mortality during fogs than so far has been suspected.

Biersteker K, de Graaf H, Nass CAG. Indoor air pollution in Rotterdam homes. *Air Water Pollut*. 1965;9:343-350.

Tip of the hat to WW Nazaroff for this.

- *International Journal of Air and Water Pollution*, 1965
- Simultaneous indoor and outdoor samples collected from 60 homes; 800 paired samples
- Indoor “smoke” ~ 80% outdoor “smoke”
- Indoor SO_2 ~ 20% outdoor SO_2
- Newer homes had lower [SO_2]

Expatica.com

Indoor chemistry and failures in telephone switches

Relation of Airborne Nitrate to Telephone Equipment Damage

Harold W. Hermance,[1] Charles A. Russell,[2] Elmer J. Bauer, Thomas F. Egan, and Harold V. Wadlow[3]

Bell Telephone Laboratories, Inc., Holmdel, N.J. 07733

■ Airborne nitrates cause stress corrosion cracking of nickel-brass telephone parts—particularly relay wire springs in the Los Angeles area. A survey of nitrate accumulation on equipment was made in California and other locations. Nitrate deposits were transferred to paper disks and determined spectrophotometrically with chromotropic acid. Nitrate deposition correlated with relay failure and a rating was established to estimate the degree of danger to equipment. A correspondence to the general patterns of smog and air pollution existing in California was indicated. Several eastern locations are marginal and some nitrate-caused component problems have occurred, but no relay failures. Air filtration and humidity control provide protection against the nitrate-caused failures.

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type of stress cracking which is different from that caused by nitric acid vapors (Uhlig and Sansome, 1964) or ammonia (Evans, 1960). Salts of other anions under the same conditions did not cause cracking. At the nitrate concentration levels found in Los Angeles (up to about 15 $\mu g/cm^2$ of surface area) an applied positive potential was necessary. Cracking without

- *Environmental Science & Technology,* 1971
- Deposition of nitrate containing fine particles of outdoor origin correlated with relay failures in telephone switching offices
- Indoor chemistry in action

Outdoor-to-indoor transport of O_3 and other pollutants

Theoretical Model for Relating Indoor Pollutant Concentrations to Those Outside

Fredrick H. Shair[1] **and Kenneth L. Heitner**

Division of Chemistry and Chemical Engineering and Environmental Quality Laboratory, California Institute of Technology, Pasadena, Calif.

■ A general ventilation model, which relates indoor pollutant concentrations to those outside, is discussed in detail. When the time interval associated with changes in the outdoor concentration is long compared to that required either to change the air within the building or to remove the pollutant by internal means, the indoor concentration of pollutant can be related to the outdoor concentration by means of a simple expression. In the case of indoor ozone associated with buildings located in photochemically smoggy regions, there is good agreement between theory and experiment. Theoretical considerations suggest that the indoor levels of ozone in many commercial buildings located in Los Angeles could be substantially reduced rather quickly and possibly with relatively little effort.

Establishing clean in
the environment for cer
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the proper legislation and enforcement needed to improve the air quality outdoors. The work up to 1972 was reviewed by Benson et al. (1972). Wallick (1973) has stressed the importance of indoor air quality among other factors associated with the indoor environment experienced within American factories.

To provide a framework useful in understanding the dependence of indoor pollutant levels upon ventilation parameters, geometric factors, and outdoor pollutant levels,

- *Environmental Science & Technology,* 1974
- Correctly observed that O_3 reactions indoors occur largely on surfaces
- Called out the potential to remove O_3 from indoor air

Organic constituents of indoor airborne particles

Characterization of Selected Organics in Size-Fractionated Indoor Aerosols

Charles J. Weschler

Bell Telephone Laboratories, Holmdel, N.J. 07733

■ A variety of organic compounds have been identified in size-fractionated indoor aerosol samples. These include aliphatic alcohols and phosphate esters not previously identified in ambient aerosols, as well as phthalate ester plasticizers whose numbers and relative abundances appear greater than those of outdoor samples. Several of the identified organics are evidence that relatively stable chemicals used within a building are likely to accumulate in the aerosol circulating throughout that building.

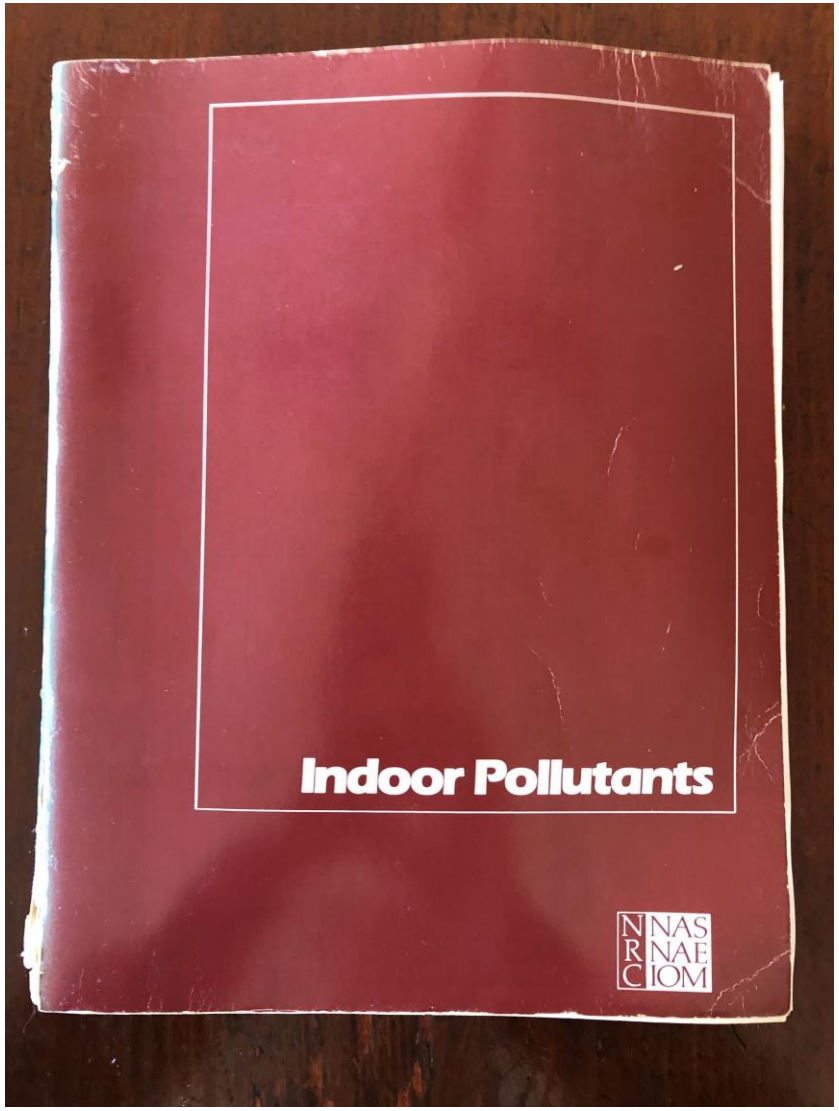
vironment. The data
certain organic comp
accumulate to signif

Experimental

Equipment. A H
graph–mass spectror
the organic mixtures
120 cm glass column
Chromosorb W-HP.
grammed to rise fron

- *Environmental Science & Technology,* 1980
- Chemicals used in a building accumulate in its airborne particles
- Organics identified in aerosols included phthalate esters, phosphate esters, & aliphatic alcohols
- $[Organics]_{indoor} > [Organics]_{outdoor}$

