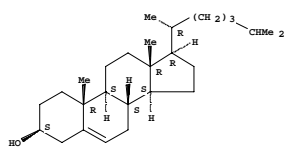


Field and laboratory experiments examining the stability of organic molecular markers used for source apportionment

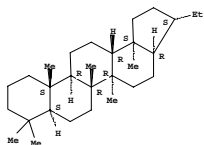
Allen Robinson, Neil Donahue, Amy
Sage, Kara Huff Hartz, Emily Weitkamp
Carnegie Mellon University

Presented at AAAR Specialty Conference: Particulate Matter, Supersites Program & Related
Studies February 7-11, 2005, Atlanta GA.

Organic Molecular Markers

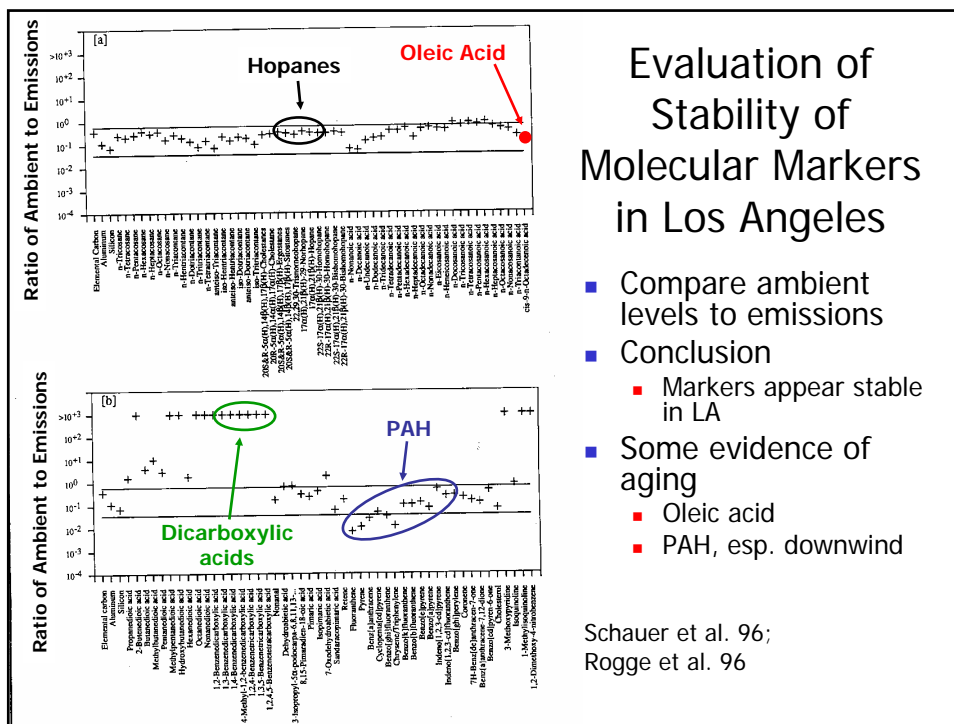


Cholesterol
(0.03 – 1% of cooking OC)



Norhopane
(0.0006% - 0.11% of vehicle OC)

- 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?



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

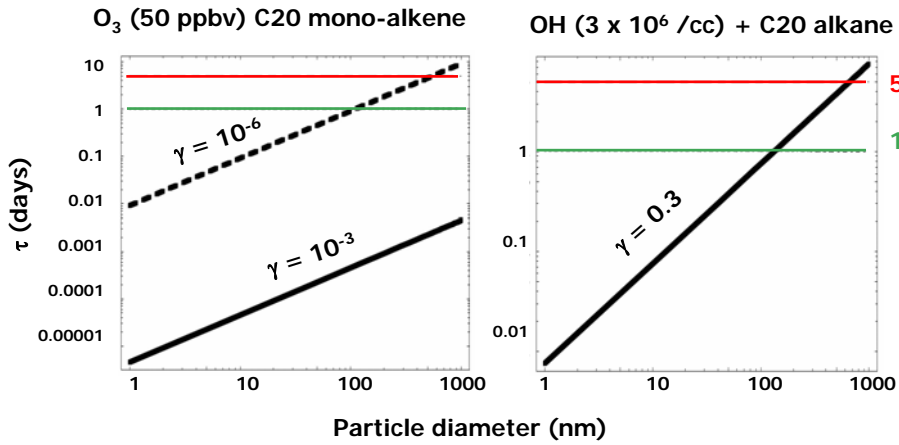
Other evidence for photochemical oxidation of tracers

