Generation of Hydrogen Peroxide by Urban Aerosols and Behavior of Hydrogen Peroxide in the VACES

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Outline

- Introduction: reactive oxygen species
- Ambient particles generate hydrogen peroxide
- A few related measurements
- Working out the mechanism
- Gas phase hydrogen peroxide in the virtual aerosol concentration enrichment system (VACES)

Reactive Oxygen Species

$O_2 \rightarrow \rightarrow O_2^{\cdot -} \rightarrow \rightarrow HO_2 \rightarrow \rightarrow$

$H_2O_2 \rightarrow \rightarrow OH^{\cdot} \rightarrow \rightarrow H_2O$

Other ROS: ClO^-, $O(^1D)$

Reactive Oxygen Species (ROS) May Play a Role in Particle Toxicity

- **ROS are generated by lung tissues in response to foreign material, but sometimes this process gets out of control, resulting in a state of oxidative stress and inflammation.**
- **ROS have been implicated in respiratory diseases such as asthma, pulmonary and circulatory morbidity and mortality and in carcinogenesis.**

Gas-Liquid Partitioning (Henry's Law)

Hydrogen peroxide, like other gasses, follows Henry's Law:

$$[X]_{aq} = H_x P_x(\text{atm})$$

- $[X]_{aq}$ = concentration of X in liquid phase
- H_x=The Henry's Law Coefficient for X;
- H(hydrogen peroxide) = 10^5 M/atmosphere
- P_x= The gas phase concentration of X, in atmospheres.

Particles Provide a Way to Deliver H_2O_2 to the Lungs

- **Most gas-phase H_2O_2 should be absorbed in the upper airways, but particles can deliver peroxide to the lungs.**
- **Due to ppb-levels of hydrogen peroxide in air, peroxides in airborne water should be ~ 0.1 mM.**
- **Our measurements indicate ambient particles *generate* H_2O_2 in aqueous solution, producing levels equivalent to > 50 mM in aerosol liquid water.**

Does H_2O_2 Contribute to Particle Associated Health Effects? *In Vitro and in Vivo Results*

- Exposure of lung epithelial cells to 20 pM - 1 μM hydrogen peroxide solutions results in significant cell damage.[1]

- Morio et al. (2001) exposed rats to ammonium sulfate aerosols (100-200 × ambient), and H_2O_2 (10 - 100 × ambient) alone or in combination, for 2 hours. These aerosols contained 10-180 ng/m^3 H_2O_2, according to our measurements & consistent with Henry's law.

- Ambient aerosols generate H_2O_2 while ammonium sulfate aerosols do not. Ambient aerosols have 10-~120 ng/m^3 H_2O_2 associated with them.

In Vivo data are Consistent with Significant Effects from Aerosol-Generated ROS at Levels Common in Urban Areas

- **All but the most minor effects were observed only when rats were exposed to H_2O_2 and particles in combination.**

- **Effects:**
  - **Increased numbers of neutrophils in pulmonary capillaries.**
  - **Production of tumor necrosis factor α by alveolar macrophages.**
  - **Increased production of superoxide by alveolar macrophages.**
  - **Increased expression of antioxidant heme oxygenase-1 by stimulated alveolar macrophages**

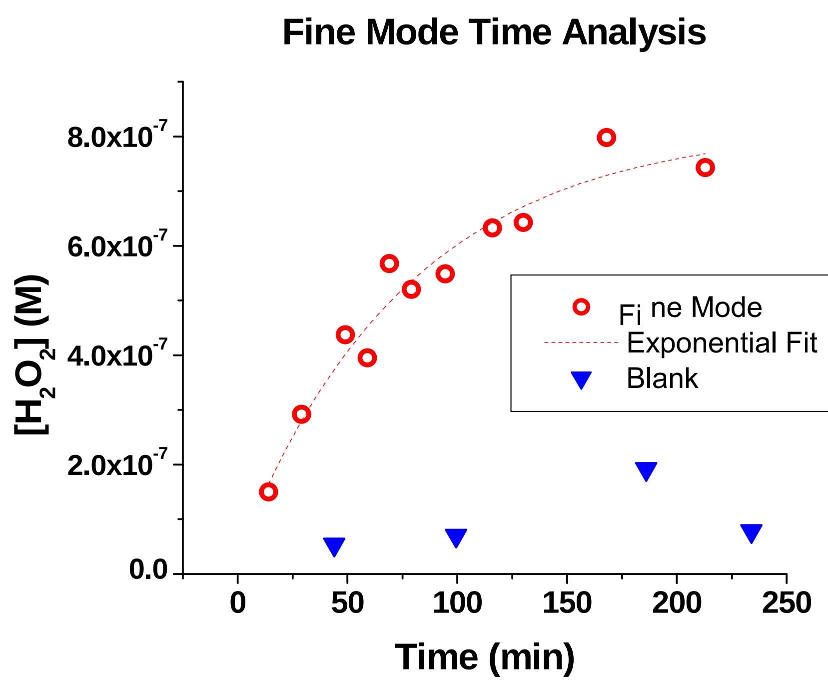
A role in aerosol aging?

The quantity of H_2O_2 produced by ambient particles is comparable (larger) than the flux of OH radicals to the surface of fine mode particles

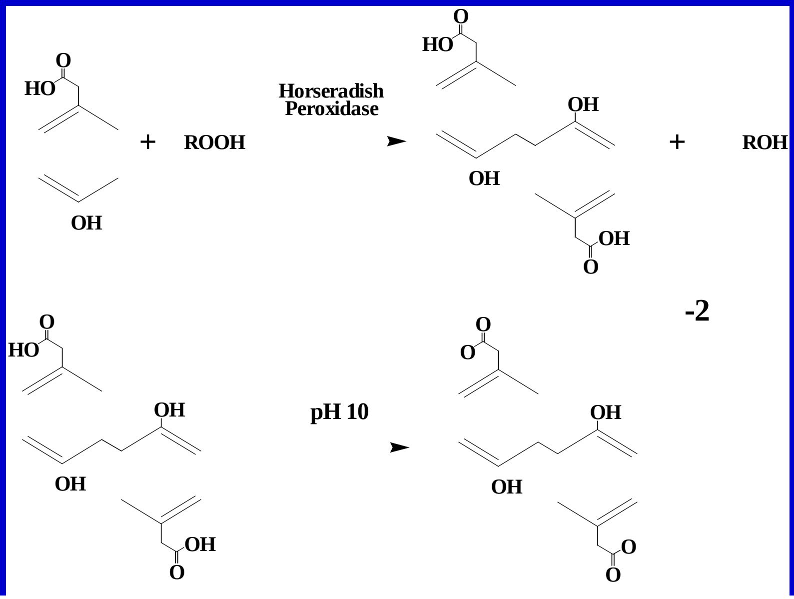
Field Measurements of Particle-Associated Hydrogen Peroxide

Measurement of Peroxides Associated with Aerosols

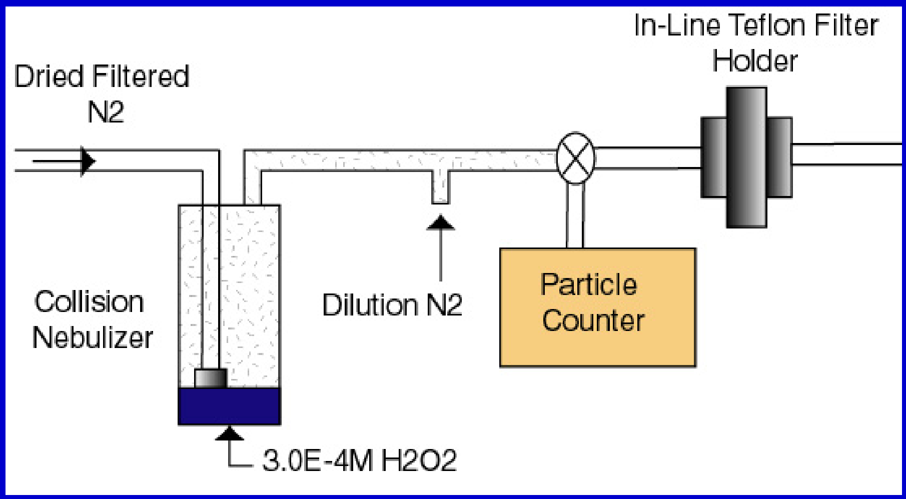
Collect particles on Teflon filters, add stripping solution (0.1 mM Na_2EDTA, various pHs, 4 mL), extract for two hours with gentle agitation.