National Academy Committee 1980-1981



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Craig D. Hollowell
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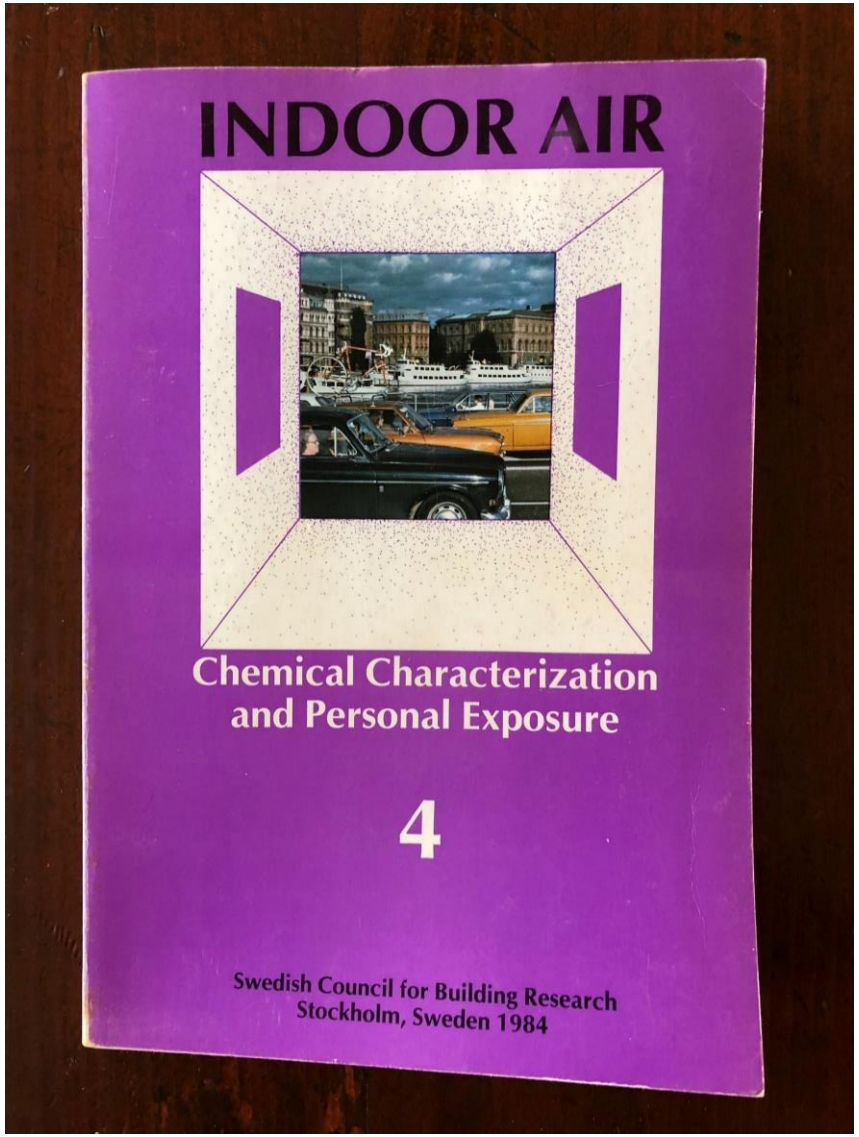
Jan A. J. Stolwijk
David L. Swift
James E. Woods

James A. Frazier – NRC Staff Officer

Indoor Air 1984, Stockholm



- *A "Woodstock" for Indoor Air*
- Organizers: Birgetta Berglund, Thomas Lindvall, & Jan Sundell
- Almost 700 participants from 31 countries
- Six volumes of conference proceedings, over 2000 pages
  - 42 papers on NO_2
  - 32 on radon
  - 29 on VOCs
  - Little on SVOCs or airborne particles

Detailed model of indoor chemistry, 1986

Mathematical Modeling of Chemically Reactive Pollutants in Indoor Air

William W. Nazaroff and Glen R. Cass*

Environmental Engineering Science, California Institute of Technology, Pasadena, California 91125

■ A general mathematical model is presented for predicting the concentrations of chemically reactive compounds in indoor air. The model accounts for the effects of ventilation, filtration, heterogeneous removal, direct emission, and photolytic and thermal chemical reactions. The model is applied to the induction of photochemically reactive pollutants into a museum gallery, and the predicted NO, NO_x–NO, and O_3 concentrations are compared to measured data. The model predicts substantial production of several species due to chemical reaction, including HNO_2, HNO_3, NO_3, and N_2O_5. Circumstances in which homogeneous chemistry may assume particular importance are identified and include buildings with glass walls, indoor combustion sources, and direct emission of olefins.

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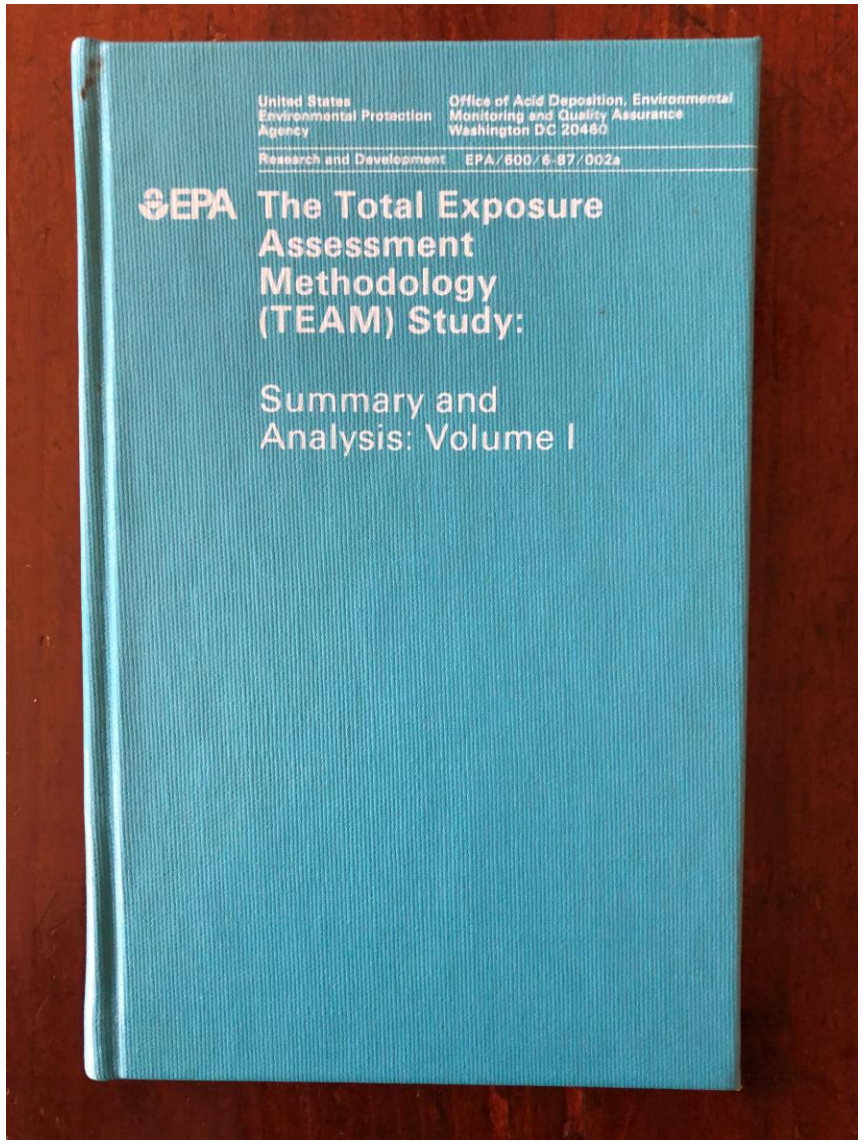
pollutants in a chen
contribution of this
explicit treatment
reactions. The mo
each species the pr
lation, chemical rea
moval rates associat
filtration, and wall loss. As a partial validation of the model, a case is simulated in which outdoor air, containing photochemically reactive air pollutants, is introduced into a museum gallery. The simulated indoor concentrations