- PAH
 - Significant evidence for oxidation from field and laboratory
 - Results illustrate complexity – composition, moisture, etc. effects
 - Kamens et al. 1988, Nielsen 1988, Finlayson-Pitts 2000
- Oleic acid
 - O₃ uptake experiments -- $\gamma \sim 10^{-3}$
 - Disconnect between laboratory results and atmospheric observations
 - Complexity of phase and mixture
 - Rudich et al. 2002, Morris et al. 2002, Smith et al. 2002
- OH uptake
 - $\gamma > 0.1$ for alkanes, alkanolic 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

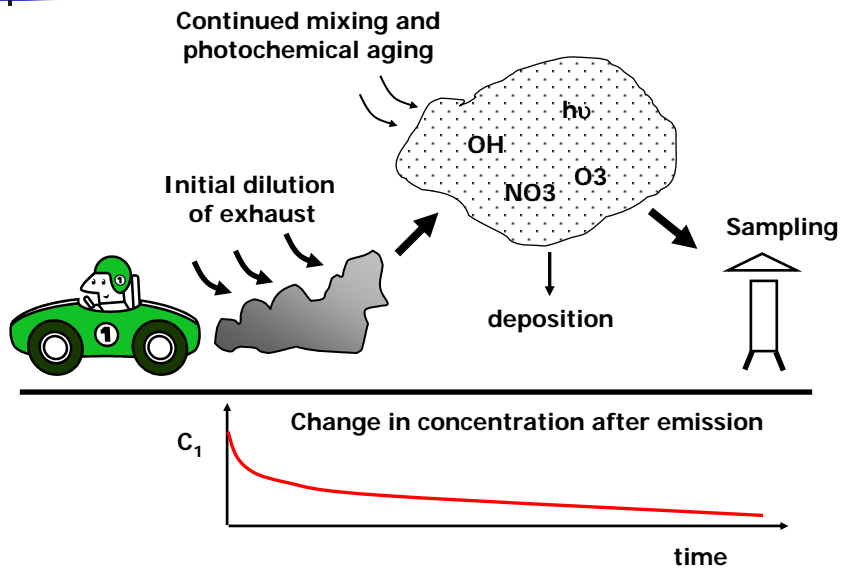


Laboratory Data from Smog Chamber

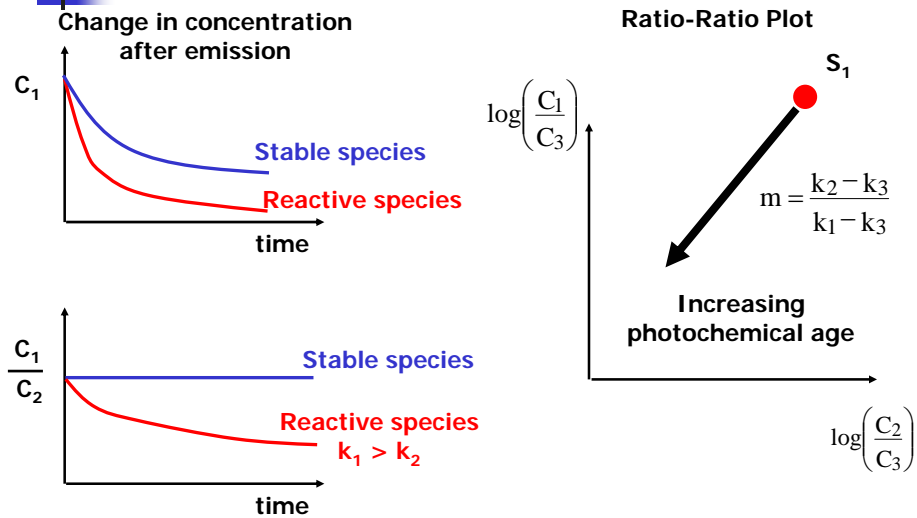


Carnegie Mellon University
10 m³ temperature-controlled chamber

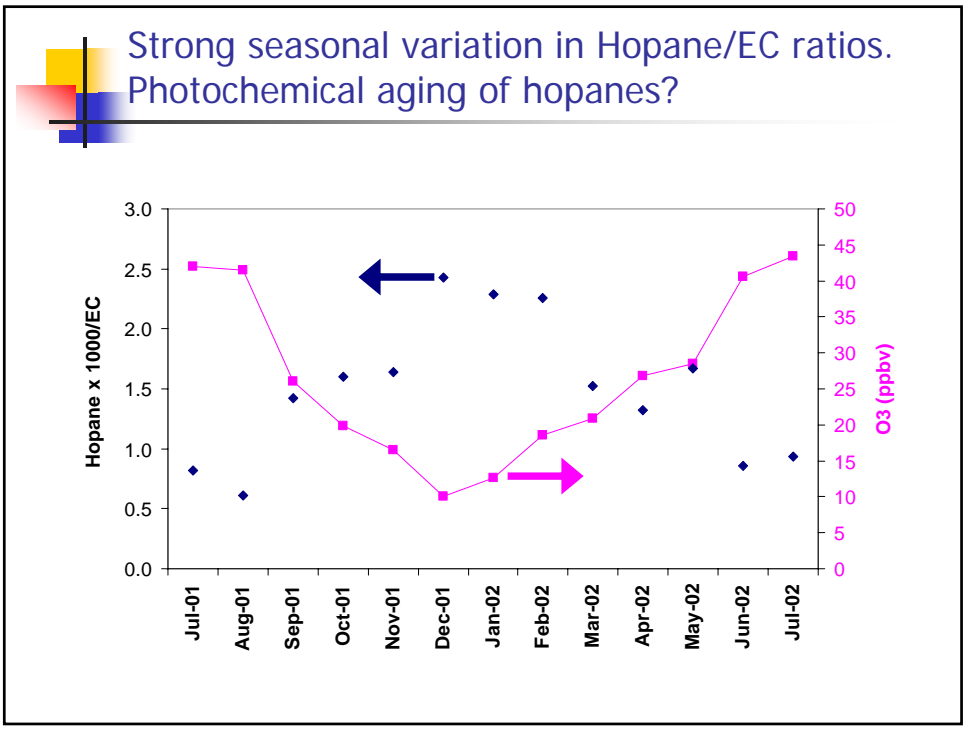
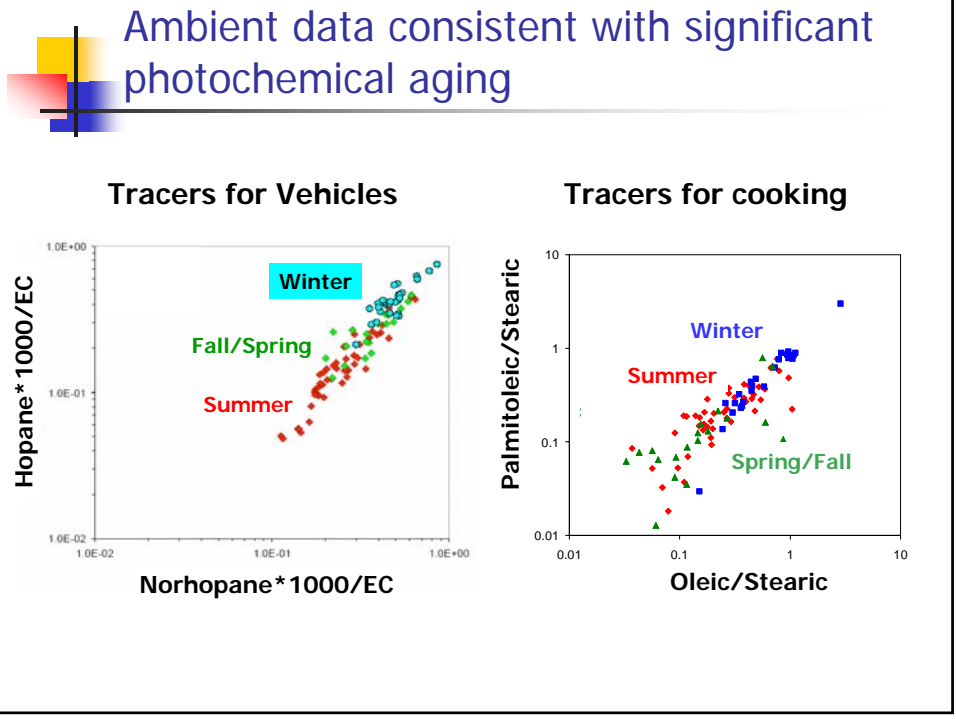
Mixing complicates examination of ambient data for evidence of photochemical aging



