Indoor chemistry and aerosols

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Chemistry

- Chemical transformations
  - $A + B \rightarrow C + D + \ldots$

- Some chemical mechanisms influencing indoor aerosols
  - Oxidation
  - Photolysis
  - Hydrolysis
  - Oligimerization
  - Acid-base
Oxidation and SOA

Oxidants convert organic compounds into secondary organic aerosols (SOA)

Volatile organic compounds + Oxidants → Molecular products

Nucleation → Condensation → Agglomeration → SOA
Outdoor chemistry

Volatile organic compounds + Oxidants → Molecular products → Nucleation, Condensation, Agglomeration → Outdoor SOA

Oxidants:
- O₃
- NO₃
- OH

Molecular products:

Volatile organic compounds:
- Alkenes
- Alcohols

Outdoor SOA (Secondary Organic Aerosol)
Indoor chemistry

Volatile organic compounds + Oxidants $\rightarrow$ Molecular products $\rightarrow$ Nucleation $\rightarrow$ Condensation $\rightarrow$ Agglomeration $\rightarrow$ Indoor SOA

O$_3$, NO$_3$, OH
Buildings and SOA

- Low sunlight intensity
- Short lifetime in building
  - SOA “fresh”
- Indoor surfaces
  - Precursor deposition and formation
  - Aerosol deposition
Indoor precursors of SOA

- **Terpenes**
  - Source: Cleaners, solvents, scented products, house plants, food

- **Ozone (O₃)**
  - Source: outdoors
  - Reacts with indoor surfaces

- **Nitrate radical (NO₃)**
  - Source: O₃ + NO₂ chemistry

- **Hydroxyl radical (OH)**
  - Source: indoor chemistry
  - Sunlight intensity lower
Evidence of SOA formation

- Many articles to date demonstrating effect
- Early, chamber experiments adding ozone + terpenes

Adapted from Sarwar et al., 2004
Evidence of SOA formation

- Any event with reactive terpenes and ozone
- Example: Painting with terpentine solvents

Lazaridis et al., 2015
Emerging Science

- Advances in measurements of indoor SOA
- Advances in modeling
- Influence of the building
- Influence of occupants
- Sunlight and photolysis
Advances in measurements

- Quantification of larger number of oxidized species by derivitization techniques
Advances in modeling

- Organic peroxides and nitrates large fraction of whole
- Sensitive to inputs such as surface deposition rates

Carslaw et al., 2012

SOA = 1 µg/m³  SOA=20 µg/m³
Reactive oxygen species (ROS)

- Formation of SOA indoors important in ROS

Table 3: Indoor to outdoor ratio of particulate ROS concentrations measured at the UTest House under different indoor (low/high ozone concentration, low/high terpene concentration) and outdoor (low/high ozone concentration) conditions. Each condition was tested in triplicate, and means ± standard error are reported.

<table>
<thead>
<tr>
<th>Indoor conditions at UTest House</th>
<th>Low Outdoor O₃</th>
<th>High Outdoor O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low O₃, Low Terpene</td>
<td>1.50 ± 0.26</td>
<td>0.77 ± 0.19</td>
</tr>
<tr>
<td>Low O₃, High Terpene</td>
<td>0.74 ± 0.05</td>
<td>0.96 ± 0.26</td>
</tr>
<tr>
<td>High O₃, Low Terpene</td>
<td>0.99 ± 0.22</td>
<td>0.93 ± 0.20</td>
</tr>
<tr>
<td><strong>High O₃, High Terpene</strong></td>
<td><strong>4.39 ± 1.11</strong></td>
<td><strong>1.23 ± 0.55</strong></td>
</tr>
</tbody>
</table>

Indoor ROS more than 4 times higher indoors when both ozone and terpene concentrations are elevated