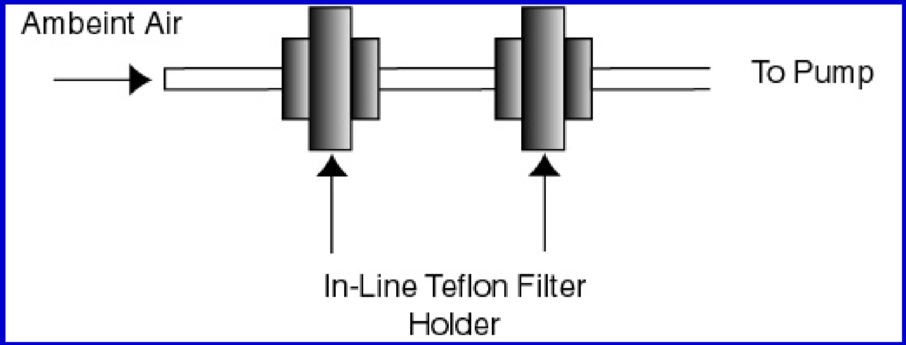


Monitor H_2O_2 using HPLC/fluorescence via the reaction of H_2O_2 with horseradish peroxidase and p-hydroxyphenyl-acetic acid



Validation of Aerosol Sampling Method

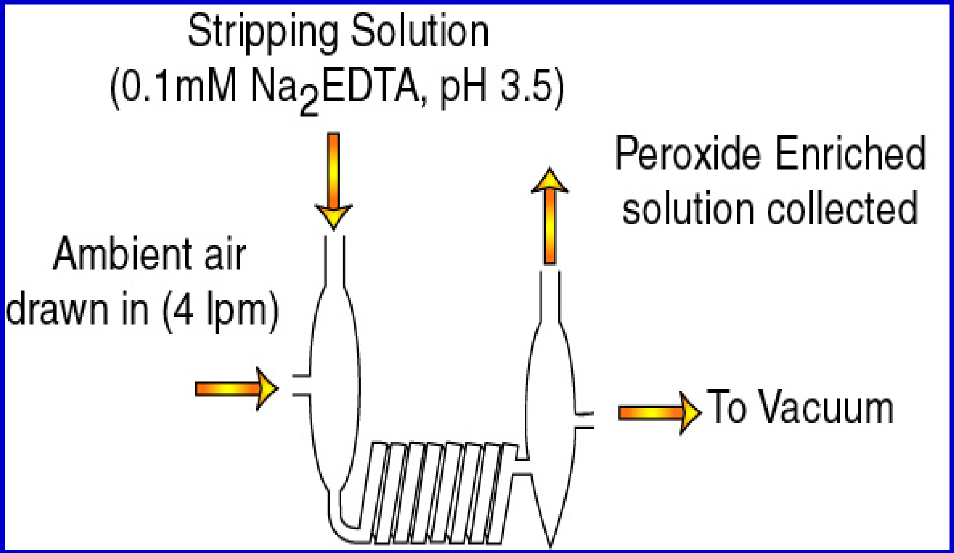




- Aqueous H_2O_2 aerosols were generated with a Collison nebulizer, diluted, collected on filters and extracted. Final [H_2O_2] were within 20 % of the expected values, indicating that H_2O_2 solutions do not decompose appreciably on Teflon filters.
- Gas Phase H_2O_2 is not collected on second filter