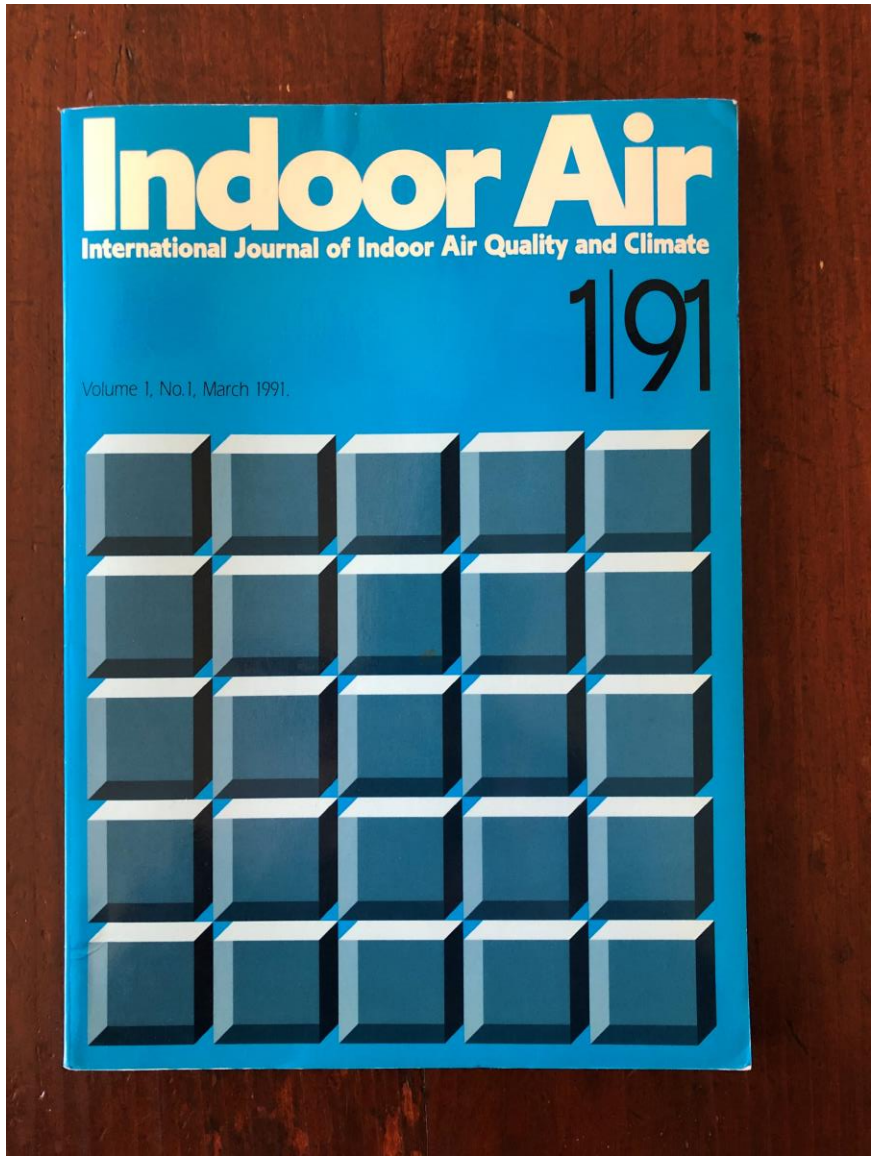
- *Environmental Science & Technology,* 1986
- Captured most of the reactions that we consider important today

U.S. EPA TEAM Study, 1979 – 1985; final report 1987



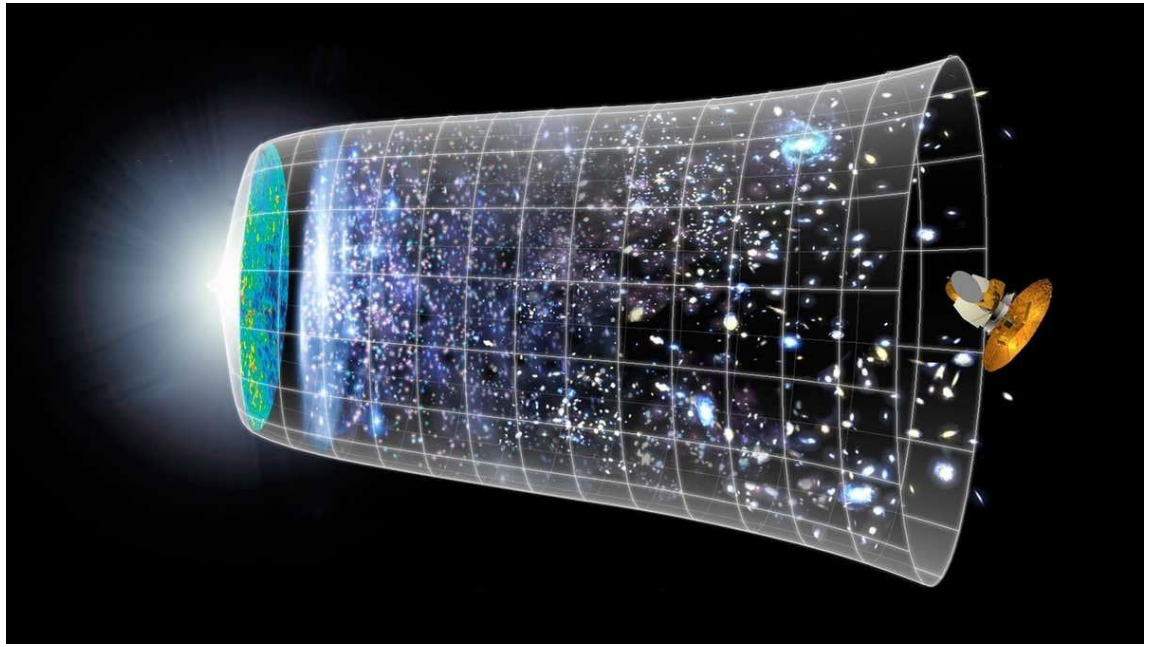
- Lance Wallace, EPA, *Project Officer*; Edo Pellizzari, RTI, *Chief chemist*
- Probability-based survey that measured personal exposures (800 people in 8 cities) to numerous toxic/carcinogenic chemicals
- Included breath analyses
- Levels of organic pollutants were elevated at home/work & tended to be much higher indoors than outdoors
- Exposures occurred mostly indoors
- Many indoor sources identified
- “Reliance on outdoor monitors to estimate exposure is contraindicated …”

First issue of *Indoor Air* published, 1991



- *David Grimsrud – Editor-in-Chief*
- Intended to cross many disciplines
- Papers in 1st issue included: “The Interaction of vapour phase organic compounds with indoor sinks”, Tichenor, Guo, Dunn, Sparks & Mason

“Indoor chemistry inflation” starting about 2015



“Cosmic Inflation”, New Scientist
https://www.newscientist.com/term/cosmic-inflation/

- 2015: first publications of research funded by Sloan Foundation’s *Chemistry of Indoor Environments* (*CIE*) program
- Paula Olsiewski – Program Manager
- *CIE* program kicked off officially in 2016
- Program has catalyzed indoor chemistry research globally

