Organic Carbon Chemistry in the Valley Atmosphere: Quinones and Peroxides

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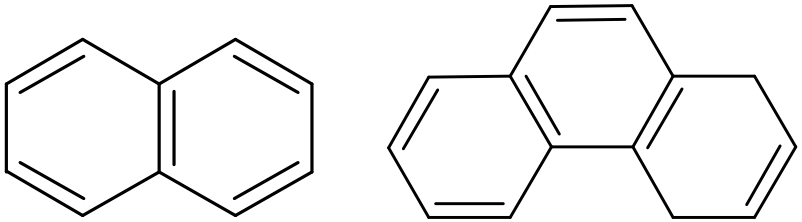
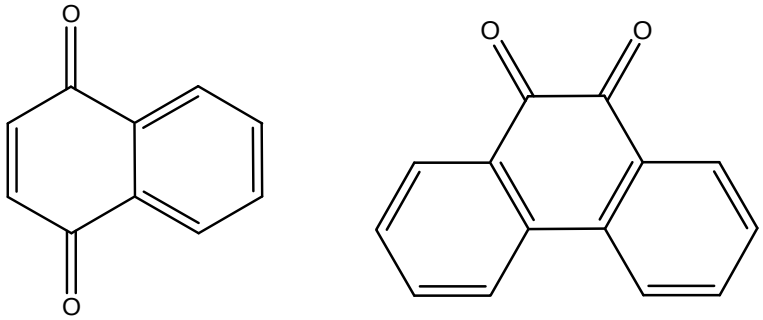
Quinones and Peroxides are minor components of PM

Polyaromatic Hydrocarbons (PAH)



Quinones



Hydrogen Peroxide (H_2O_2)

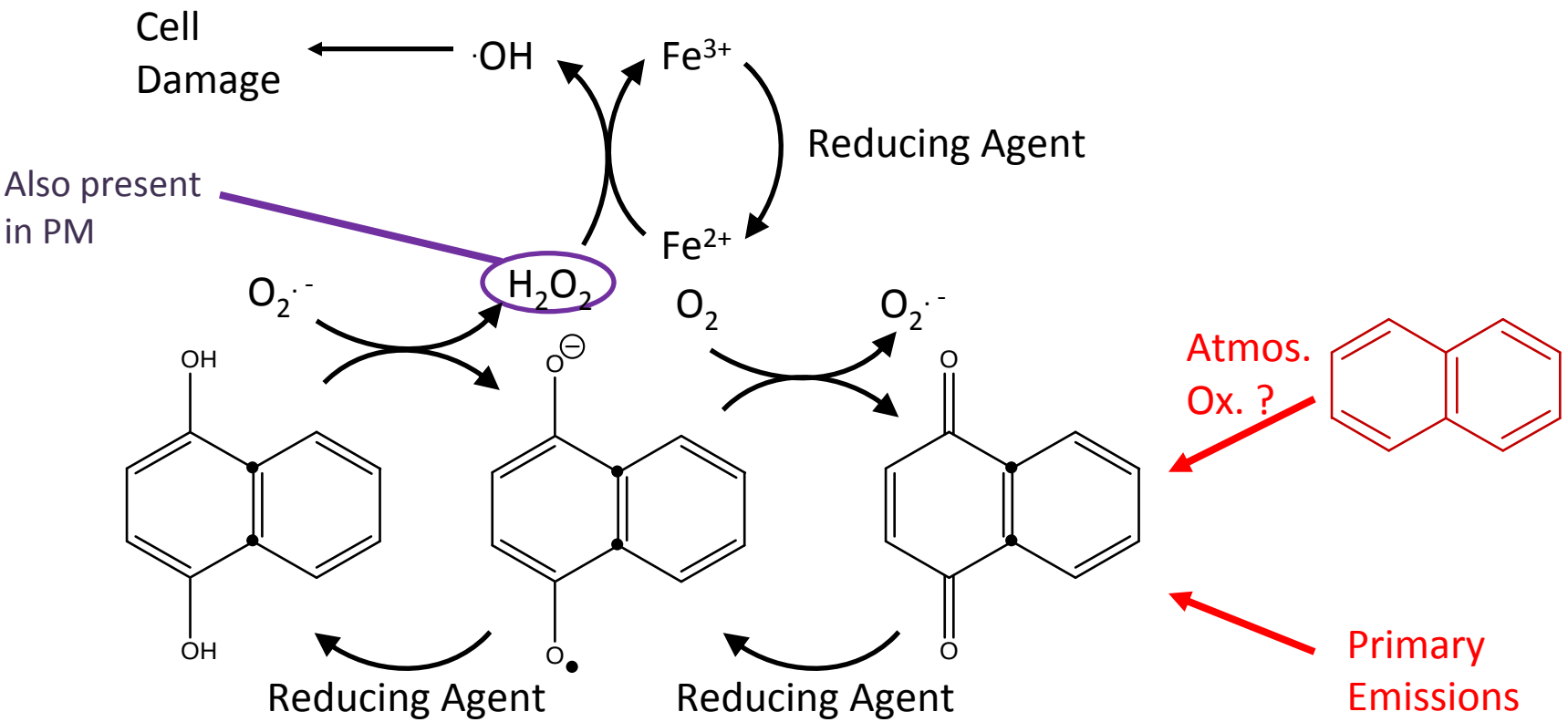
Annual Average $PM_{2.5}$ ~25 $\mu g.m^{-3}$

Typical mass loading for quinones and PAH < 1 $ng.m^{-3}$ (0.004% of PM mass)

Typical mass loading for H_2O_2 < 30 $ng.m^{-3}$ (0.1% of PM mass)*

(* for Southern California)

Quinones and Hydrogen Peroxide



Key Questions to address:

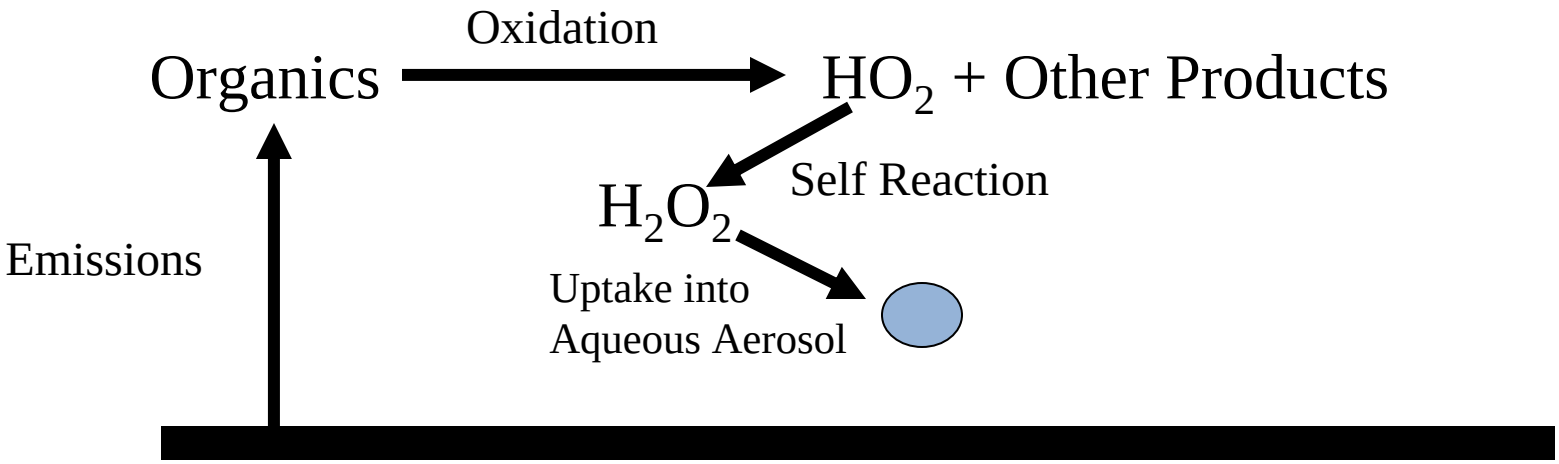
1. Do all quinones behave the same?
2. What is the relative importance of emissions vs. chemistry?
3. What is the relative importance of H_2O_2 production in atmosphere vs. in lung?