Hasson, A.S. and Paulson, S.E. *J. Aerosol. Sci*. **34**, 2003, 459

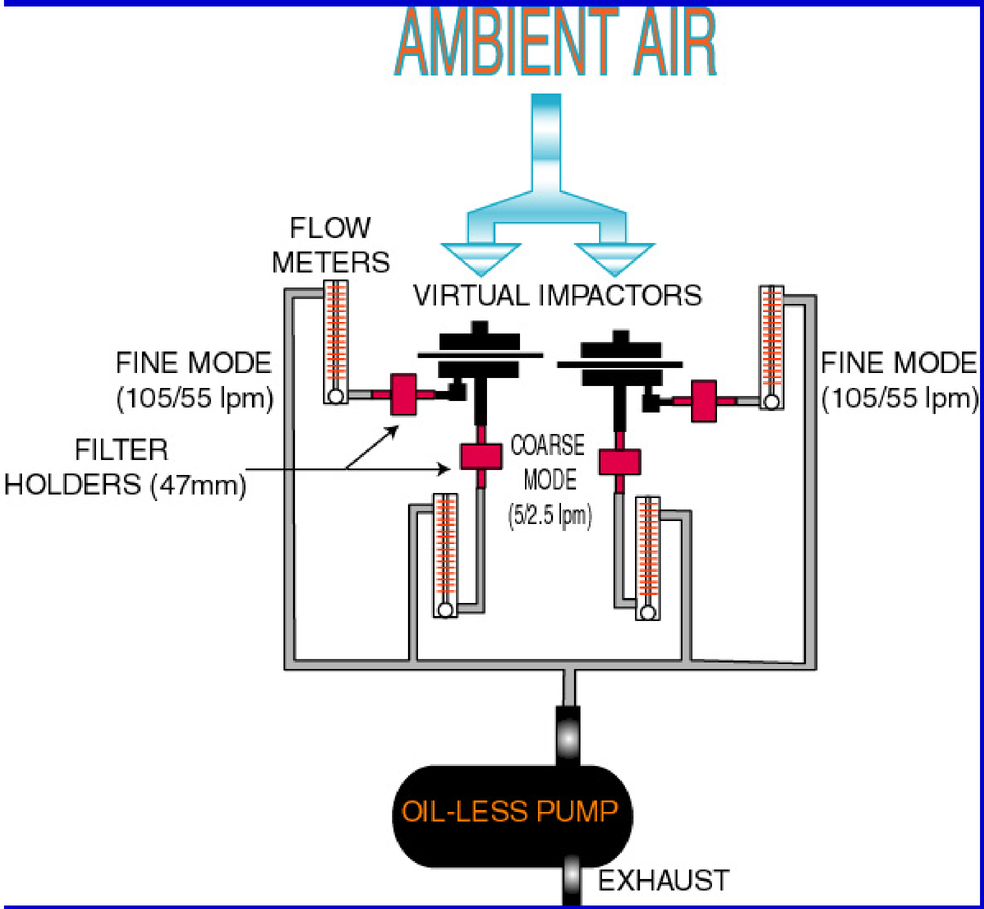
PEROXIDE SAMPLING: GAS PHASE

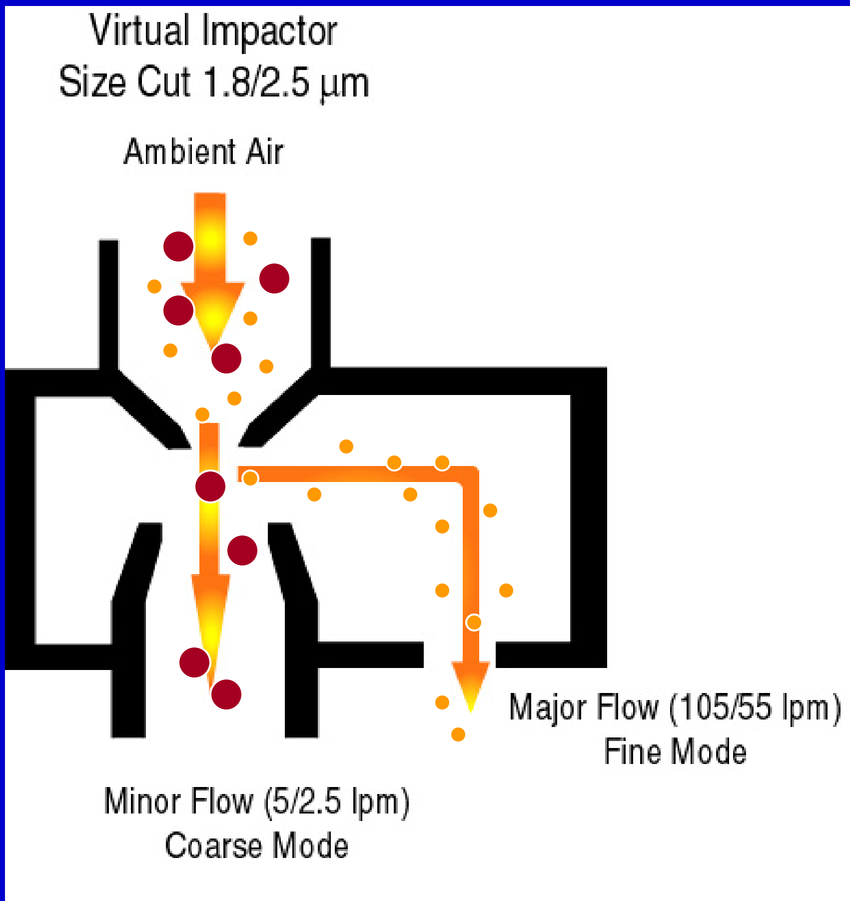


- **Gas phase peroxides are partitioned into the aqueous phase**
- **Collection efficiency >95%**

Source: Hartkamp & Bachhausen *Atmos. Environ.*, 1987, **21**, 2207

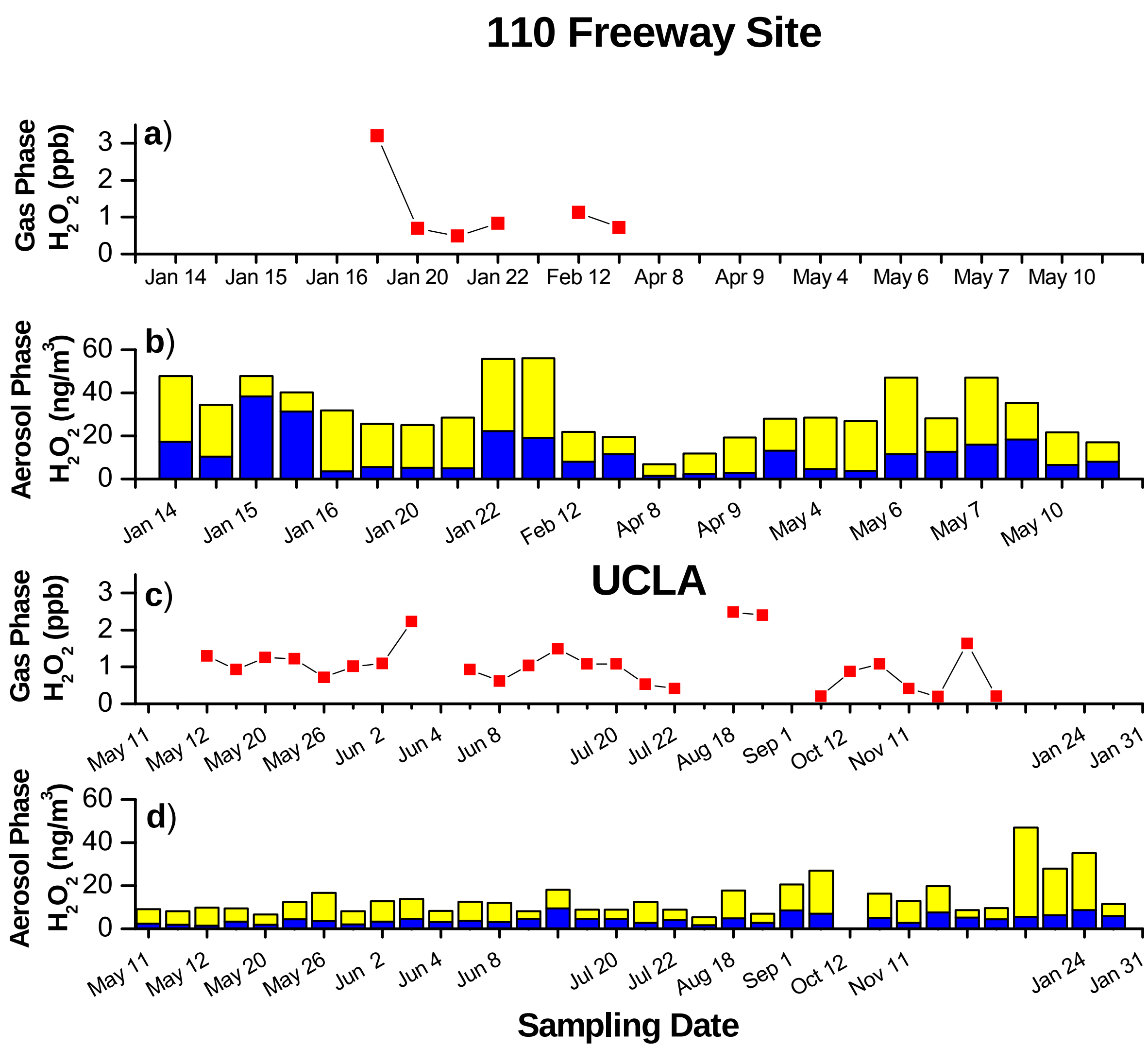
Virtual Impactor Sample Collection





H_2O_2 Generation by Aerosols Varies by Site

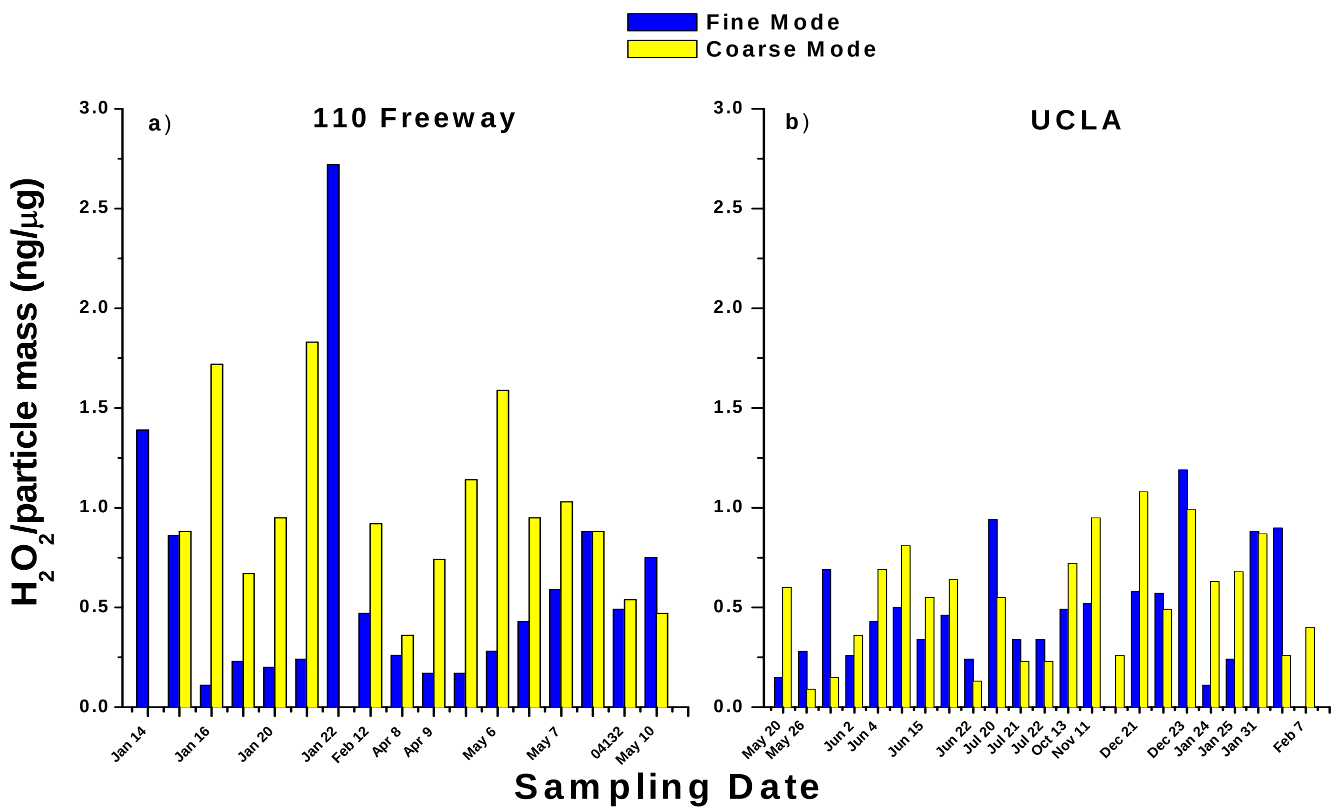
Fine (blue), **Coarse** (yellow) Hydrogen Peroxide