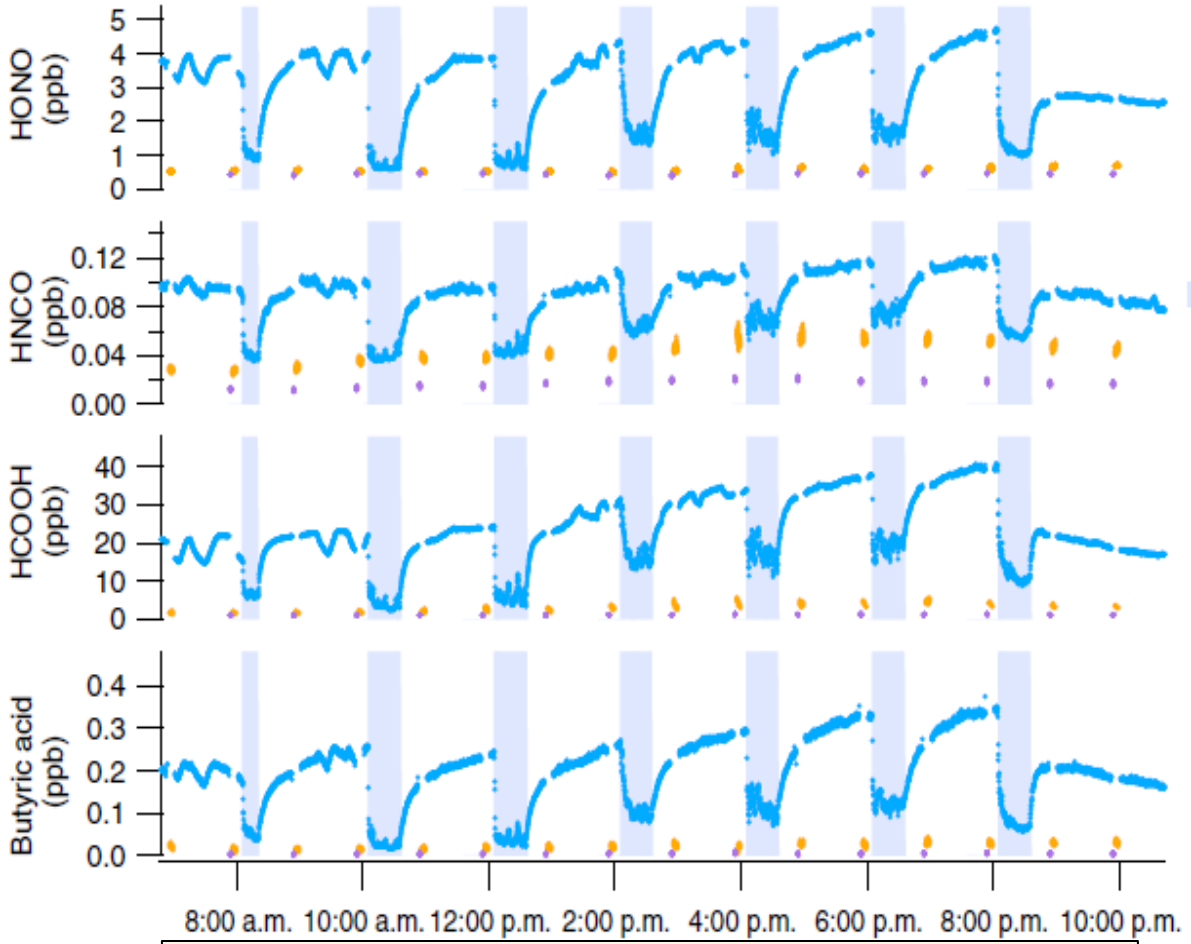
Emerging research/discoveries

Highlights from post-2015 research addressing topics of importance

Just the tip of impactful results that have been reported

theactivetimes.com

Indoor surfaces as reservoirs



Ventilation experiments demonstrate that numerous chemicals reside in surface reservoirs

- Gas/surface partitioning examined for broad suite of compounds in indoor air
- Chemicals that are “volatile” outdoors are “semivolatile” indoors, reflecting much larger surface-to-volume ratios indoors
- Air/surface partitioning is faster than air exchange

Collins et al., ES&T 2018; Kristensen et al., Indoor Air 2019; Lunderberg et al., ES&T 2019; 2020; Wang et al., Sci. Adv. 2020

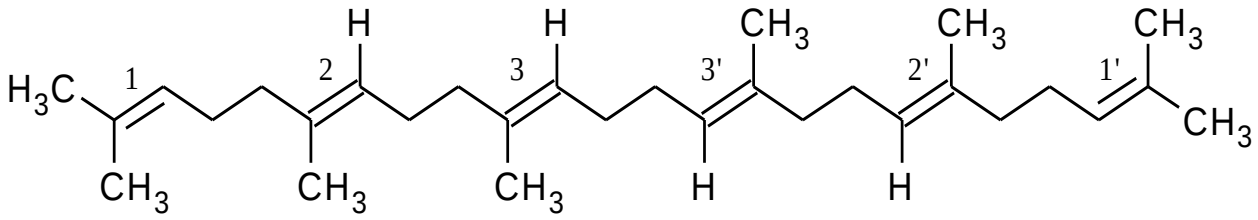
Soiling promotes commonality among indoor surfaces

- Organic film growth > 0.05 nm/day measured on vertically placed substrates over a 17 day period[a]
- Growth fueled by natural sources (skin oils) & consumer products (e.g., plasticizers)[a,b]
- Double bonds (−C=C−) measured in surface wipes from in situ vertical glass- & painted-surfaces within various types of buildings[c]
- Alkenes comprised ~ 20% of the surface film constituents[c]
- Lifetime of alkenes in films ~ 1 hour; replenished quickly – highly dynamic[c]
- Emission rates of O_3/squalene products were ~ 4 times larger from soiled surfaces than from the skin, hair & clothing of two occupants[d]

thespruce.com

[a]Lim & Abbatt, ES&T, 2020; [b]Gall & Rim, B&E 2018, [c]Deming & Ziemann, Indoor Air 2020; [d]Liu et al., PNAS, 2021

O_3/squalene chemistry: products, kinetics, branching ratios



Dominant O_3-reactive compound in human skin oil (~ 10% by Wt)

- O_3/squalene chemistry occurs on skin, soiled clothing, soiled surfaces, settled dust & airborne particles in all occupied indoor environments
- Criegee Intermediates + carbonyls → Secondary ozonides (SOZ) – long lived, if dry
- CIs + carboxylic acids → α-acyloxyalkylhydroperoxides (α-AAHP)
- CIs + H_2O → α-hydroxyhydroperoxides (α-HHP)
- α-HHP & α-AAHPs thermally stable, react with water to form carbonyls & H_2O_2
- Fraction of gas-phase products increases as water vapor concentration increases

Since 2015: *Fooshee et al., ES&T, 2015; S Zhou et al., ES&T Letters, 2016; S Zhou et al., ES&T, 2016; Jacobs et al., J Phys Chem A, 2016; Heine et al., ES&T, 2017; Arata et al., ES&T, 2019; Lakey et al., Chem Comm, 2019; Xiong et al., ES&T, 2019; S Zhou et al., ES&T Letters, 2019; J Zeng et al., ES&T, 2020; Morrison et al., 2021; M Zhang et al., ES&T, 2021; Z Zhou & Abbatt, ES&T Letters, 2021*