Hydrogen Peroxide Generation in the Atmosphere

Hydrogen Peroxide in PM

- Fine aerosols contain high concentrations of liquid water, so H_2O_2 may partition between the gas phase and the aerosol according to Henry's law:

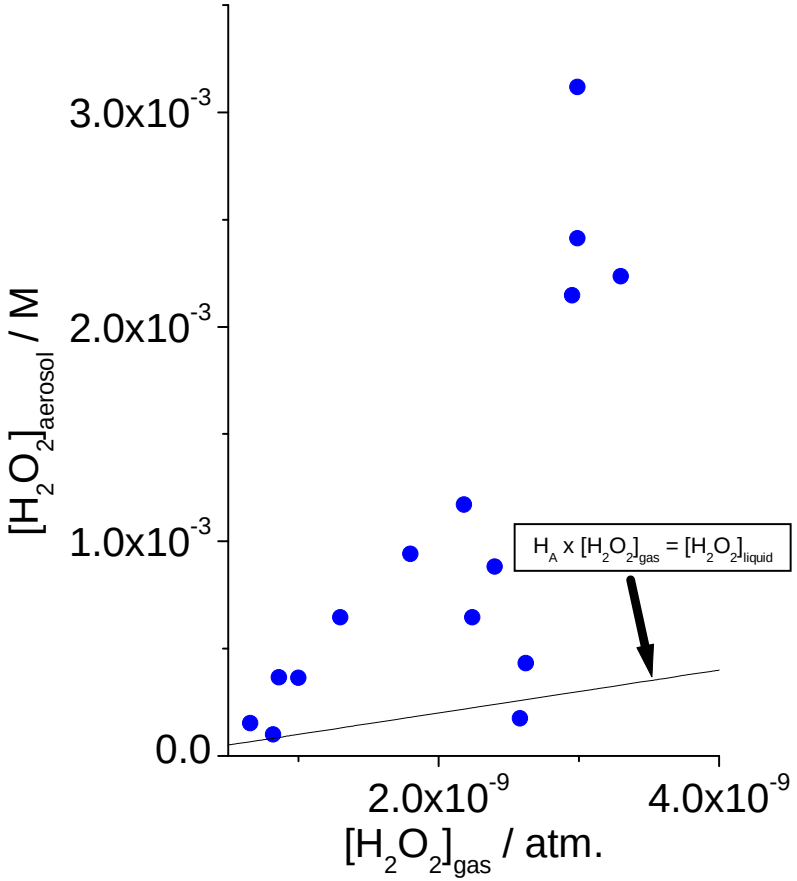
$$H_2O_2(g) \leftrightarrow H_2O_2(l) \qquad H_A.P_{H_2O_2} = [H_2O_2]_{aq}$$

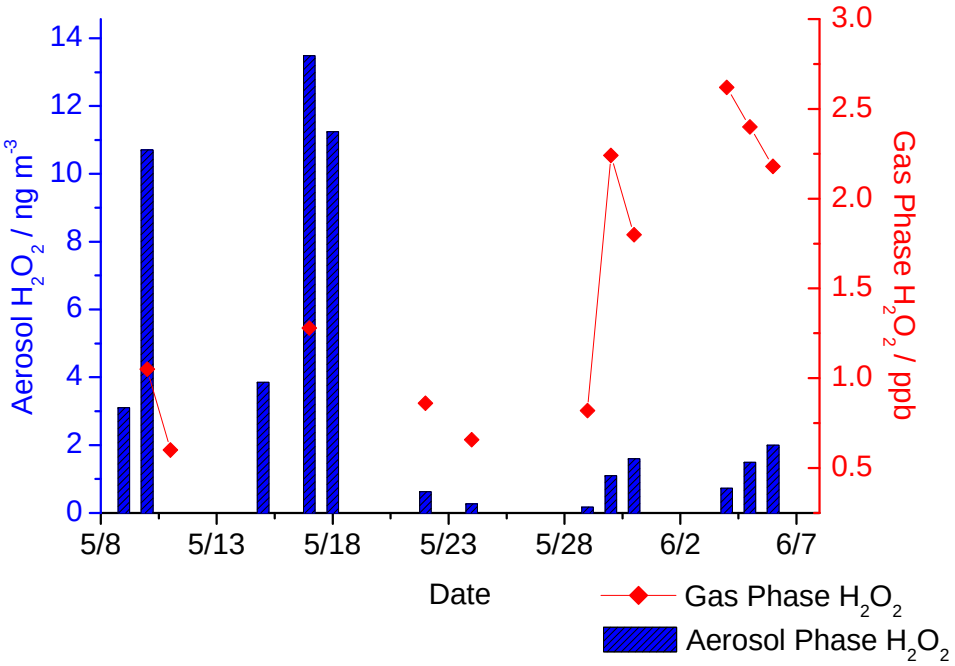


Hydrogen Peroxide

- H_2O_2 levels are up to 100 times higher in PM than expected in LA basin.

(*Hasson and Paulson, J. Aerosol Sci, 459-68, **2003.**)*

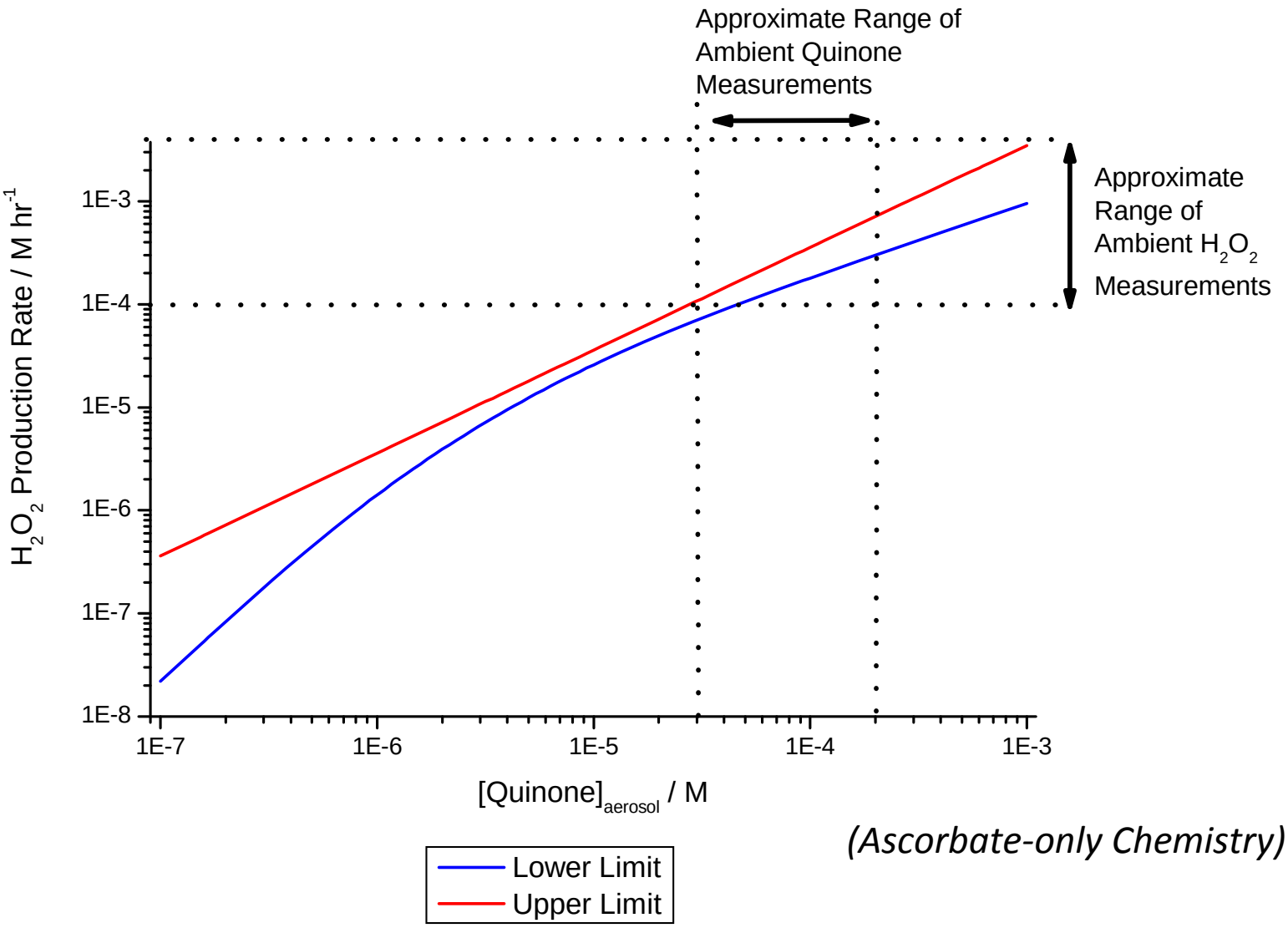




- Measurements imply that H_2O_2 is generated within the particles themselves.