H_2O_2 Generation by Aerosols Normalized to Mass Varies by Site

Fine (blue), **Coarse** (yellow)

Hydrogen Peroxide

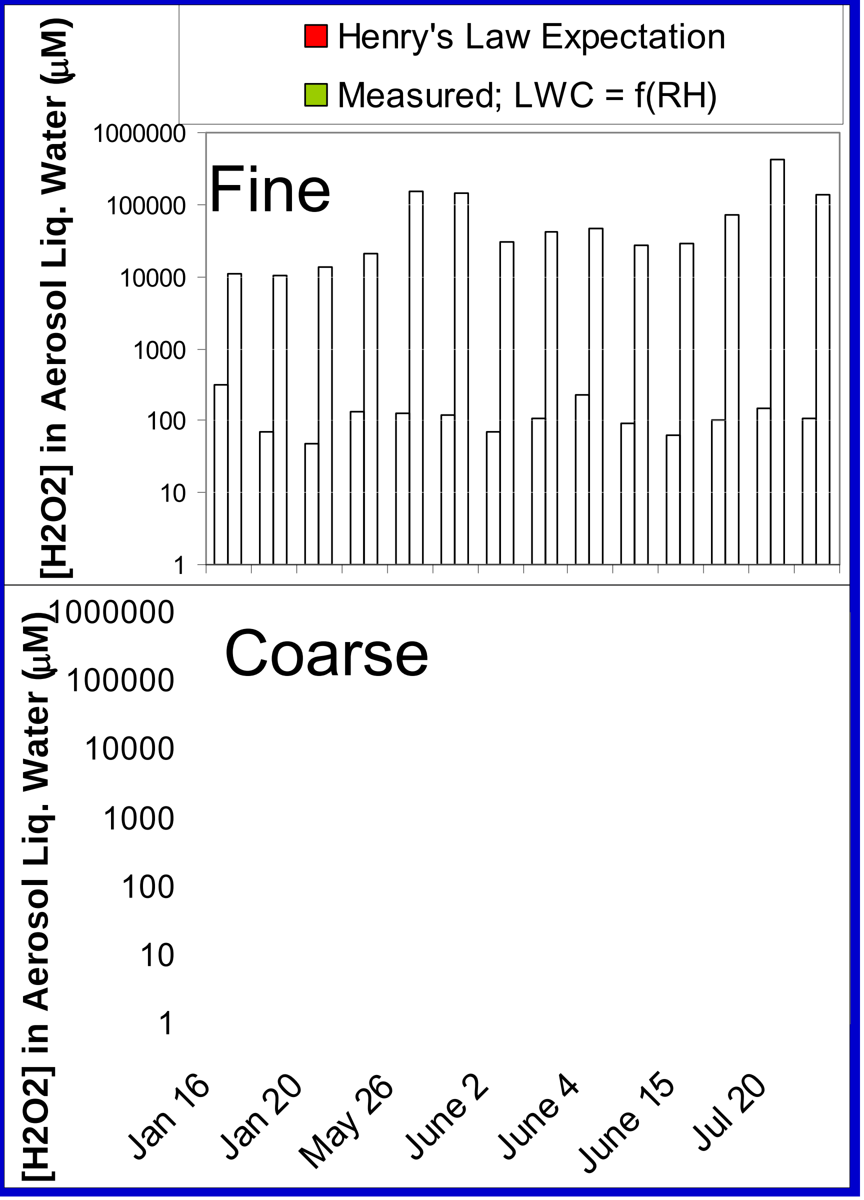


Hydrogen Peroxide is Generated in Aqueous Solution

Peroxides exceed levels predicted by Henry's law by a factor of ~700.

Henry's Law Expectation **(red):**
$[H_2O_2]$ = P_{H2O2} (measured) × H_{H2O2} (known)

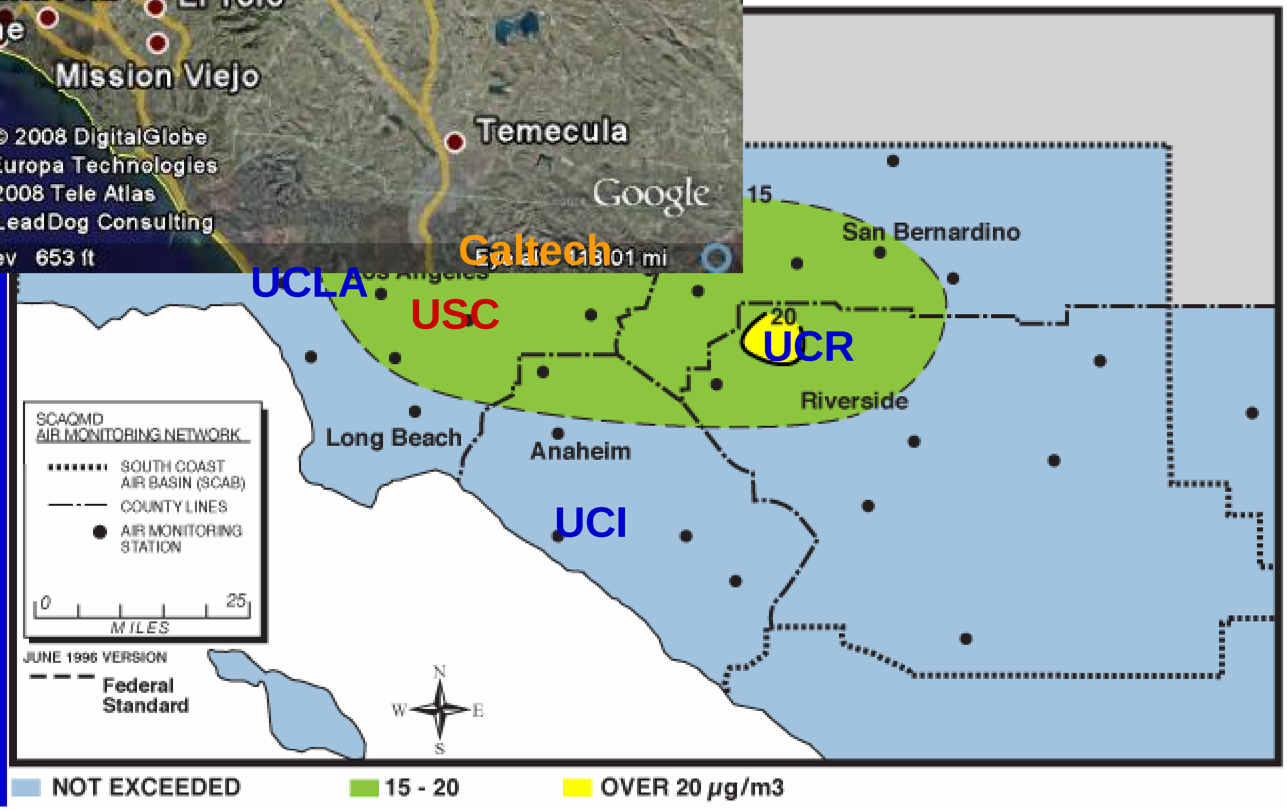
Equivalent measured aerosol H_2O_2 "concentration" **= measured aerosol phase H_2O_2 ÷ aerosol liquid water content (which is calculated from the measured aerosol mass × f(RH)*)**



*LWC dependence on RH from Slone and Wolff, 1985.