Painted surfaces

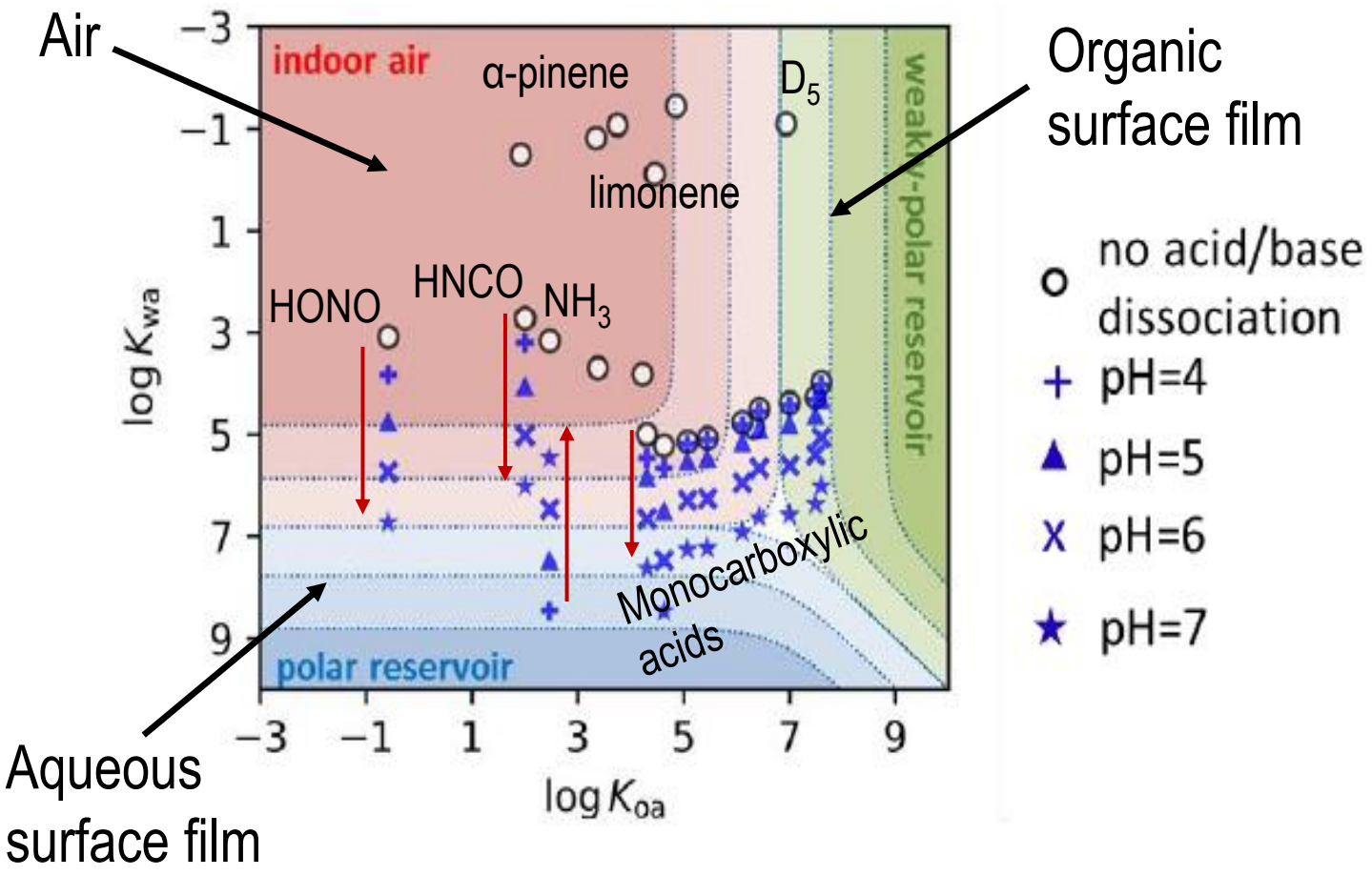
- Painted surfaces account for 60% to 70% of exposed surfaces in residences[a]
- *Paint*/*Air* partition coefficients for C_3- to C_7-carboxylic acids: 4×10^5 to 40×10^5 — close to the corresponding K_{oa} for these acids[b]
- Diffusion coefficient of C_3- to C_7-carboxylic acids in paint films correlate with vapor pressure[b]
- Large fraction of these acids penetrate paint film, implying that uptake by underlying substrate is common[b]
- Surface wipes of vertical painted vs. glass surfaces not that different[c]
- At 50% RH, typical paint layer contains H_2O equal to ~ 1 µm thick film[d]

"Painted Surfaces"
Berit Morgensen Lopez

[a]*Manuja et al., Environ Sci Proc & Impt 2019;* [b]*Algrim et al., Indoor Air 2020;* [c]*Deming and Ziemann, Indoor Air 2020;* [d]*Nazaroff and Weschler, Indoor Air 2020.*

Acid/base chemistry: impact on partitioning to surface films

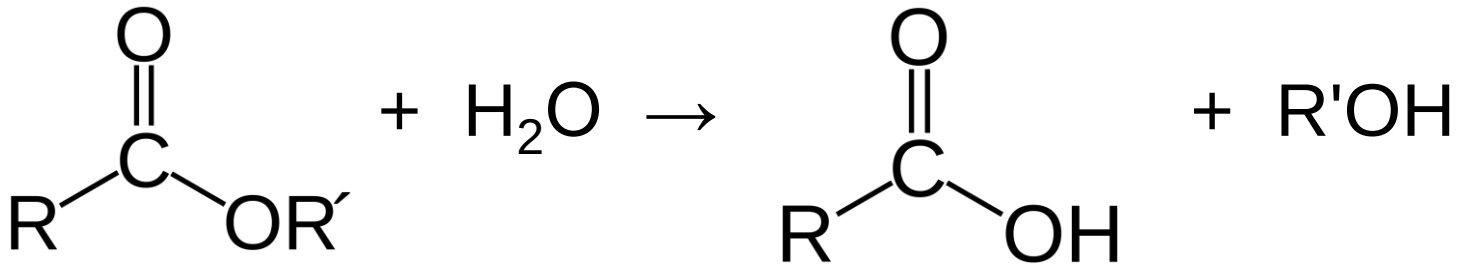
- Mass of acids & bases sorbed to indoor surfaces/bulk water >> mass in air (CO_2 is exception)
- pH strongly affects fraction of acidic & basic species in air vs. sorbed to surfaces
- pH also impacts aerosols
- Hence, pH of aqueous surface films & aerosols impacts what occupants inhale



Wang et al., Sci. Adv. 2020; Nazaroff & Weschler, Indoor Air 2020

Hydrolysis

- Esters are ubiquitous indoors – phthalates, adipates, sebacates, organophosphates – used as plasticizers, flame retardants, pesticides … and esters hydrolyze