- Metals and/or organics (including quinones) may undergo reactions to form H_2O_2 in particles.

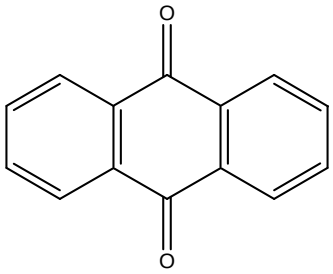
Endo- vs. Exo-ROS Generation



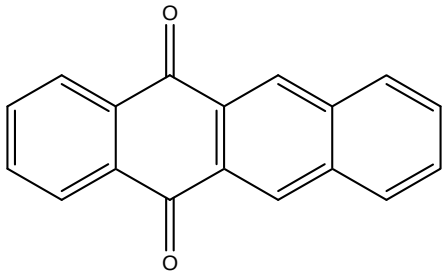
(Ascorbate-only Chemistry)

Hydrogen peroxide in PM *may* be as important as hydrogen peroxide formed by PM.

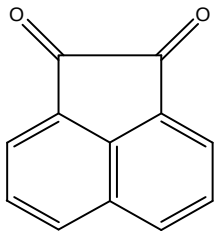
Quinones Identified in Fresno Air: Do they all behave in the same way?



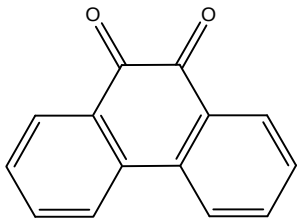
Anthraquinone



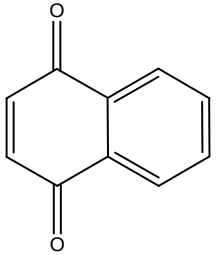
5,12-Naphthacenequinone



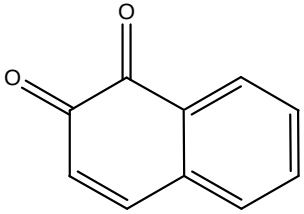
Acenaphthenequinone



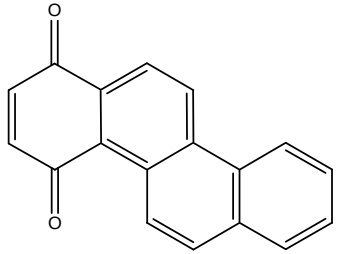
Phenanthraquinone



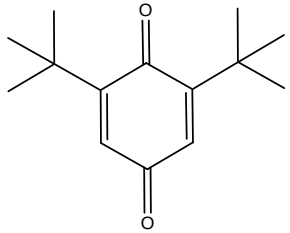
1,4-Naphthoquinone



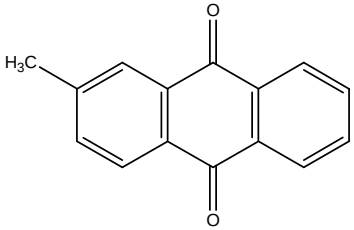
1,2-Naphthoquinone



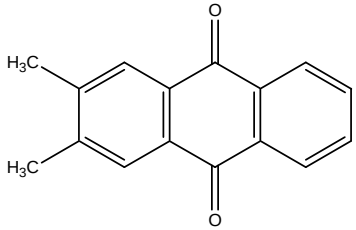
1,4-Chrysenequinone



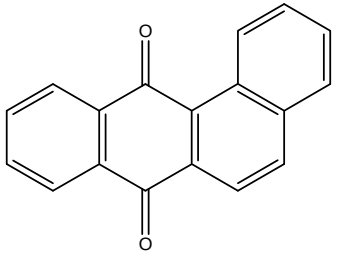
2,6-Dtb-1,4-Benzoquinone



2-Methyl Anthraquinone



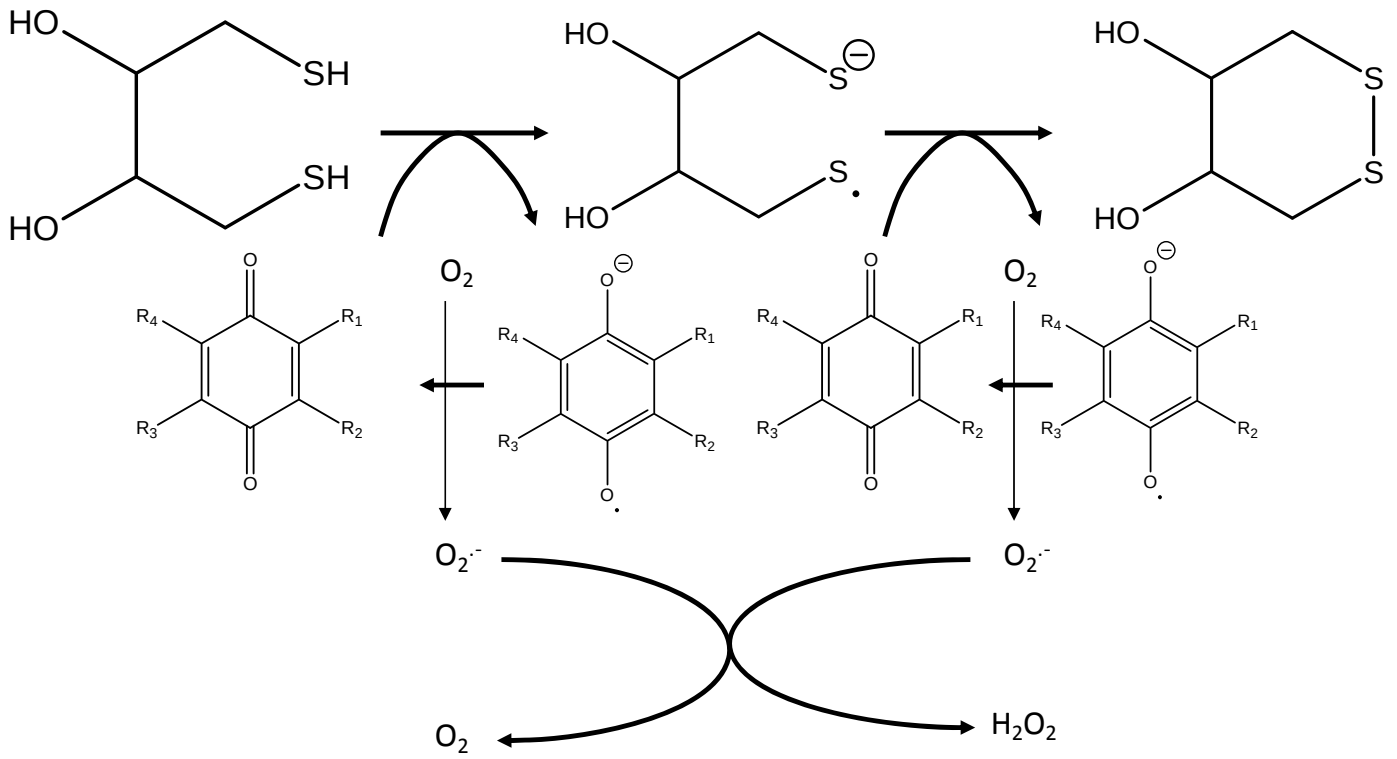
2,3-Dimethyl Anthraquinone