More Field Data

Sampling Sites



2006 Annually Averaged Fine Particles (μg/m^3); Standard = 15 (μg/m^3)

Summary of Multi-Day Averages

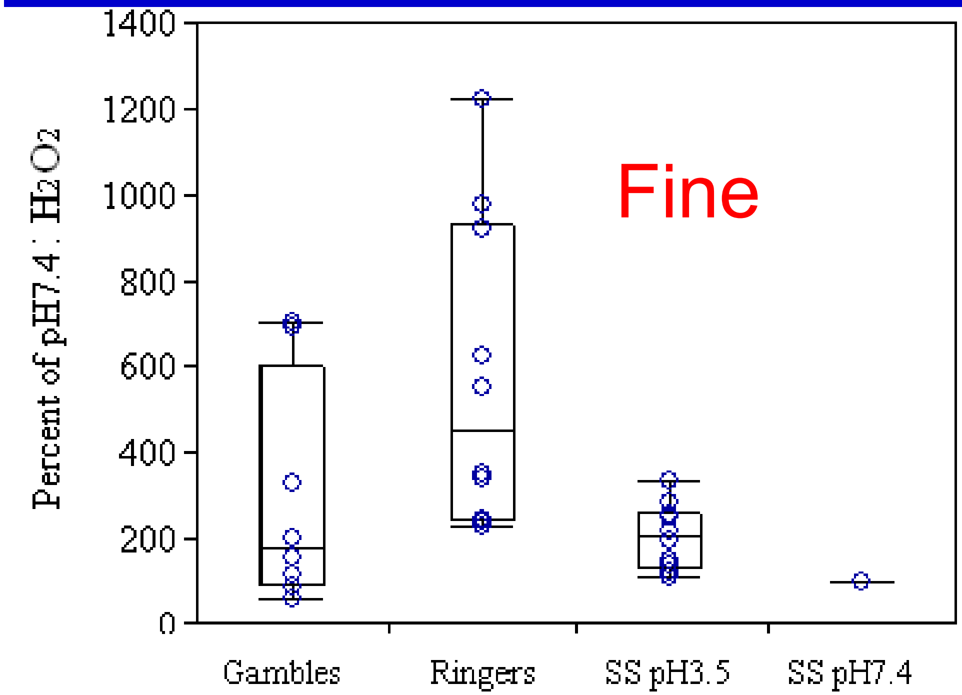
	UCLA 05	110 Fwy	UCLA 09 fine Riv. 1 crse	Riv. 2 (Orange Grove)
Ultrafines (PM 0.15 to 0.18)				
Mass (μg/m^3)	~0.8	--	--	--
H_2O_2 (ng/m^3)	~0.4	--	--	0.9 ±0.35
H_2O_2/mass	~0.5	--	--	--
PM 2.5				
Mass (μg/m^3)	13 ± 10	23 ± 8	18 ± 7 (UCLA)	19 ± 6
H_2O_2 (ng/m^3)	5.4 ± 6	12 ± 9	1.8 ± 1.4	8 ± 8
H_2O_2/mass**	0.42 ± 0.3*	0.58 ± 0.3	0.11 ± 0.08	0.5 ± 0.6*
PM > 2.5				
Mass (μg/m^3)	26 ± 15	27 ± 33	98 ± 26 (Riv)	50 ± 21
H_2O_2 (ng/m^3)	13 ± 10	20 ± 9	33 ± 13	17 ± 8
H_2O_2/mass**	0.58 ± 0.3*	1.05 ± 0.3	0.37 ± 0.2*	0.48 ± 0.32

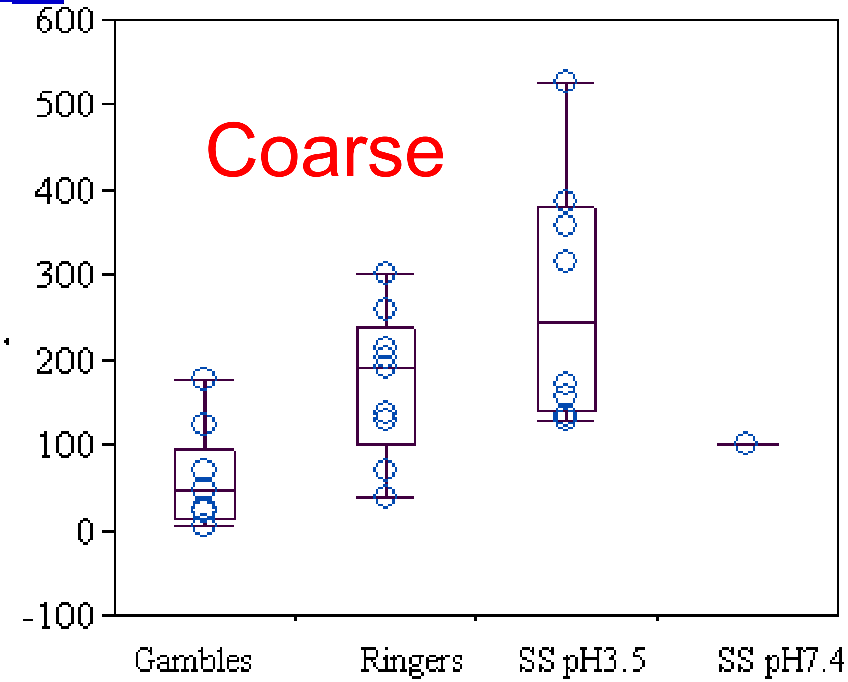
*Correlation between H_2O_2 and particle mass not significant

** in ng/μg

Extraction in Simulated Lung Fluid, Normalized to Extraction at pH 7.4

Chemical	Molar Concentration (mM) Gamble's	Ringer's
NaCl	116	114
NH_4Cl	10	-
$NaHCO_3$	27	31
Na_2HPO_4	1.2	14.6
NaH_2PO_4	-	2
$Na_3Citrate$	0.2	-
Glycine	6	-
$CaCl_2$	0.2	-
pH	7.4	7.4
Ionic Strength	160	190

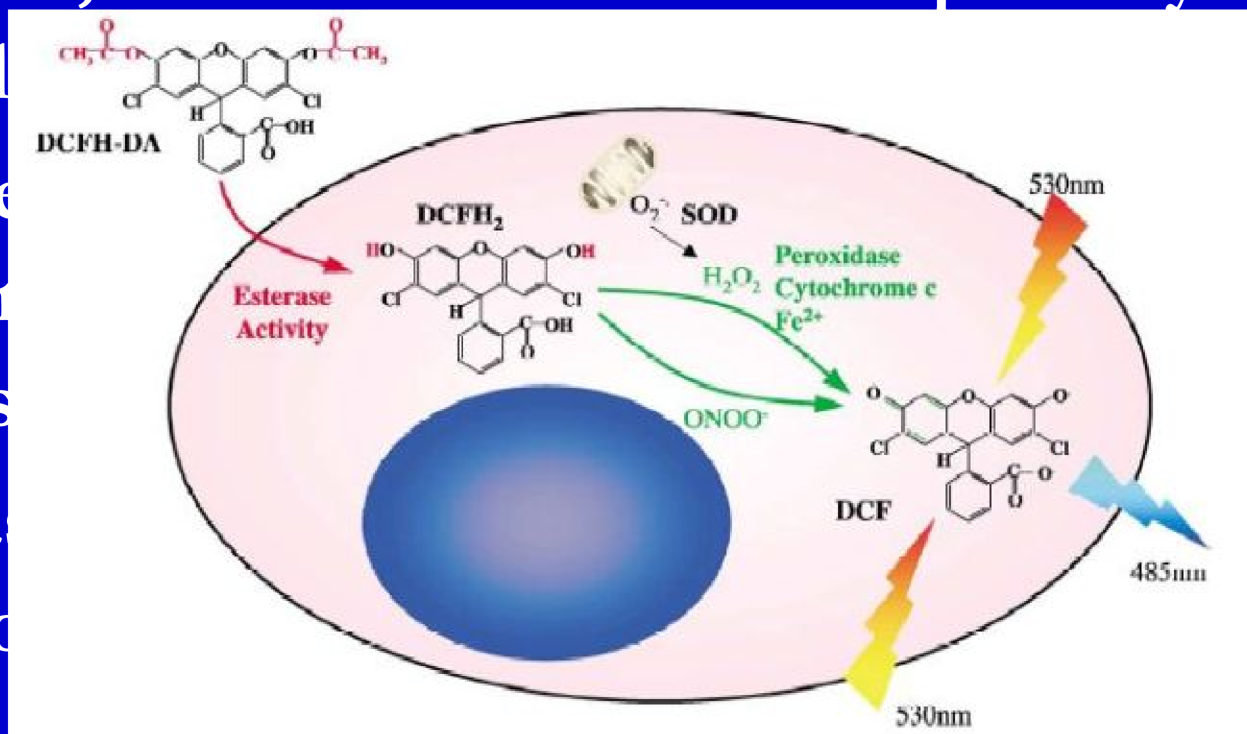




Closely Related Measurements

Dichlorofluorescin Assay for ROS

- **Used to monitor ROS in cells since at least the early 1990's**
- **Due to its indiscriminate nature to various free radicals, DCF can be useful in quantifying overal**
- **Fluore oxida with others**
- **The a aeroso**