Using a relative rate approach to separate mixing and aging

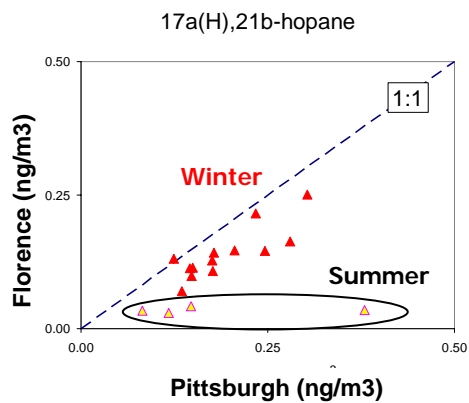
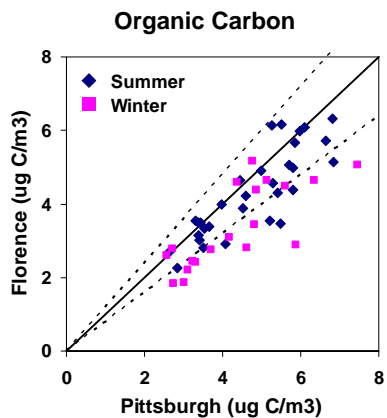


Assuming compounds emitted by a single source

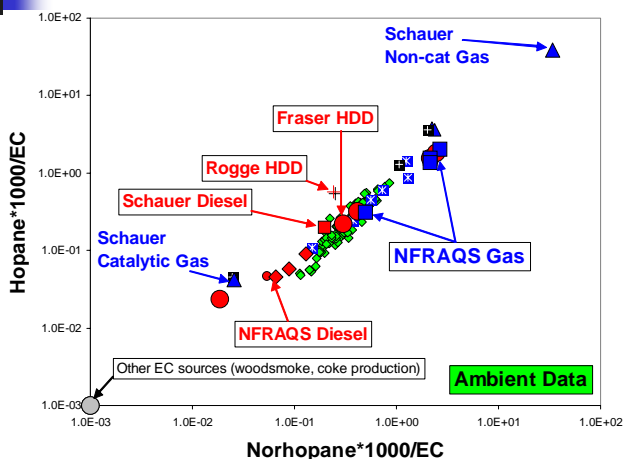


Upwind measurements of hopanes also suggest photochemical aging in summer

Much lower levels of hopanes in regional aerosol during summer.