Benz[a]anthracene -7,12-dione

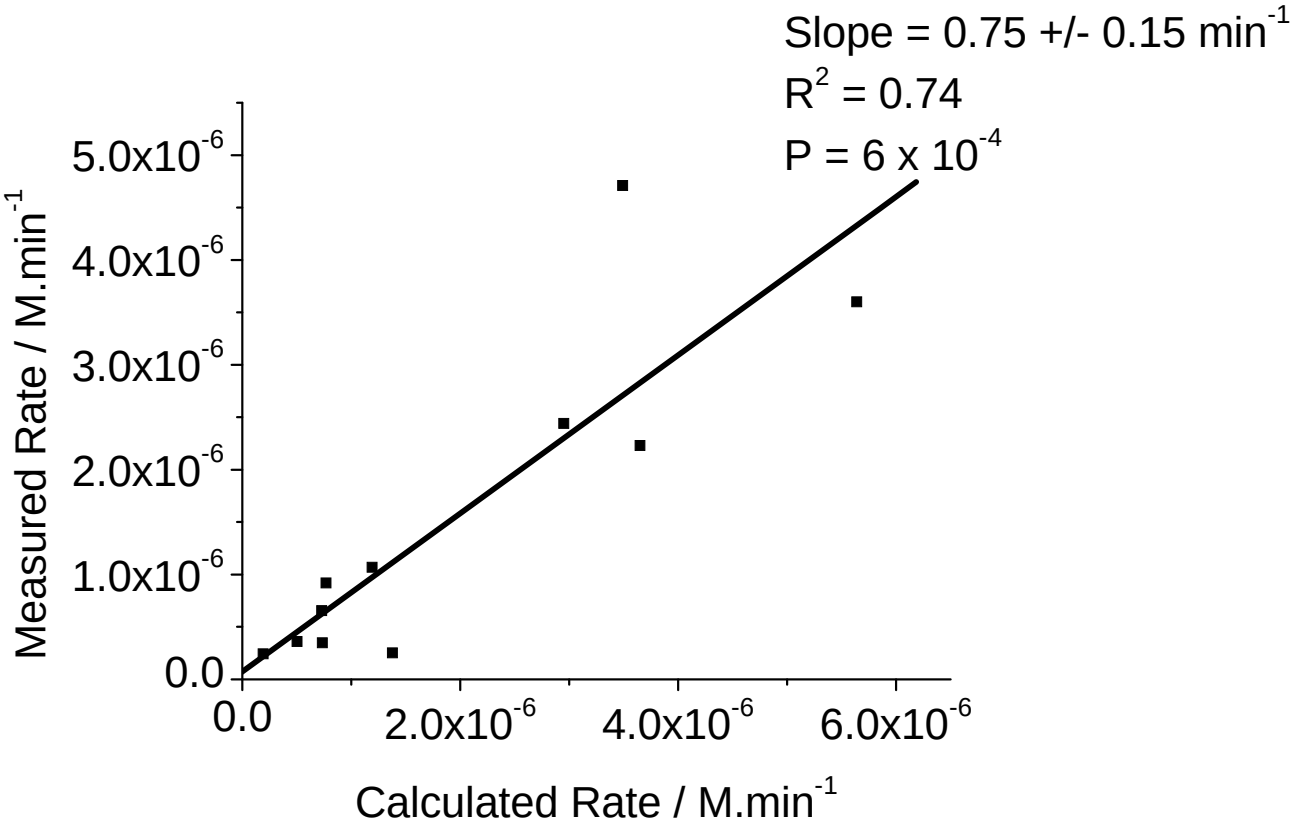
DTT (Dithiothreitol) Assay

- Provides information on the potential of PM extracts to cause cell injury.
- Quinones/PM oxidize DTT, generating H_2O_2.
- The reaction rate is correlated with bronchial epithelial cell injury by ROS (*Li et al., Environ. Health Perspect. 2003*).



DTT (Dithiothreitol) Assay

$$\text{Rate} = k'_{PQ}[PQ]_0 + k'_{1,4\text{-}NQ}[1,4\text{-}NQ]_0 + k'_{1,2\text{-}NQ}.[1,2\text{-}NQ]_0$$



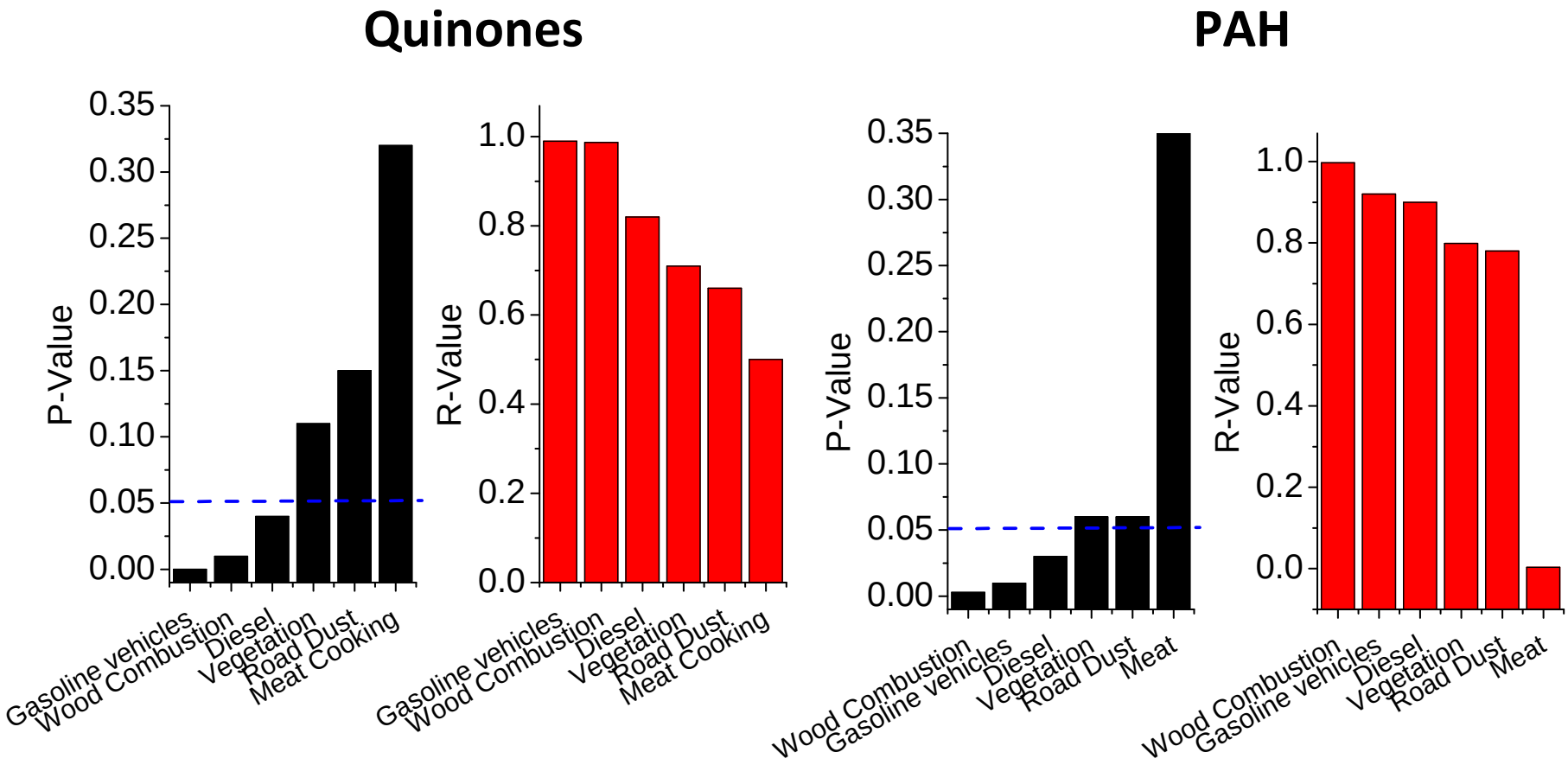
Measured quinones account for all of the reactivity of the PM samples collected. Phenanthraquinone dominates the reactivity of these samples.

Origins of Atmospheric Quinones: Emissions vs. Chemistry

Sources of Quinones and PAH

- Samples Collected at Fresno State (November 2005 – June 2006).
- Lundgren Impactor with four size cuts (10, 3, 1 and 0.3 μm).
- ~50 chemical compounds monitored.

Sources of Quinones and PAH: 11/2005 – 7/2006



Wood combustion correlation is strongly dependent on a few data points.