Sources: MEDICINA INTERNA E TERAPIA MEDICA, H. WANG & J. A. JOSEPH, 1999

H_2O_2 and ROS generation by ambient coarse mode aerosols at several locations

Site		PM Mass ($\mu g/m^3$)	PM ROS or H_2O_2 (ng/m3)	PM ROS or H_2O_2 /Mass (ng/µg)	Ref.
Riverside, CA	upwind	46 ± 22	17 ± 8	0.48 ± 0.32	UCLA
	downwind	97 ± 27	34 ± 14	0.37 ± 0.18	
Los Angeles, CA	UCLA campus	26 ± 15	14 ± 10	0.58 ± 0.3	UCLA
	110 freeway	27 ± 33	20 ± 9	1.05 ± 0.3	
Taipei, Taiwan	sidewalk	8 ± 3	2 ± 1	0.28 ± 0.11	Hung and Wang 2001
	underpass	14 ± 8	6	0.43 ± 0.15	
Rubidoux, CA	urban	-	26	-	Venkatachari et al 2005
Flushing, NY	campus	-	5	-	“ 2007

White = H_2O_2 Orange = ROS by dichlorofluorescin

H_2O_2 generation by ambient fine PM

Site		PM Mass ($\mu g/m^3$)	PM H_2O_2 (ng/m^3)	PM H_2O_2/Mass ($ng/\mu g$)	Ref.
Riverside, CA	(orange grv)	19 ± 6	8 ± 7	0.49 ± 0.4	UCLA Wang et al
Los Angeles, CA	UCLA 2005	15 ± 17	4 ± 2	0.50 ± 0.28	UCLA Arellanes et al., Wang et al.
	UCLA 2009	18 ± 7	1.8 ± 1.4	0.11 ± 0.08	
	110 freeway	27 ± 22	8 ± 6	0.45 ± 0.25	
Taipei, China	sidewalk	16 ± 8	11 ± 8	0.57 ± 0.16	Hung & Wang
	underpass	99 ± 27	37	0.37 ± 0.18	
Singapore	campus	19 ± 2	194 ± 70	10 ± 3	See et al.
	curbside	33 ± 6	513 ± 25	16 ± 2	
Rubidoux, CA	urban		193		Venkata-chari et al
Flushing, NY	campus		29		“

White = H_2O_2 Orange = ROS by dichlorofluorescin

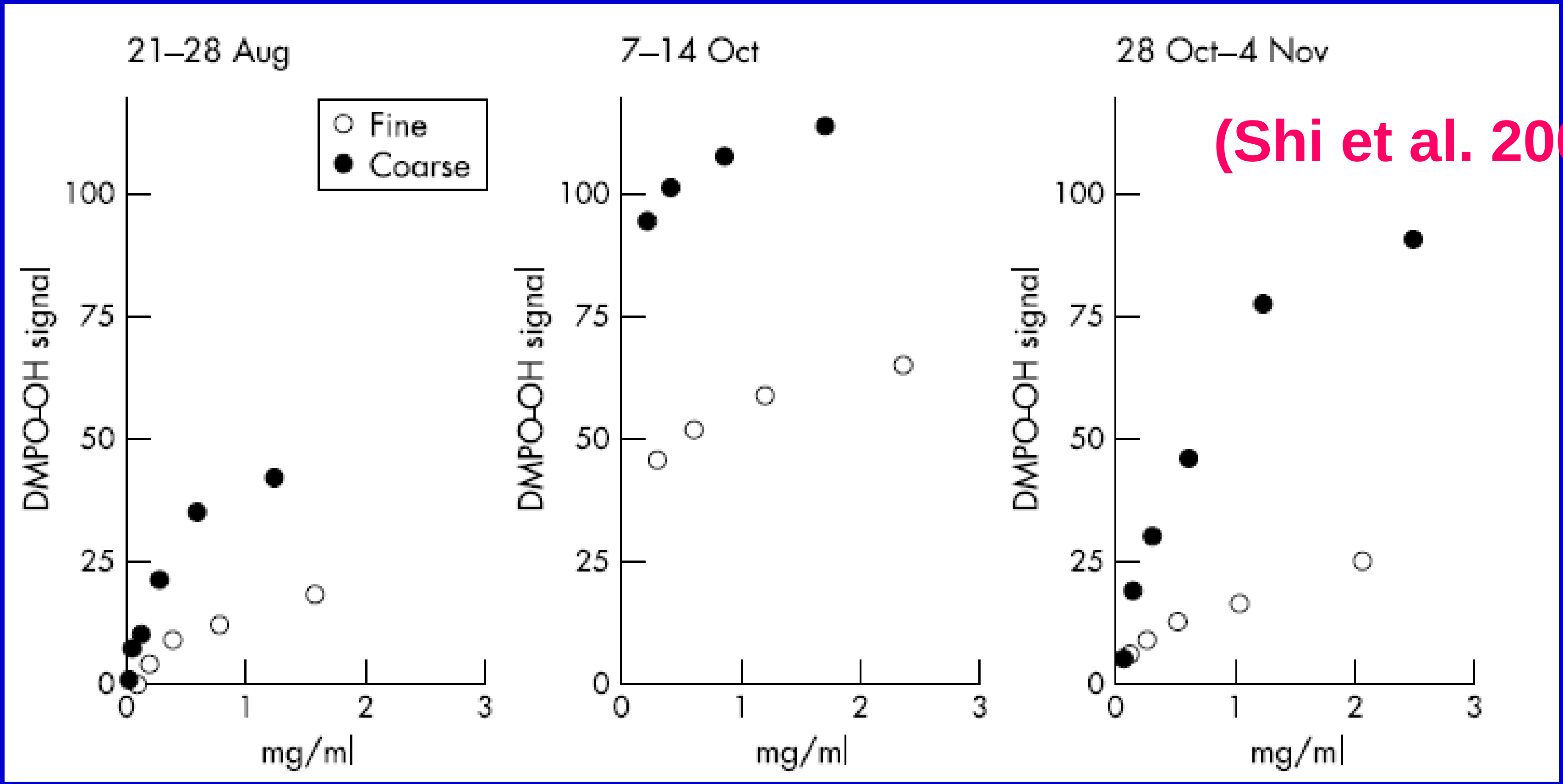
OH radical assays: usually add and electron donor or H_2O_2, detect w/ scavenger technique.