Khurshid et al., 2015
Building operation

- Influence of air exchange rate on peak SOA

Youssefi and Waring, 2015
Chemistry induced particle nucleation at surfaces

Nucleation, growth

+ $O_3$ → products

Secondary organic aerosol formation from ozone reactions with single terpenoids and terpenoid mixtures

Waring et al., 2011

Terpene-surface reactions FAST
Shu and Morrison, 2011

Secondary organic aerosol formation from ozone-initiated reactions with nicotine and secondhand tobacco smoke

Sleiman et al., 2010
Occupancy reduces indoor $O_3$ concentration

Desquamation

Weschler, 2015
Occupancy, chemistry and aerosols

Fadeyi et al., 2013

Impact of Human Presence on Secondary Organic Aerosols Derived from Ozone-Initiated Chemistry in a Simulated Office Environment
Moshood O. Fadeyi, Charles J. Weschler, Kwok W. Tham, Wei Y. Wu, and Zuraimi M. Sultan
HONO and OH

Light enhanced heterogeneous reactions with household cleaners (Alvarez et al. 2014)

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]

\[ \text{HONO} \rightarrow \text{OH} + \text{NO} \]

\[ \text{OH Concentration} \sim 10^6 \text{ mol/cm}^3 \]

(Alvarez et al., 2013)
Knowledge gaps and opportunities

- Advances in field analysis and instrumentation
- Models
- Surface chemistry
- Building characterization
Field analysis

- Application of field instruments
  - High resolution Aerosol Mass Spectrometry (PM)
  - FAGE (OH)
  - Cavity Ring-down Spectroscopy (NO$_3$)
  - DART-MS for real-time surface film characterization

Romonosky et al., 2014
Improving Models

- Current models based on ambient chemistry models
- Better account for
  - Surface phenomena
  - Building characteristics
  - Occupancy
  - Activities
Surface composition/chemistry

- Acid-base chemistry
  - pH, solubility, partitioning, ionization
  - High CO₂ decreases pH
  - High NH₃ increases pH

- Surface aging, composition over time, exchange with aerosols
  - Extent of oligimerization
  - Generation of toxicants, carcinogens → aerosols

Mohamad Sleiman et al. 2010
Buildings

• Buildings highly heterogeneous
  • Building materials
  • Occupancy/activities
  • Air composition
  • Air exchange
  • Temperature gradients
  • Humidity gradients

• Air paths
  • Interstitial spaces

• Identifying parameters
  • Which are most important with respect to chemistry?
Thank you
Extra slides
Cleaning events and SOA

A mechanistic study of limonene oxidation products and pathways following cleaning activities
Nicola Carslaw
Environment Department, University of York, York YO10 5DD, UK
Advances in modeling

Graph showing:
- Outdoor Chemistry
- Exchange with outdoors
- Indoor Sources
- Total PM2.5

Diagram illustrating:
- Biogenic species (e.g., limonene and α-pinene) + oxidant
- OUTDOORS
- INDOORS
- GPP
- GPP
- GPP
- New SOA formation from outdoor GPP
- Indoor emissions
The lasting effect of limonene-induced particle formation on air quality in a genuine indoor environment

Carolin Rösch¹ · Dirk K. Wissenbach² · Martin von Bergen¹,² · Ulrich Franck⁴ · Manfred Wendisch⁵ · Uwe Schlink¹
Advances in modeling

- Relative oxidation rates

Volatile organic compound conversion by ozone, hydroxyl radicals, and nitrate radicals in residential indoor air: Magnitudes and impacts of oxidant sources

Michael S. Waring, J. Raymond Wells
Advances in modeling

- SOA yields from terpenoid ozonolysis variable, dependent on presence of organic aerosols and indoor ozone concentration

Youssefi and Waring, 2012
Building surfaces and reaction rates

- Ozone reactions rates with terpenes enhanced on buildings surfaces

\[ \text{Dihydromyrcenol oxidation rate} \geq 20 \times \text{faster at painted surface than in air} \]

Shu and Morrison, 2011