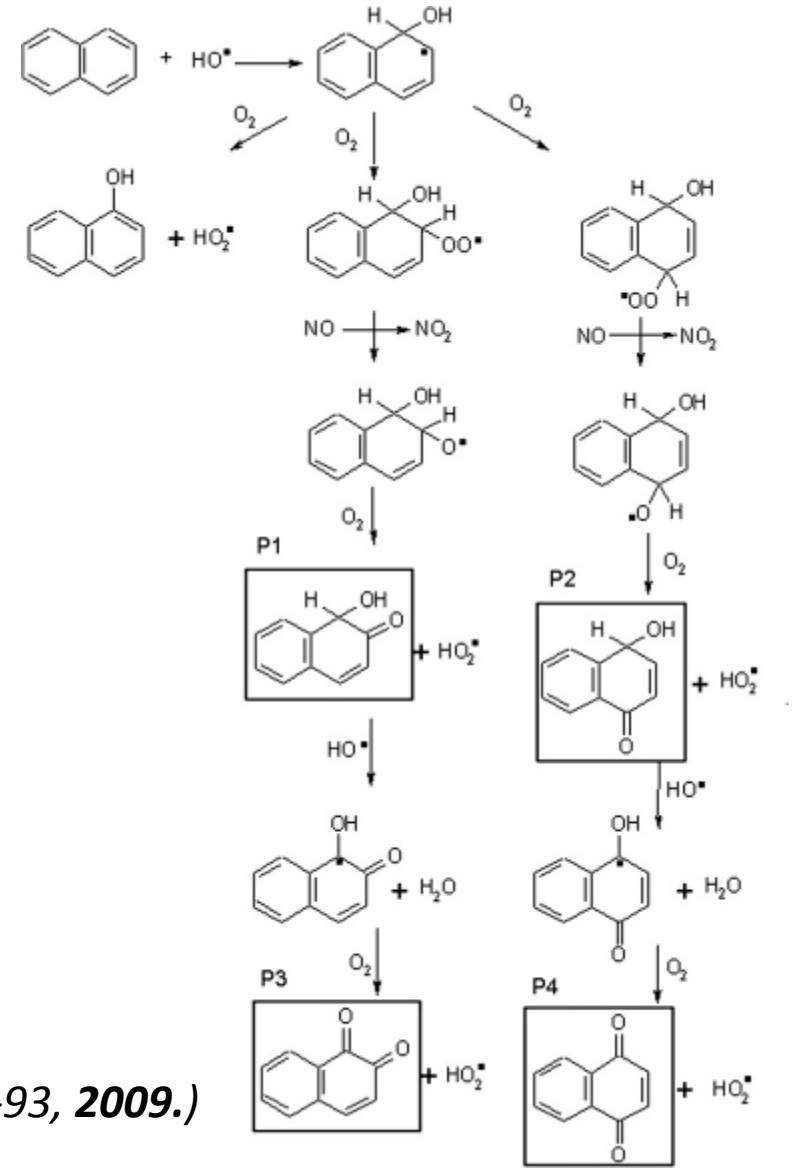
PAH and quinone mass loadings are strongly correlated ($R^2 = 0.98$; $P = 2 \times 10^{-4}$).

Some Quinones Expected From PAH Oxidation Chemistry

- PAH oxidation chemistry is complicated.

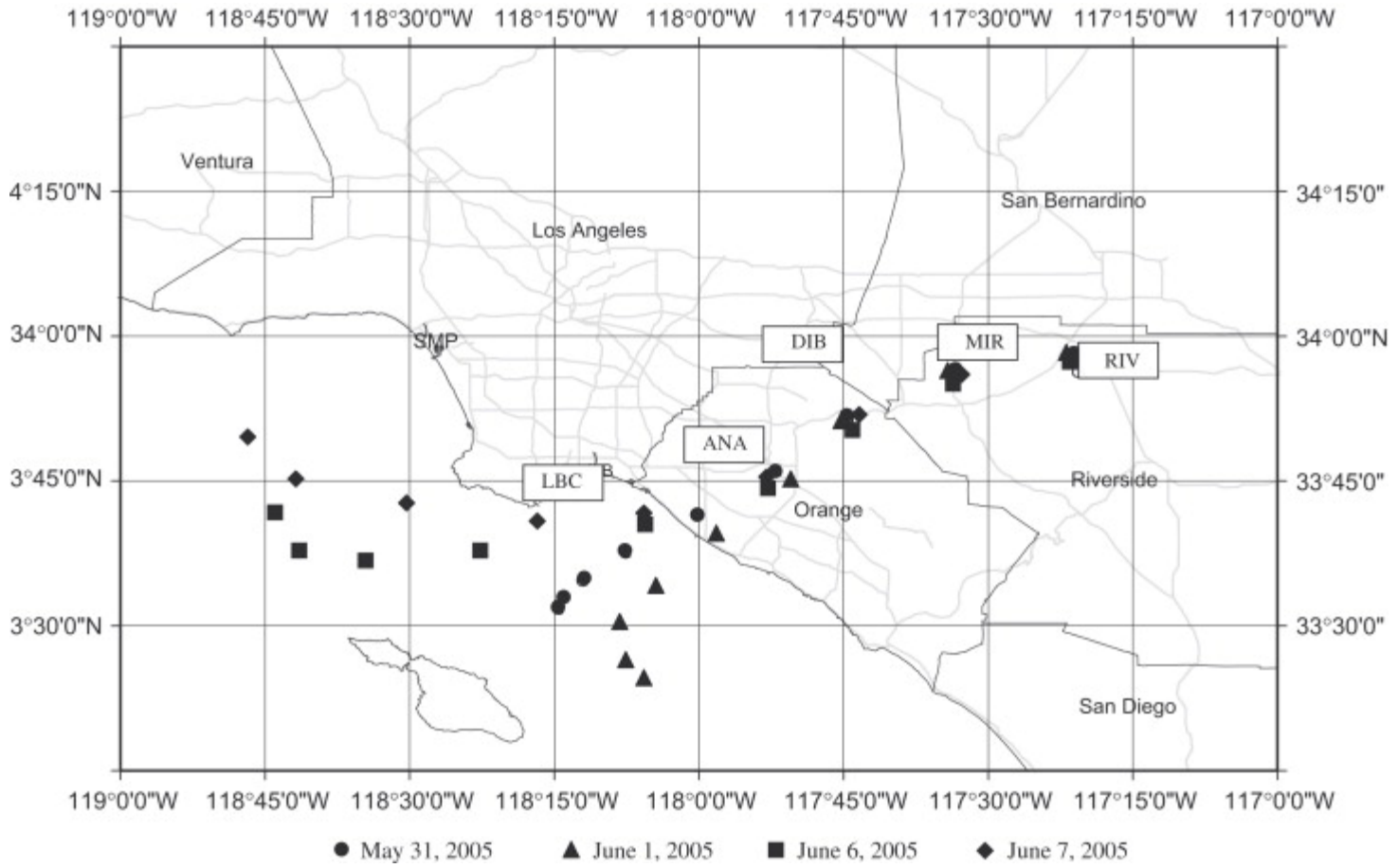
- Quinones have been observed in low yield (a few percent or less) from several PAHs.

- Because PAH emissions are much greater than quinone emissions, chemical formation of quinones in the atmosphere may exceed primary emissions.