- Electron spin resonance
  - e.g., Shi et al. 2003, others
- 2-Deoxyribose + OH → Malondialdehyde
  - e.g., Ball et al. 2000
- Benzoate + OH → p-Hydroxybenzoate
  - e.g., Vidrio et al. 2008)
- Others (Valavanidis et al. 2005, DiStefano et al. 2009)

Methods are mostly sensitive to transition metals;

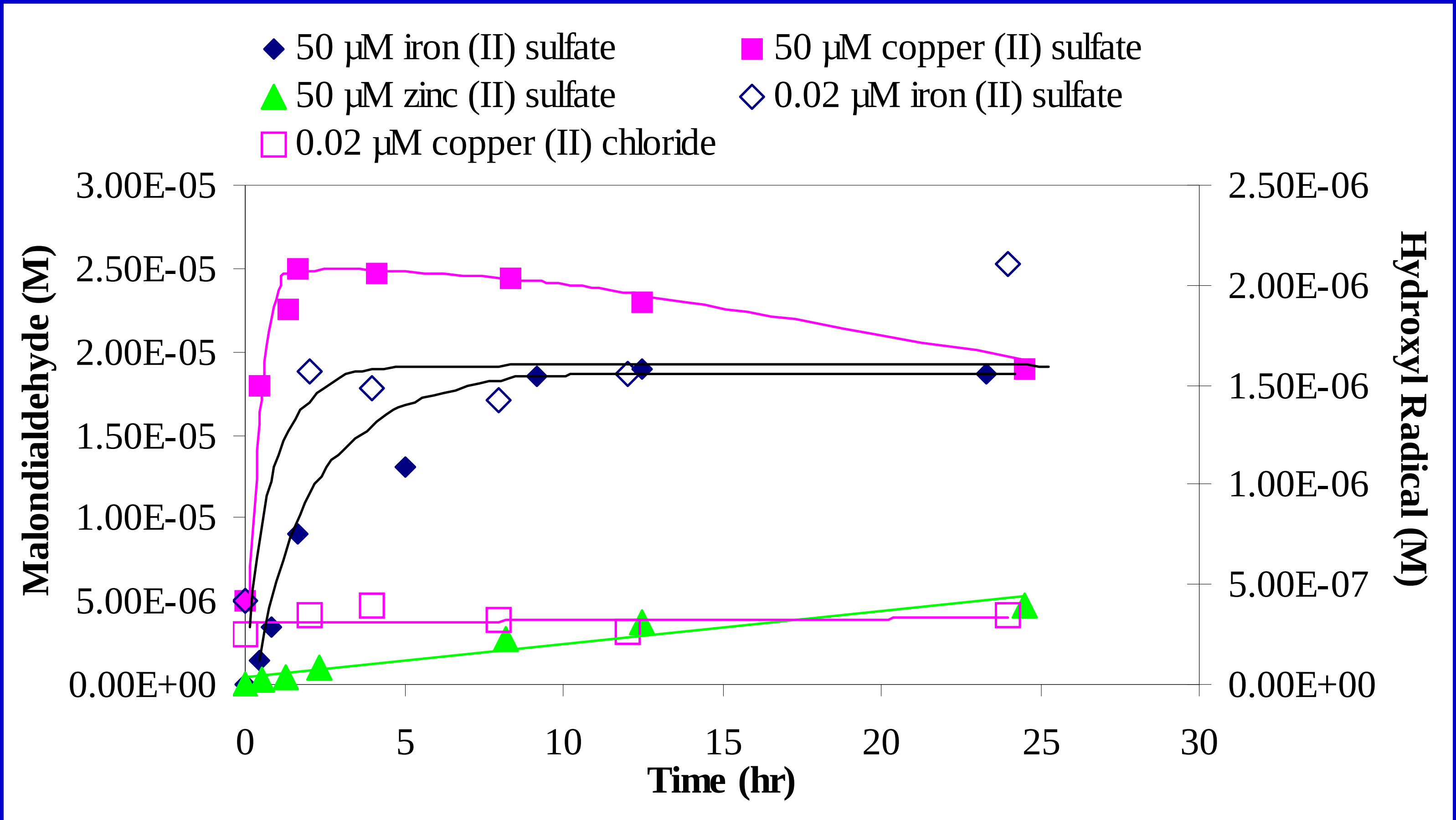
e.g., $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$

Transition metal mediated OH formation with added H_2O_2 is larger in coarse particles



Hydroxyl radical generation by serial dilutions of suspensions of coarse and fine PM

Metal-mediated OH generation with added ascorbate or H_2O_2 (large excess)



Filled symbols: left axis, study from Ball et al. (2000)

Open symbols: right axis, study from Vidrio et al. (2008)

What Generates the Oxidants?

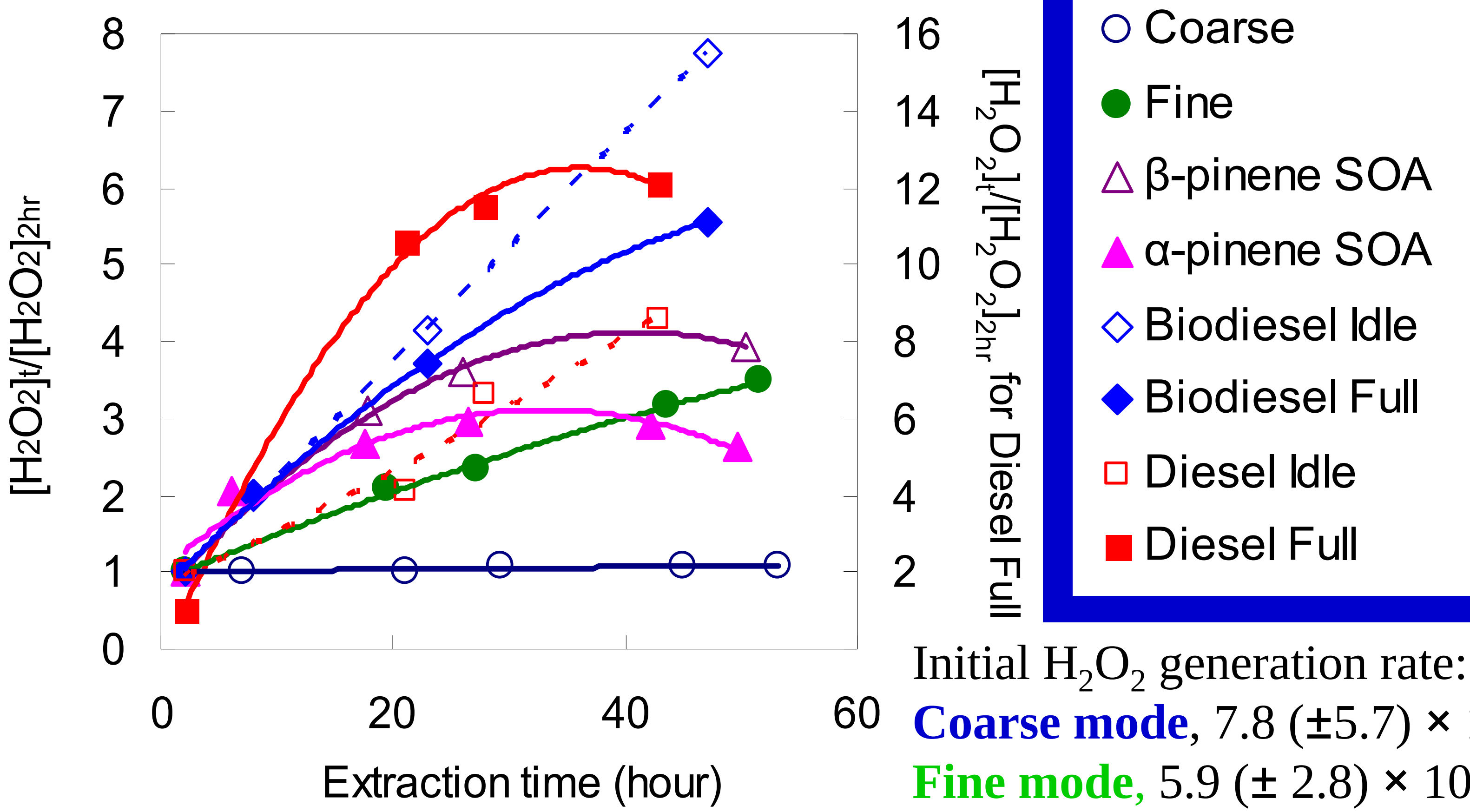
What is the Mechanism?

