Field and laboratory experiments examining the stability of organic molecular markers used for source apportionment

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Organic Molecular Markers

- Reduced organic compounds used as tracers for sources of organic carbon
  - Highly source specific
  - Small fraction of emissions

- Are these compounds stable under conditions of long range transport?

**Cholesterol**
(0.03 – 1% of cooking OC)

**Norhopane**
(0.0006% - 0.11% of vehicle OC)
Evaluation of Stability of Molecular Markers in Los Angeles

- Compare ambient levels to emissions
- Conclusion
  - Markers appear stable in LA
- Some evidence of aging
  - Oleic acid
  - PAH, esp. downwind

Schauer et al. 96; Rogge et al. 96

Other evidence for photochemical oxidation of tracers

- PAH
  - Significant evidence for oxidation from field and laboratory
  - Results illustrate complexity – composition, moisture, etc. effects
- Oleic acid
  - \( \text{O}_3 \) uptake experiments \( \gamma \sim 10^{-3} \)
  - Disconnect between laboratory results and atmospheric observations
  - Complexity of phase and mixture
- OH uptake
  - \( \gamma > 0.1 \) for alkanes, alkanoic acids, PAH, etc.
- Levoglucosan
  - No evidence of acid catalyzed hydrolysis
  - Fraser et al. 2000
- Cholesterol
What are chemical time scales?

\[ \tau = \frac{N}{\phi} = \frac{4}{3} r \frac{\rho Na}{M \gamma Cs} \]

### Field Data from Pittsburgh Air Quality Study

**PAQS Main Site**

### Laboratory Data from Smog Chamber

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10 m³ temperature-controlled chamber
Mixing complicates examination of ambient data for evidence of photochemical aging.

Using a relative rate approach to separate mixing and aging.

Assuming compounds emitted by a single source:

\[ \log\left(\frac{C_1}{C_3}\right) \]

Increasing photochemical age

\[ m = \frac{k_2 - k_3}{k_1 - k_3} \]
Ambient data consistent with significant photochemical aging

Strong seasonal variation in Hopane/EC ratios. Photochemical aging of hopanes?
Upwind measurements of hopanes also suggest photochemical aging in summer.

Much lower levels of hopanes in regional aerosol during summer.

What about mixing?

- Seasonal variation in some non-vehicular source of EC.
- Seasonal variation in fleet composition.
- Seasonal variation in hopane/EC ratio of motor vehicle emissions
Seasonal variations in vehicle emissions?

**CASS**

- Vehicle OC
  - Non Cat Gas
  - Cat. Gas
  - Diesel

**NFRAQS**

- Vehicle OC
  - Gas
  - Diesel

Ambient Data
- Summer
- Spring/Fall
- Winter

- Schauer catalytic gas
- Non-catalytic gas

**Laboratory Aging Experiments in a Smog Chamber**

- CMU smog chamber
- 1500 µg/m³ aerosol
- Non-reactive tracer: pentane
- Reactive: 1-butene, propene

- T=22 ± 2 °C,
- RH= 7 ± 3%

- Model Meat Smoke Aerosol
  - 4 & 14 component mixtures – alkanoic acids, alkenoic acids, sterols, alkanes, ...

- Gas phase tracers
- 2-butanol (radical scavenger)

- Ozone Monitor
- GC-MS
- Quartz Filter Samples
- GC-FID
- SMPS
Ozonolysis of oleic acid and cholesterol in model meat smoke aerosols

4-mix (30% oleic acid, 30% cholesterol)
O3 ~ 350 ppbv

14-mix (17% oleic acid, 4% cholesterol)
O3 ~ 100 ppbv

The rate constant for ozone aging of cholesterol and oleic acid depends on the mixture composition.

Relative rate analysis of 14 component model meat smoke mixture

Condensed-phase relative rates

- palmitic acid
- cholesterol
- pentacosane

Mixed-phase relative rates

- oleic acid
- nervonic acid

- \( \frac{k(\text{cholesterol})}{k(\text{oleic})} = 0.19 \pm 0.08 \)
- \( \frac{k(\text{palmitic})}{k(\text{oleic})} = 0.05 \pm 0.06 \)
- \( \frac{k(\text{pentacosane})}{k(\text{oleic})} = 0.006 \pm 0.009 \)

- \( \frac{k(\text{oleic})}{k(\text{propene})} = 6.4 \pm 0.8 \)
- \( \frac{k(\text{nervonic})}{k(\text{propene})} = 6.8 \pm 0.8 \)
Decay of cholesterol may be significant under conditions of regional transport

Rate constant from 14 component mixture experiment

Are molecular markers stable?

- Both field and laboratory data suggest that molecular markers may not be stable under conditions of regional transport.
- Dependence of oxidation rates on mixture composition complicates interpretation of laboratory experiments
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