*(Lee and Lane, Atmospheric Environment, 43, 4886-93, **2009.**)*

Evidence for Photochemistry from Southern California

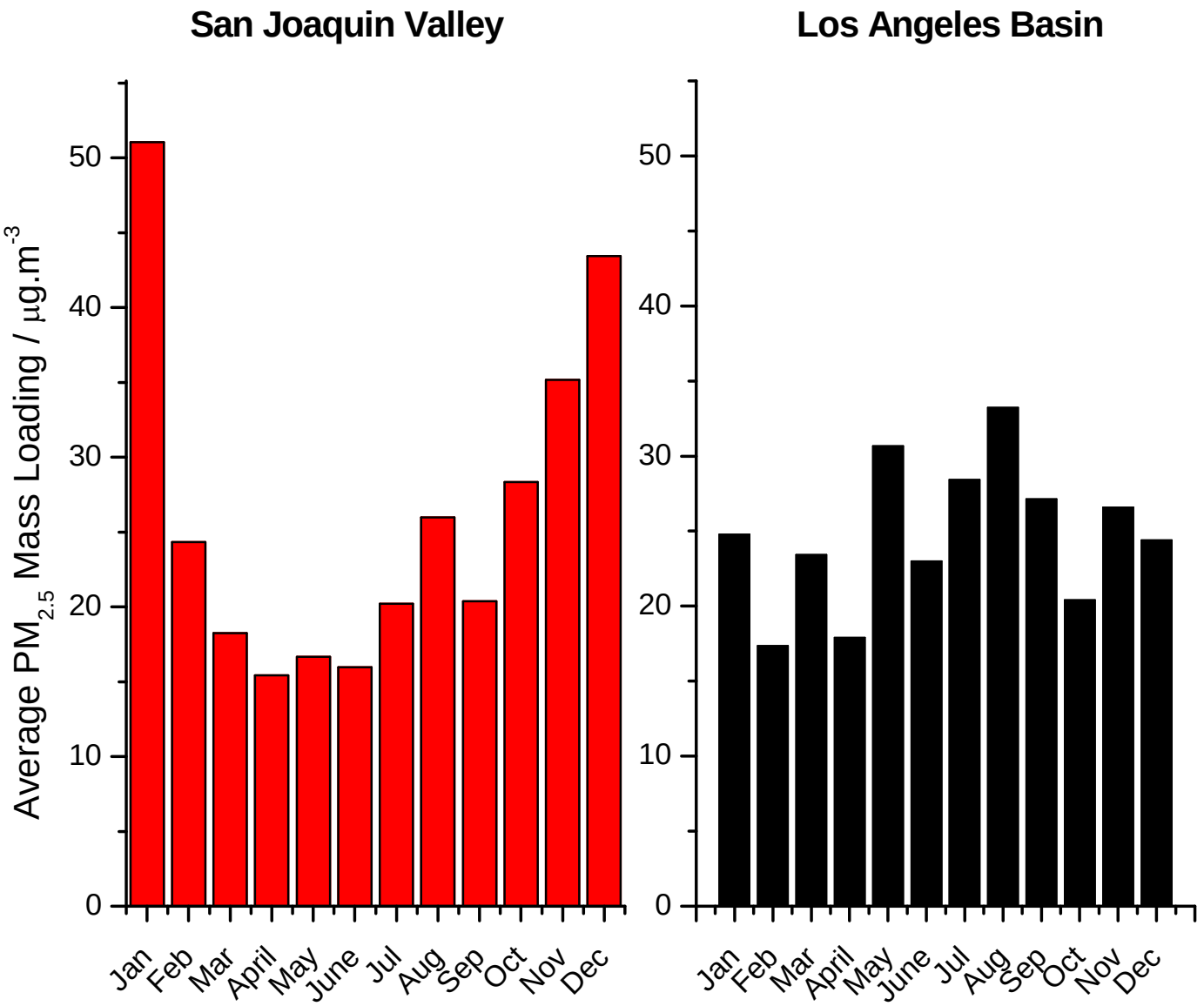


• Role of photochemistry estimated from relative levels of phenanthrene, phenanthraquinone and benzo[g,h,i]perylene.

• ~90% of phenanthraquinone is from phenanthrene oxidation.

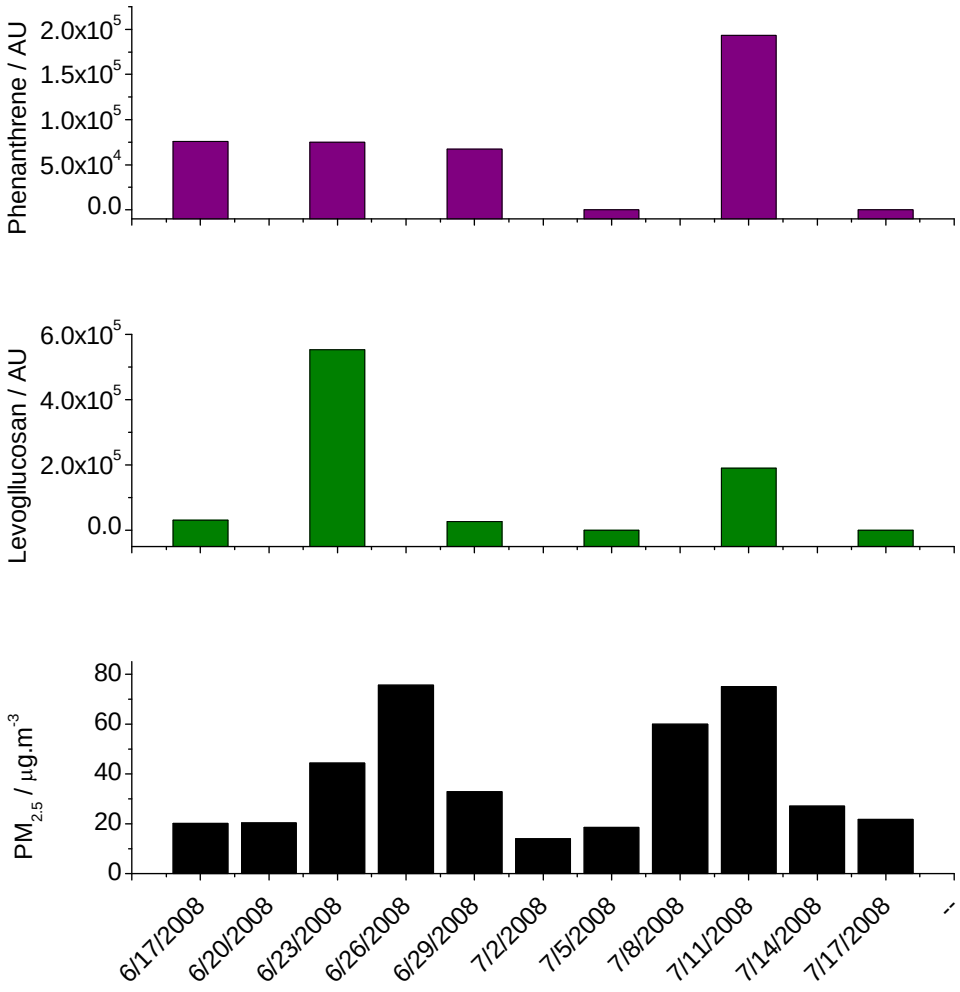
*(Eiguren-Fernandez et al, Atmospheric Environment, 42, 2312-19, **2008.**)*

PM in Southern and Central California not the same



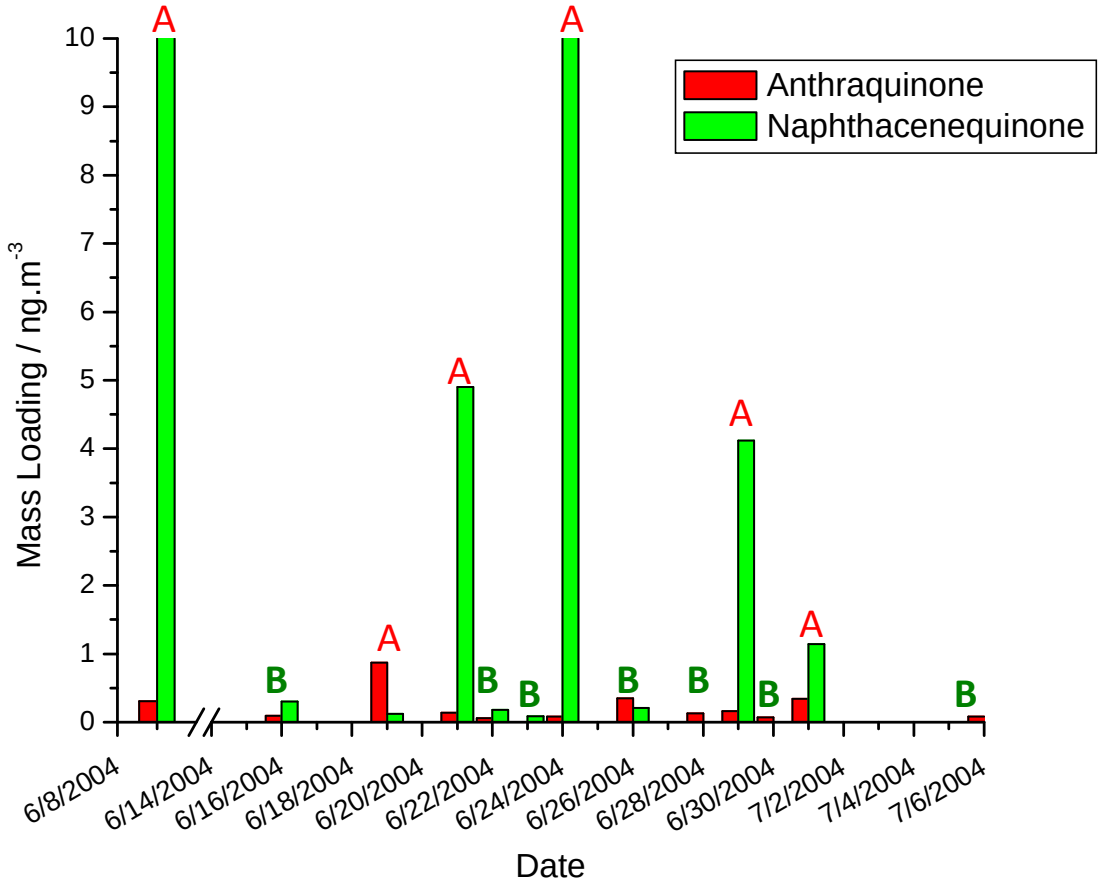
Mass Loadings for 2009 (California Air Resources Board)