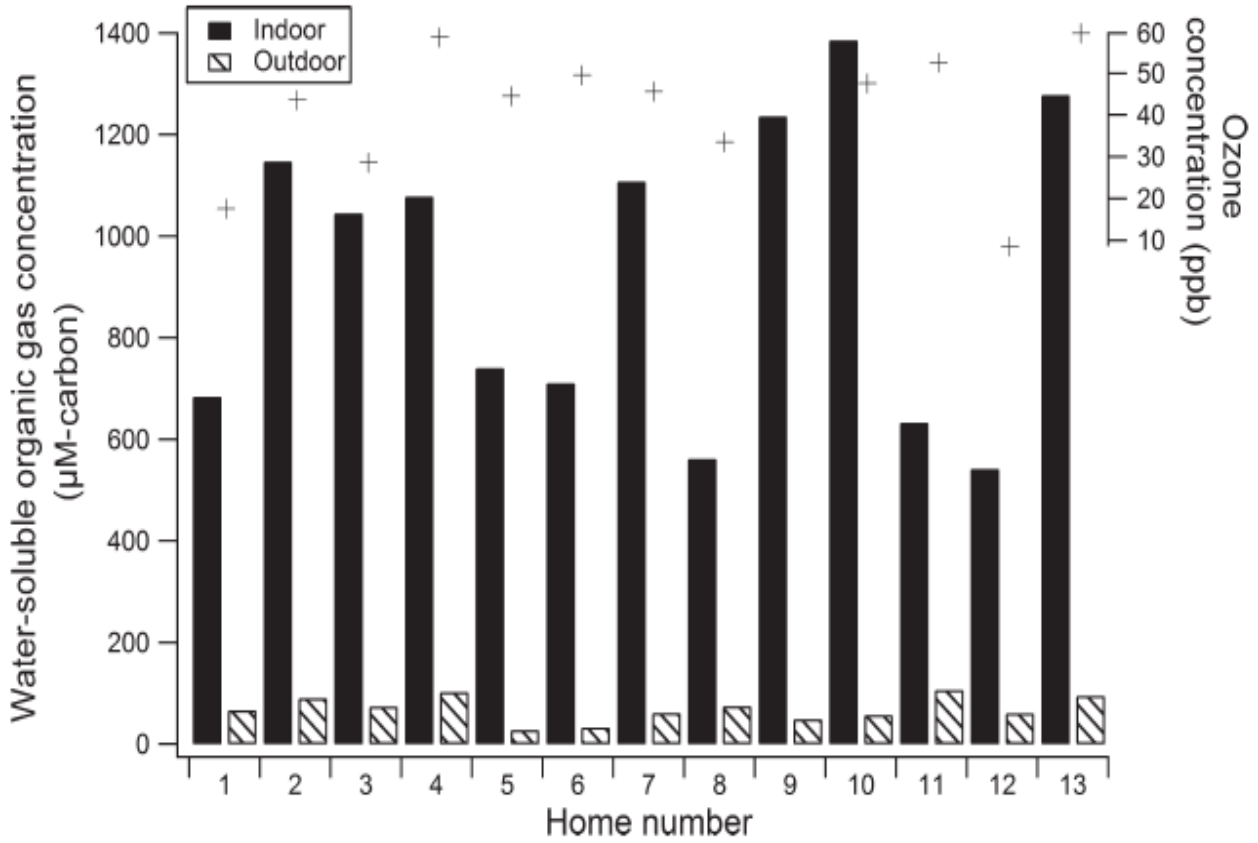


Ester Water Carboxylic acid Alcohol

- Hydrolysis products can be more toxic than precursors
- Hydrolysis reactions tend to be slow, but there is time for such chemistry on indoor surfaces and settled dust
- Kinetics & products of hydrolysis reactions anticipated to occur indoors are being measured[a]

[a]*Prof. F. McNeill group (Columbia Univ), in preparation*

Water soluble organic gases (WSOG)



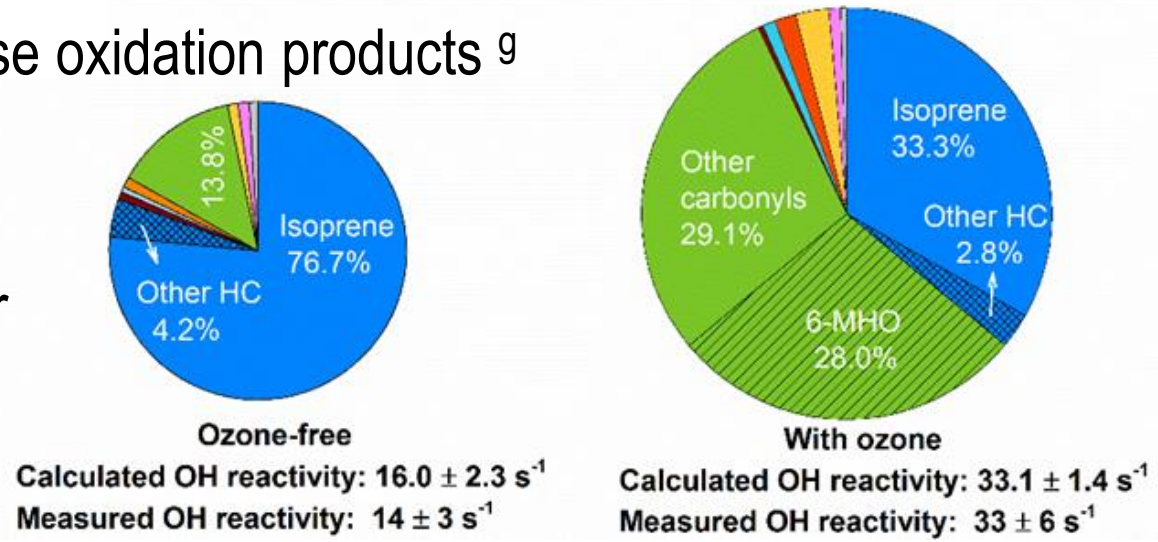
Duncan et al., Indoor Air 2017

- Net [WSOG] ~ 15 times higher indoors than outdoors at 13 NJ & NC homes [a]
- Acetic, lactic, & formic acid ~ 40% of total WSOGs in these homes [a]
- [Gas-phase carboxylic acids] ~ 7X higher indoors than outdoors in a CO classroom [b]
- Acetic acid, formic acid & methanol ~ 75% of organic emissions in a CA home … ?wood decomposition? [c]
- WSOG sources: materials/furnishings, O_3 chemistry, human emissions

[a]*Duncan et al., Indoor Air 2017; ES&T 2019; Environ Sci Proc Imp 2019;* [b]*S Liu et al., ES&T, 2017;* [c]*Y. Liu et al., Indoor Air, 2019*

Impact of chemicals emitted by humans (breath & skin)

- CO_2 (breath), NH_3 (breath & skin), acetic & formic acid (O_3/skin oil chemistry) affect pH of indoor aqueous surface films and bulk water [a]
- Humans are large sources of NH_3; emission rate very sensitive to temperature [b,c]
- Skin oils and skin flakes contribute to soiling of indoor surfaces [d,e,f]
- Skin surface + O_3 → gas- and condensed phase oxidation products [g]
- Emissions contribute to indoor *Total OH Reactivity* & influence OH concentration [b,h]
- Ozone/skin oil chemistry generates nanocluster aerosols that may contribute to SOA formation indoors [i,j]

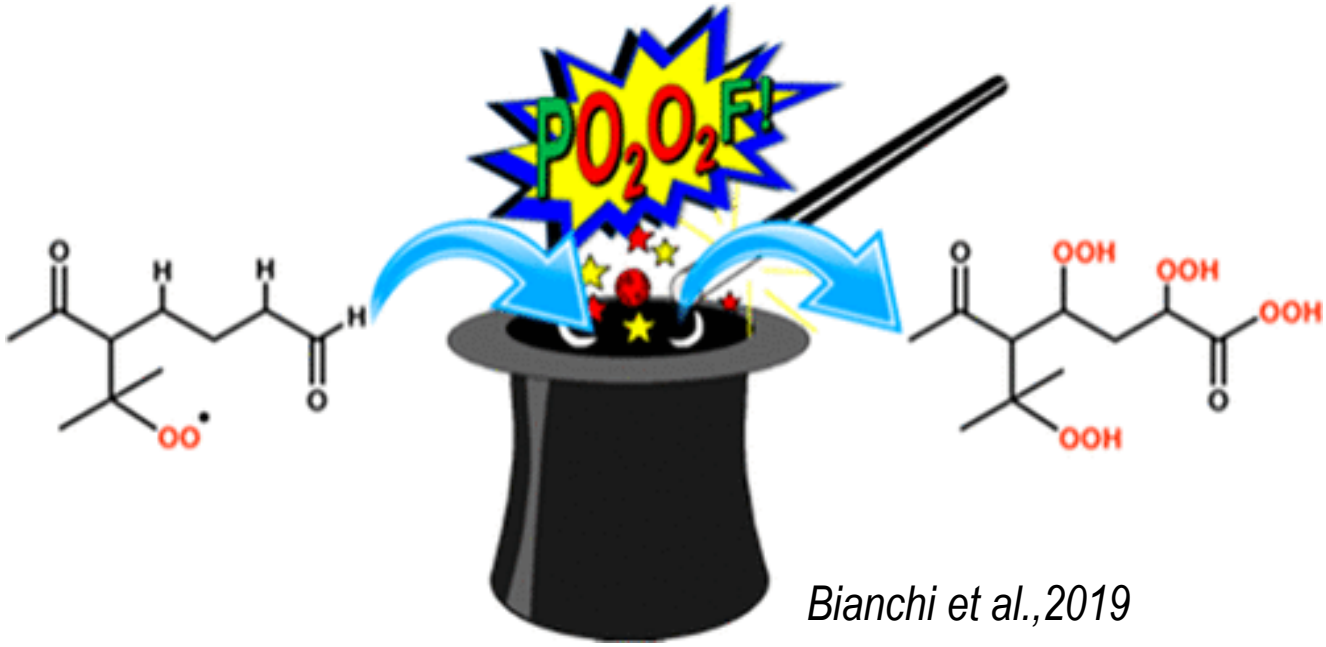


Total OH Reactivity

[a]Nazaroff & Weschler, Indoor Air 2020; [b]Beko et al., Indoor Air 2020; [c]Li et al., ES&T 2020; [d]Lim & Abbatt, ES&T, 2020; [e]Gall & Rim, B&E 2018; [f]Liu et al., PNAS, 2021; [g]Morrison et al., ES&T 2021; [h]N Wang et al., ES&T 2021; [i]Avery et al., Environ Sci Proc Imp 2019; [j]S Yang et al., submitted 2021