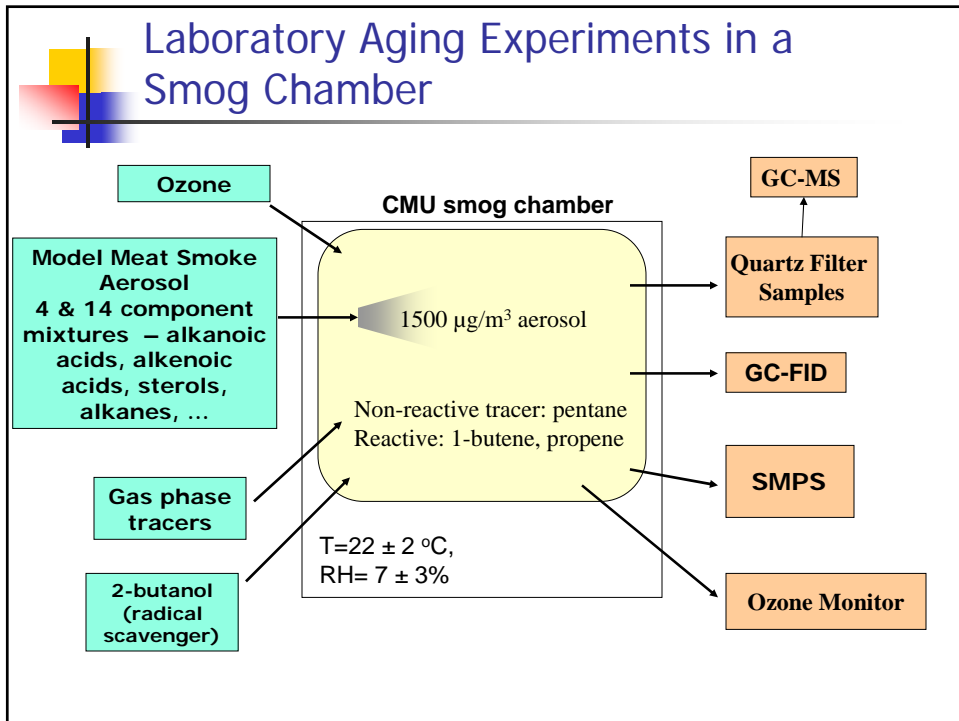
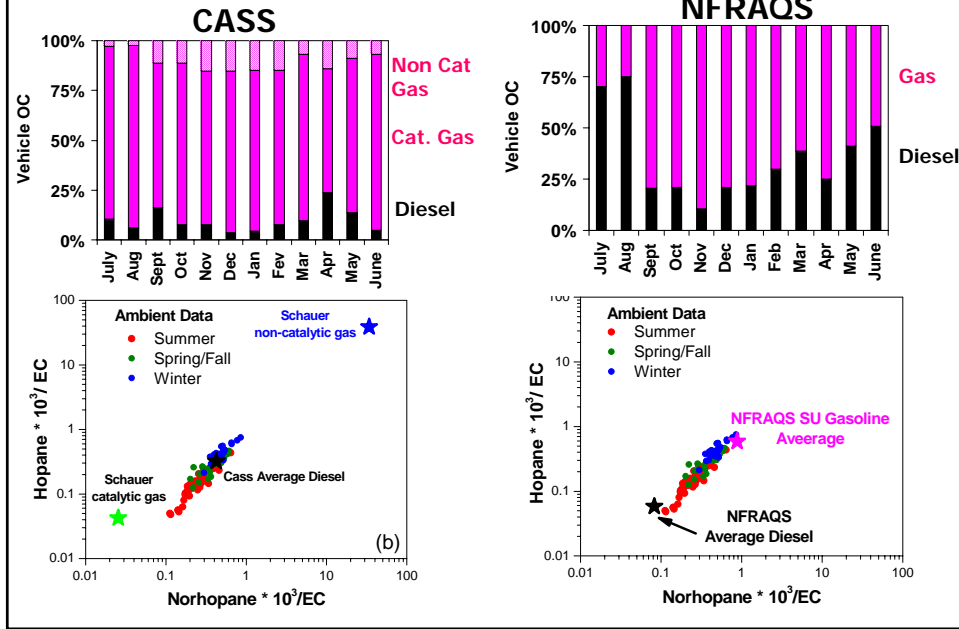


What about mixing?