Field Data – Summer 2008

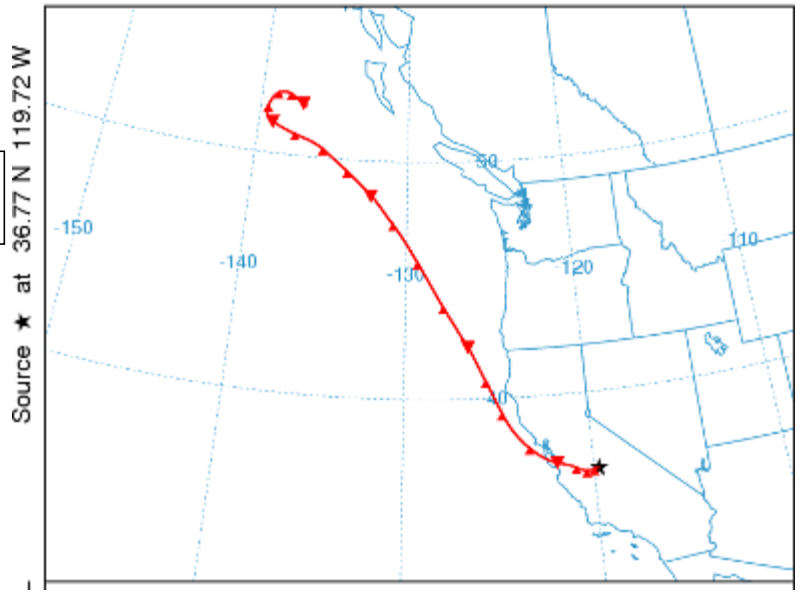


No Phenanthraquinone observed: Not present or all in the gas phase?

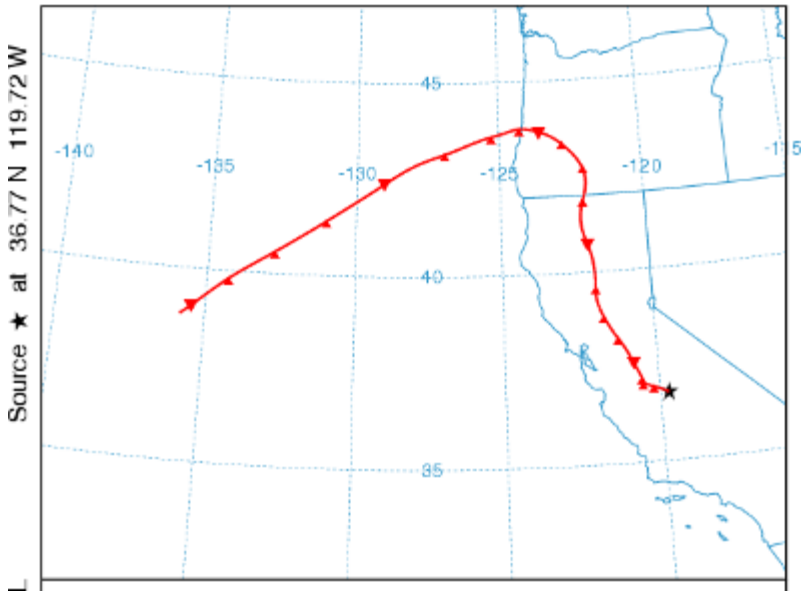
Field Data – Summer 2004



Summer A



Summer B



Daytime vs. Nighttime Chemistry

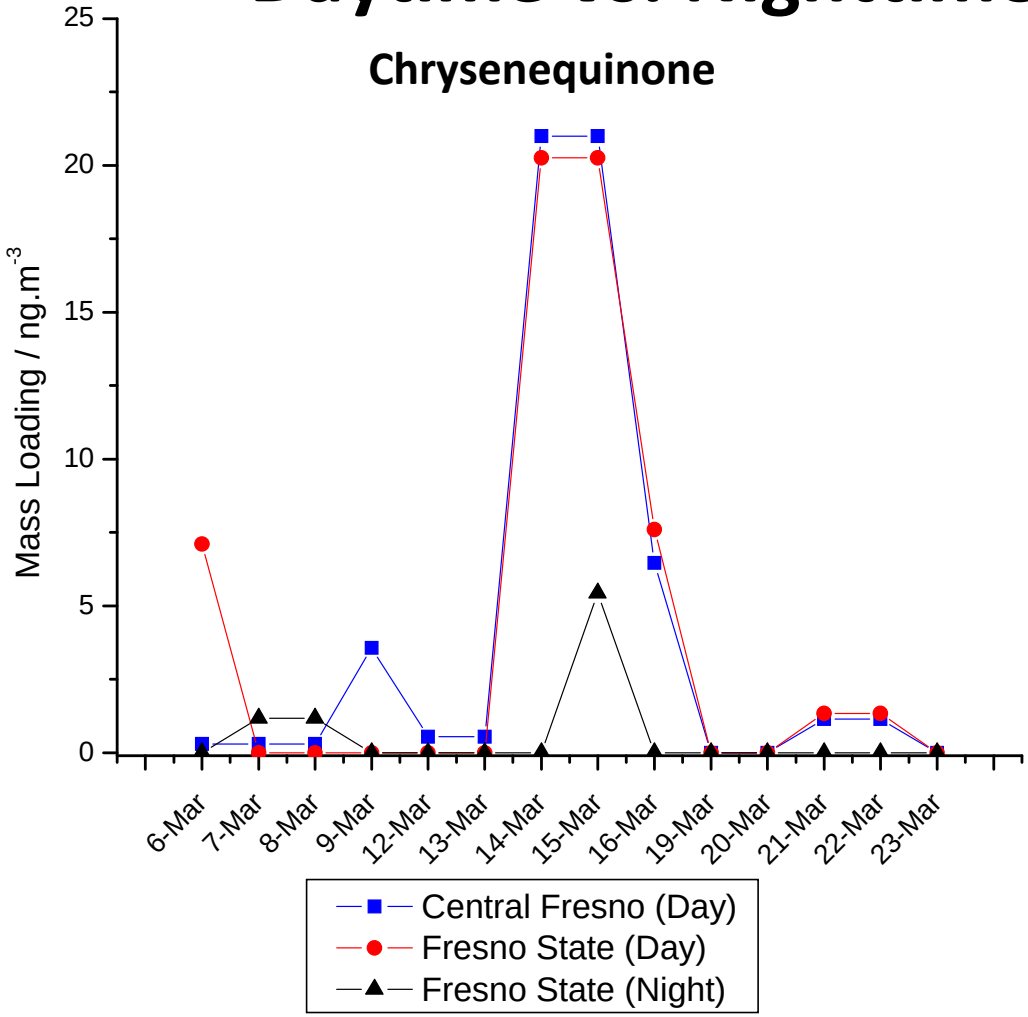
- OH and O_3 are the major daytime oxidants; NO_3 is the main nighttime oxidant.