Autoxidation

- Oxidation reactions typically proceed through alkylperoxy radicals (RO_2•)
- Indoors, when [NO] is low, lifetime of RO_2• can be long enough for isomerization (H-shifts)
- This H-shift is called “autoxidation” & produces products with large O/C [a]
- Autoxidation of limonene observed in university art museum [b]
- Criegee intermediates drive autoxidation in unsaturated lipids such as squalene [c]
- Autoxidation indoors being studied by P Wennberg & H Kjærgaard [d,e]



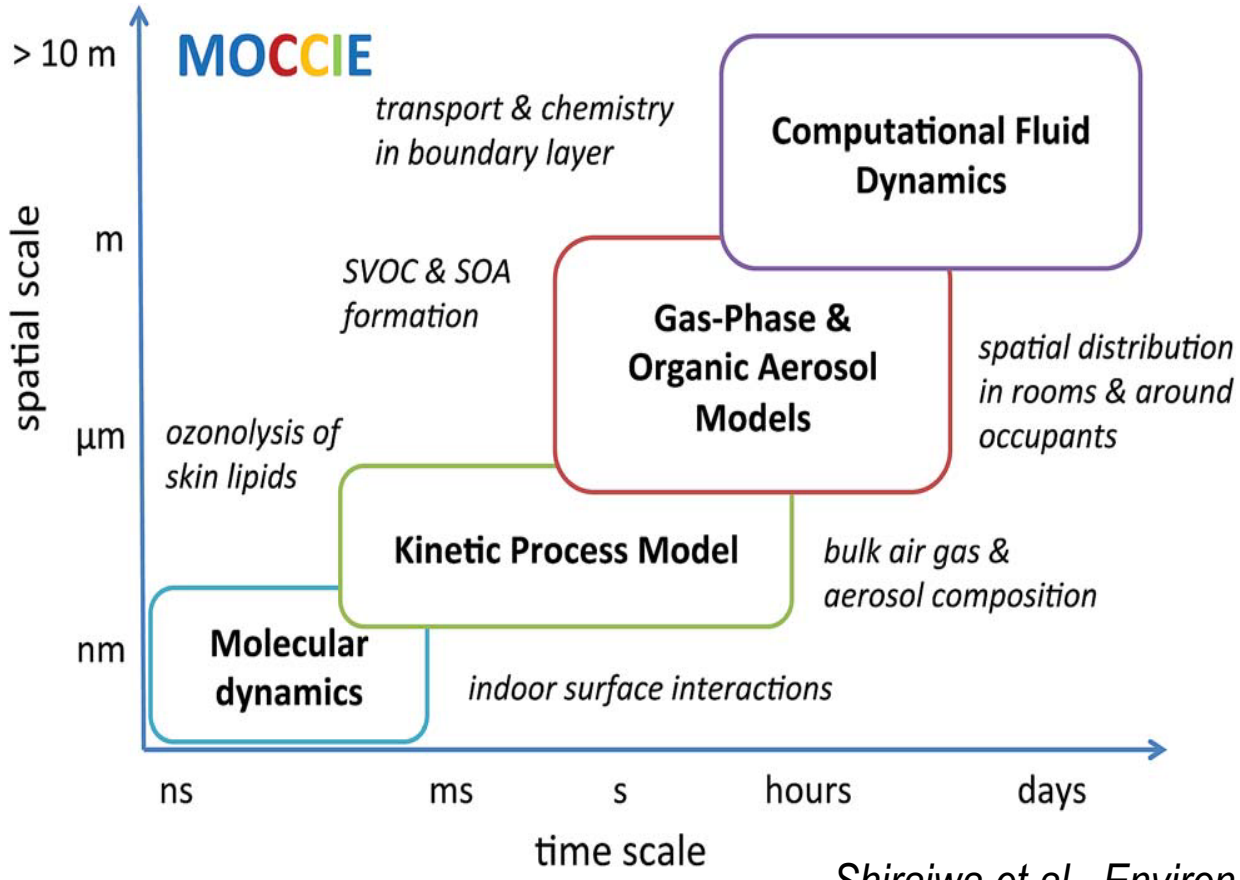
Bianchi et al.,2019

[a]*Bianchi et al., Chem Rev 2019;* [b]*Pagonis et al., ES&T Letters 2019;* [c]*M. Zeng et al., PNAS 2020;* [d]*Møller et al., J Phys Chem A 2020;* [e]*C Jing et al., J Phys Chem Letters 2020*

Modeling

- Modeling integrates emerging discoveries & contributes to the generalization of the specific
- MOCCIE (modelling consortium for chemistry of indoor environs)
- SURF-CIE (Surface consortium for chemistry of indoor environs) includes a modeling component
- Collaboration has been strong -- links formed between modelers and experimentalists

Models connected over range of spatial & temporal scales



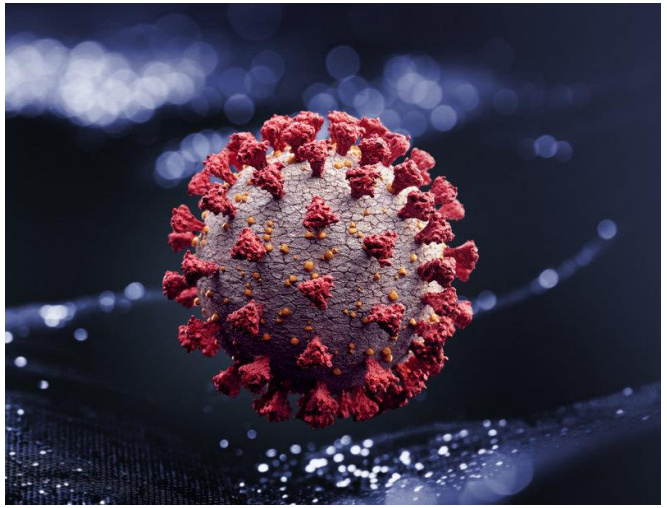
Shiraiwa et al., Environ Sci Proc Impacts 2019

Indoor chemistry related to the pandemic

Cleaning with bleach

Disinfecting with ultraviolet C (photochemistry)

Disinfecting with other approaches (H_2O_2, O_3, free radicals, ion generators, plasma)