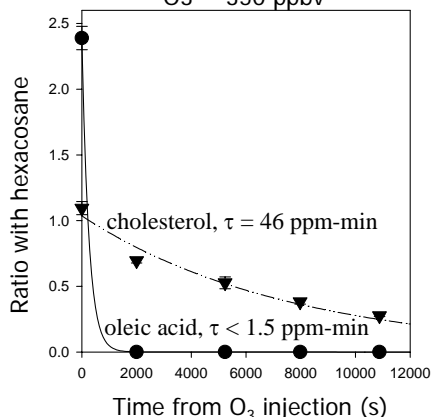
- Seasonal variation in some non-vehicular source of EC.
- Seasonal variation in fleet composition.
- Seasonal variation in hopane/EC ratio of motor vehicle emissions

Seasonal variations in vehicle emissions?

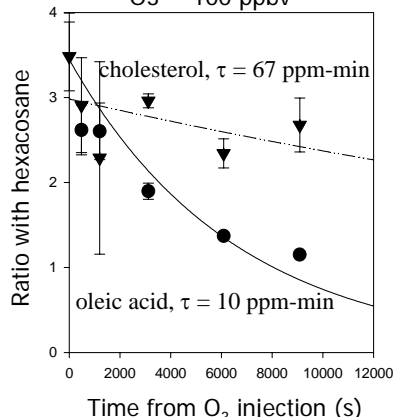


Ozonolysis of oleic acid and cholesterol in model meat smoke aerosols

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



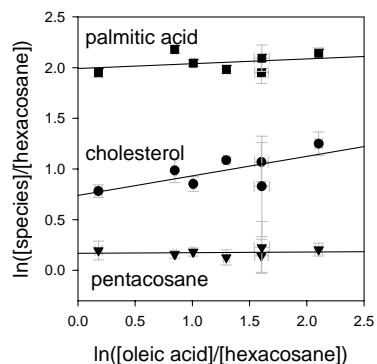
14-mix (17% oleic acid, 4% cholesterol)
O₃ ~ 100 ppbv



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

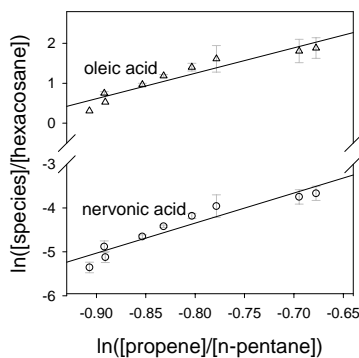
Relative rate analysis of 14 component model meat smoke mixture

Condensed-phase relative rates



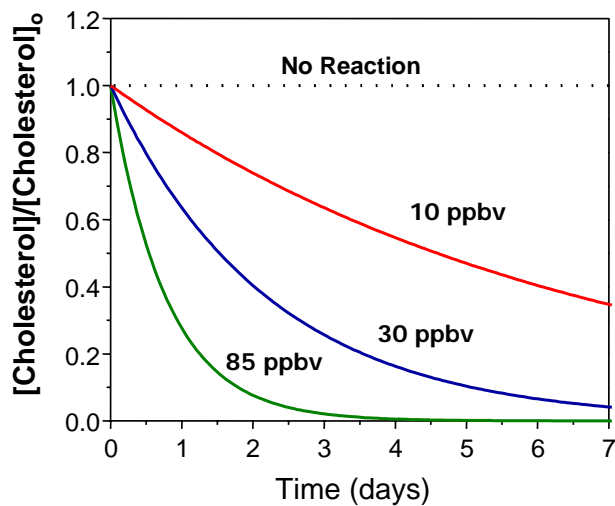
- $k(\text{cholesterol})/k(\text{oleic}) = 0.19 \pm 0.08$
- $k(\text{palmitic})/k(\text{oleic}) = 0.05 \pm 0.06$
- $k(\text{pentacosane})/k(\text{oleic}) = 0.006 \pm 0.009$

Mixed-phase relative rates



- $k(\text{oleic})/k(\text{propene}) = 6.4 \pm 0.8$
- $k(\text{nervonic})/k(\text{propene}) = 6.8 \pm 0.8$

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



Acknowledgments

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- Everyone who worked on Pittsburgh Air Quality Study