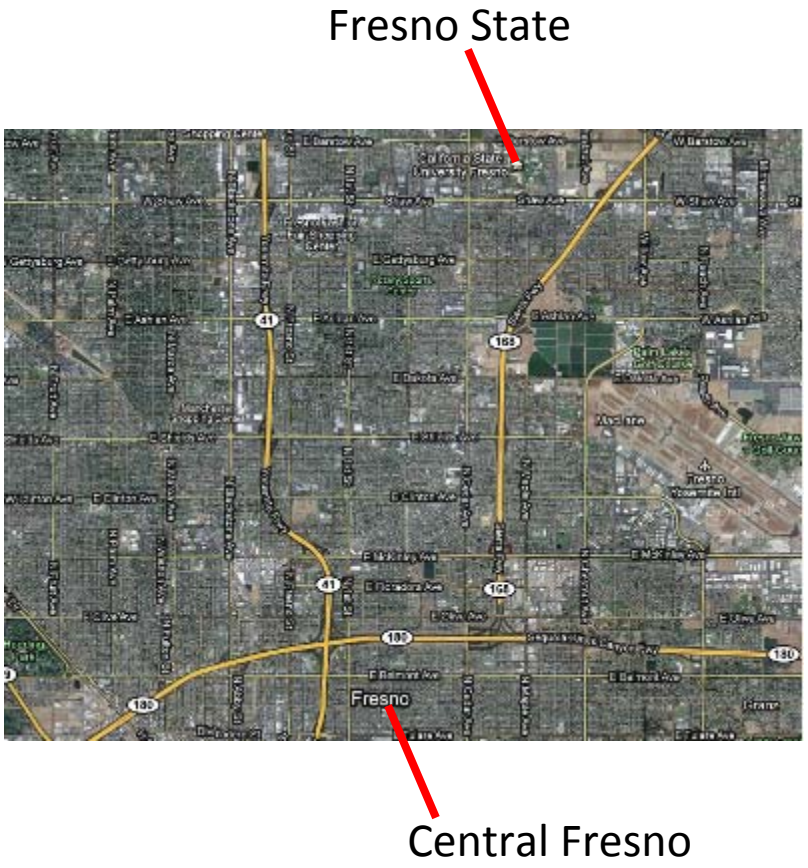
  Gas Phase Phenanthraquinone from Phenanthrene

	Gas Phase Reaction with		
	OH	***NO_3***	***O_3***
Yield	3%	33%	2%
Reaction Rates ($cm^3.mol^{-1}.s^{-1}$)	3.2×10^{-11}	1.2×10^{-13}	4.0×10^{-19}
Formation Rate ($pg.m^{-3}.hr^{-1}$)	80	800	0.2

*(Wang et al, Atmospheric Environment, 41, 2025-35, **2007.**)*

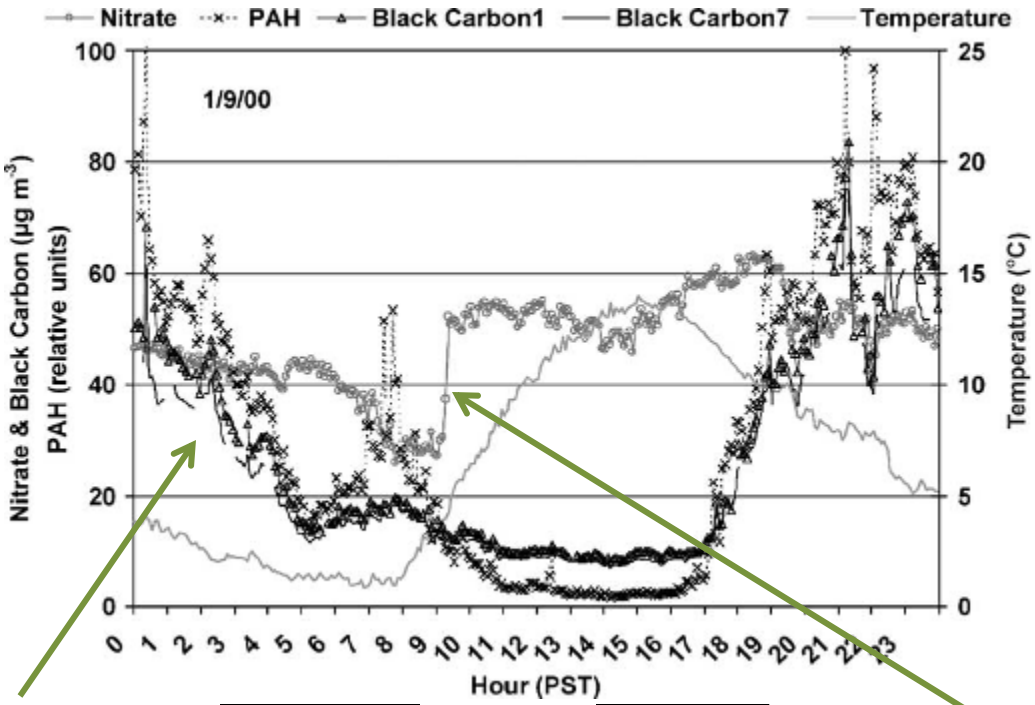
Daytime vs. Nighttime Quinone Levels

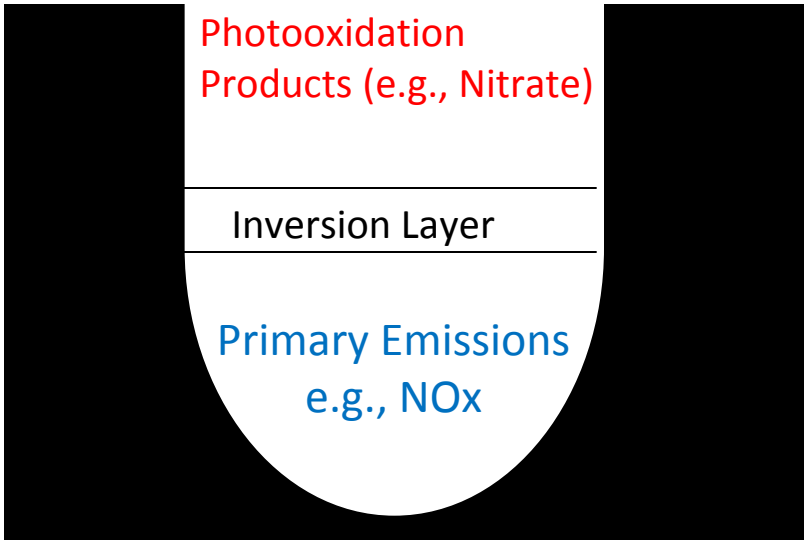


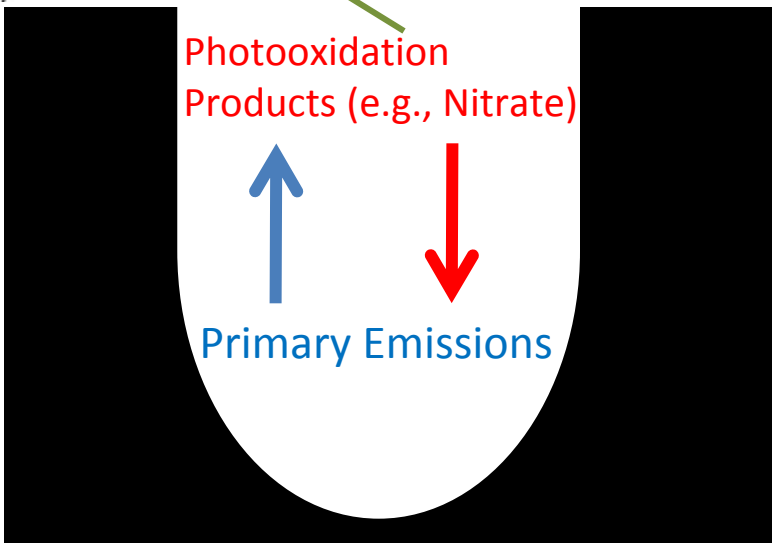


- Samples collected at both sites 6:00 am – 6:00 pm. Samples also collected at Fresno State site 6pm – 6 am.
- Chrysenequinone, Phenanthraquinone and 1,2-Naphthoquinone levels were higher during day (although not statistically significant).

Conceptual Model for Secondary PM Formation







(Watson and Chow, Atmospheric Environment, 36, 177-201, ***2002.****)*

Summary

- Certain quinones such as phenanthraquinone likely play a greater role in ROS production than others.
- Some evidence for quinone production from chemical reactions, but more work is needed to understand this.
- Hydrogen Peroxide in atmospheric particles may play an important role in particle chemistry and health effects, but levels and origins are not well understood.

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