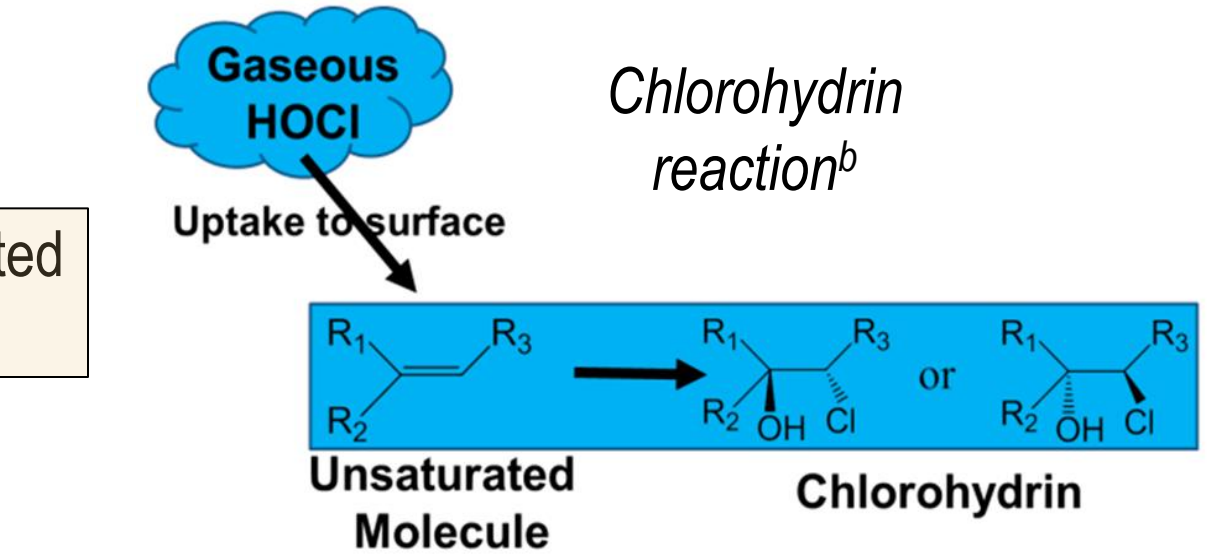


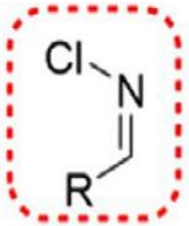
NPR.org

Unintended consequences!

Cleaning with bleach

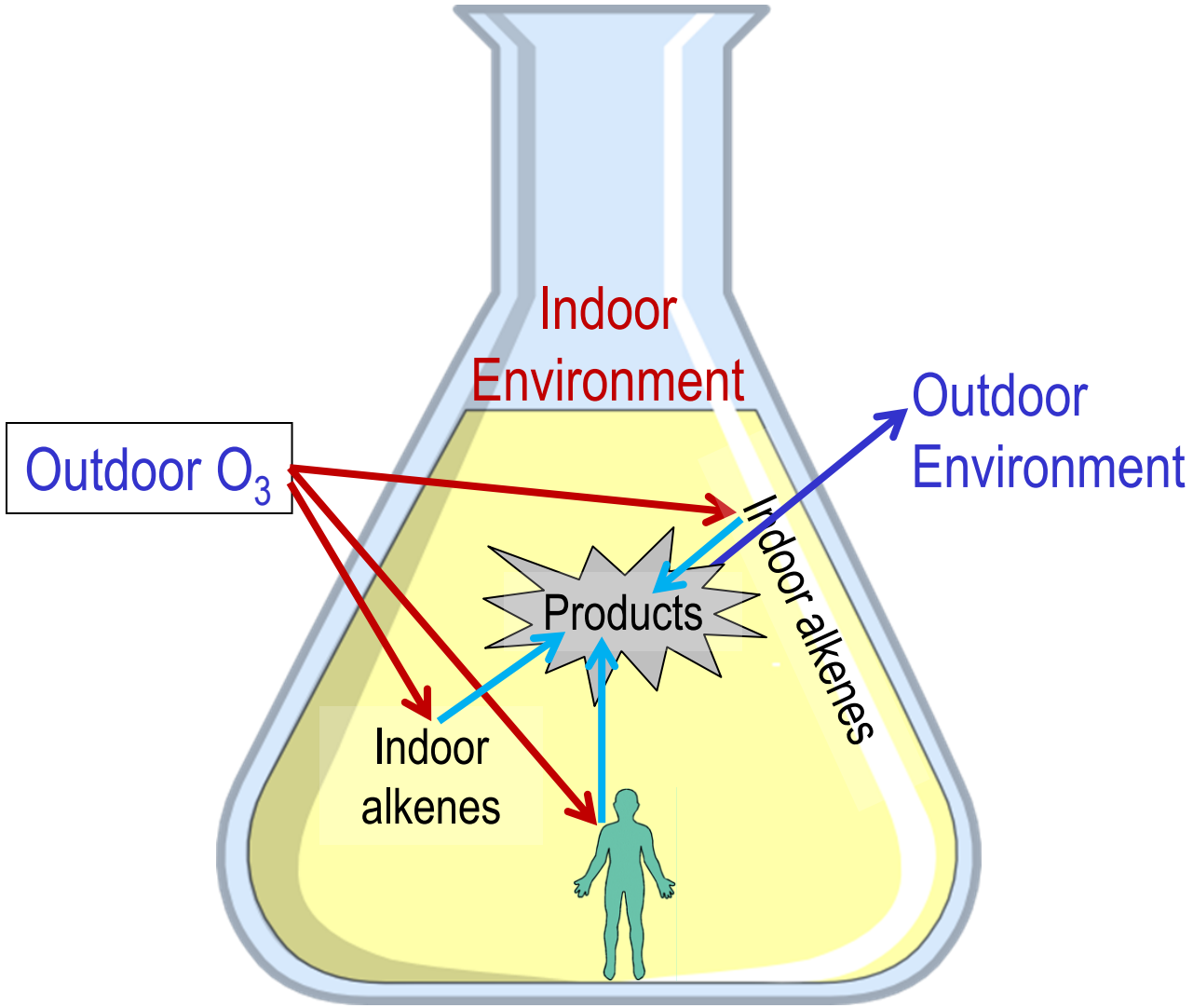
- Using bleach releases HOCl, Cl_2, $ClNO_2$, Cl_2O, $NHCl_2$ & NCl_3 to indoor air [a]
- Chlorinated & nitrogenated VOCs produced [b]
- HOCl reacts with −C=C− as fast as O_3 [c]
- HOCl + squalene → chlorohydrins[c]
- HOCl reacts with all surfaces, not just treated surfaces[a,c]
- Photolysis of Cl_2 → 2 Cl• [a,d]
- OH•, Cl• & ClO• increase with bleach use
- HOCl + amino acids → N-chloraldimines [e]





[a]JPS Wong et al., Indoor Air 2017; [b]Mattila et al., ES&T Letters 2020; [c]Schwatrz-Narbonne et al., ES&T 2018; [d]Mattila et al., ES&T 2020; [e]Finewax et al., Indoor Air 2020

Indoor environments: Chemical reactors feeding outdoor air



- Organic compounds emitted indoors are a substantial source of VOCs in outdoor urban air [a]
- A large fraction of outdoor O_3 that is transported indoors reacts to generate oxidation products that are then transported outdoors.
- Do products generated by indoor O_3 chemistry have a meaningful impact on outdoor air quality?

[a] *McDonald et al., Science 2018*

Summary – emerging science on indoor chemistry

- This was a small subset of the research & discoveries that have emerged over the past several years
- Indoor chemistry has a large impact on the chemicals we inhale, dermally absorb, and even ingest
- If the chemical transformations that occur indoors are overlooked, we have an incomplete picture of the chemicals to which humans are exposed
- The more completely we see, the more we detect, the better we understand

M51,
C.J. Weschler

M51,
NASA, Beckwith & Hubble Heritage Team

Better instruments enable us to see more

Acknowledgements

- Paula Olsiewski and the Sloan Foundation for their interest in and support of indoor chemistry

- Dr. Charles (Bud) A. Russell, Bell Labs, for encouraging my early interest in indoor chemistry

- Dr. Joan M. Daisy, Lawrence Berkeley Laboratories, for a 1991 sabbatical focused on indoor chemistry