- ***Redox chemistry.*** **Quinones and metals (such as $Fe^{2+/3+}$, $Cu^{+/2+}$) mediate redox chemistry that could generate H_2O_2.**

- **Several other sources, many likely minor: decomposition of larger hydroperoxides and other complexes, high ionic strength-induced enhancements to gas-liquid partitioning, and photochemistry.**

- **Data suggest different mechanisms for the fine and coarse modes.**

H_2O_2 Generation past t = 2 hours, normalized to the 2 hour level



Initial H_2O_2 generation rate:

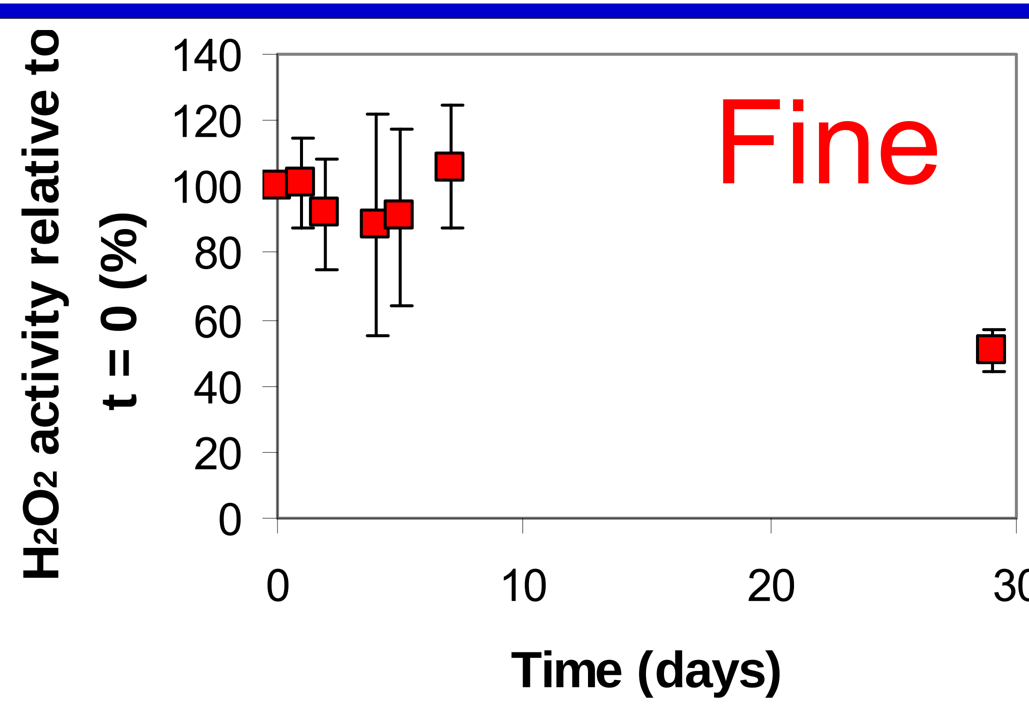
Coarse mode, 7.8 (±5.7) × 10^{-8} M min^{-1}

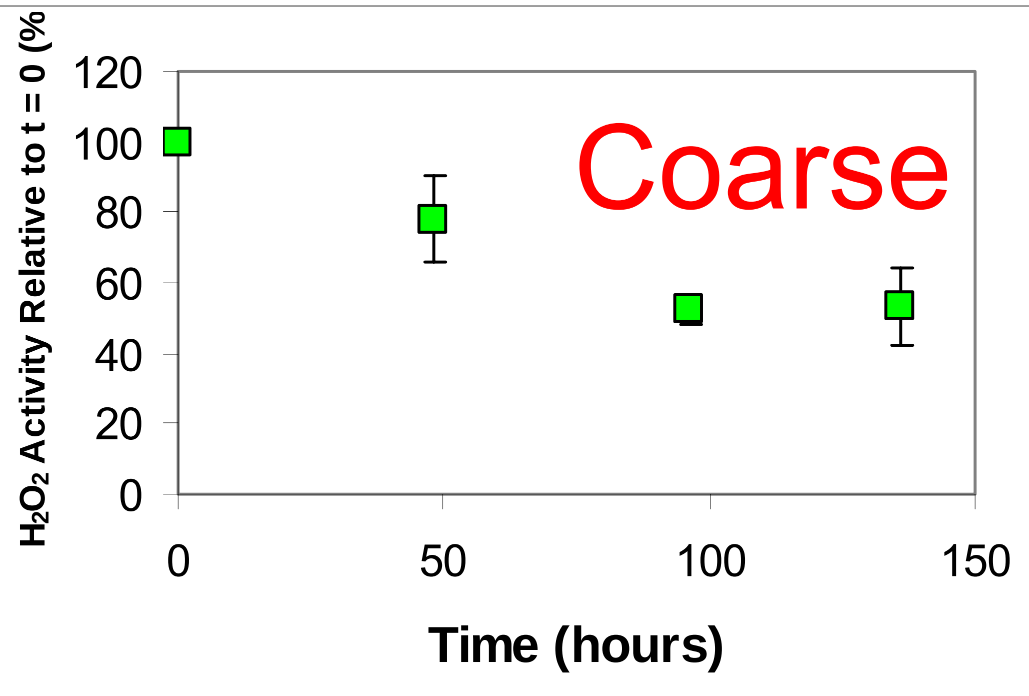
Fine mode, 5.9 (± 2.8) × 10^{-9} M min^{-1}

Quinones, 5 × 10^{-9}-1× 10^{-7} M min^{-1}

Iron/copper/zinc solution (OH radical with added H_2O_2) (0.14-20) × 10^{-8} M min^{-1} (with added H_2O_2

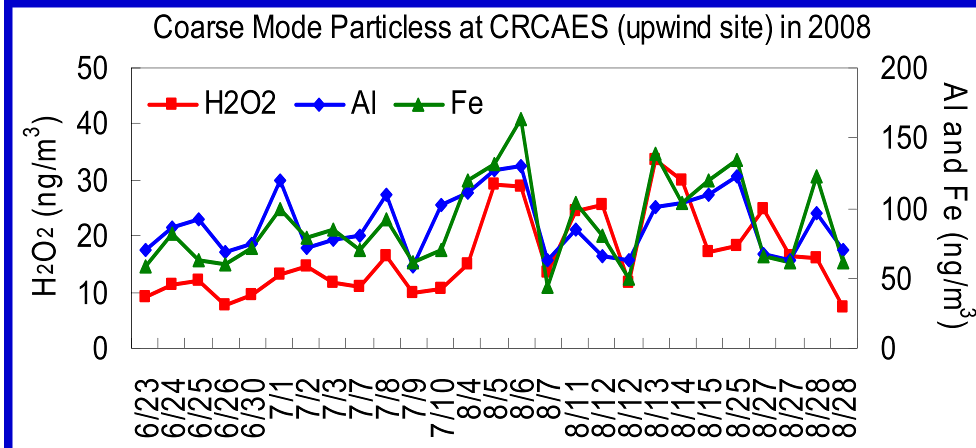
Signal Persistence Over Days to Weeks

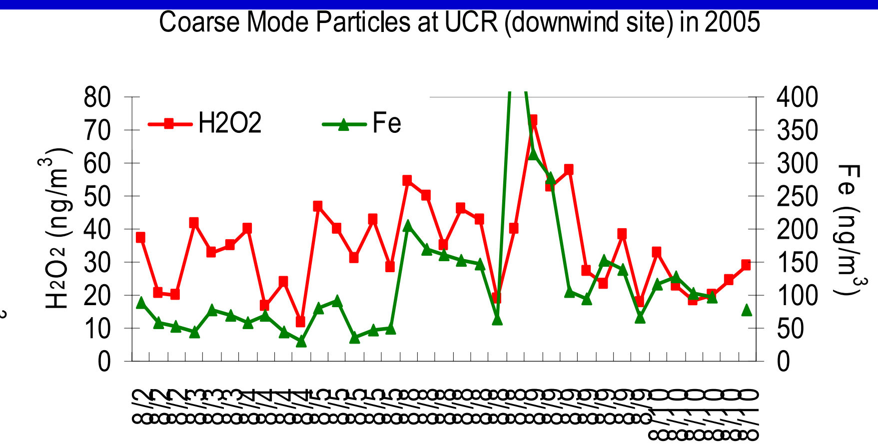




Coarse Particles: Transition Metals

Evidence for metal-mediated H_2O_2 production in the Coarse mode

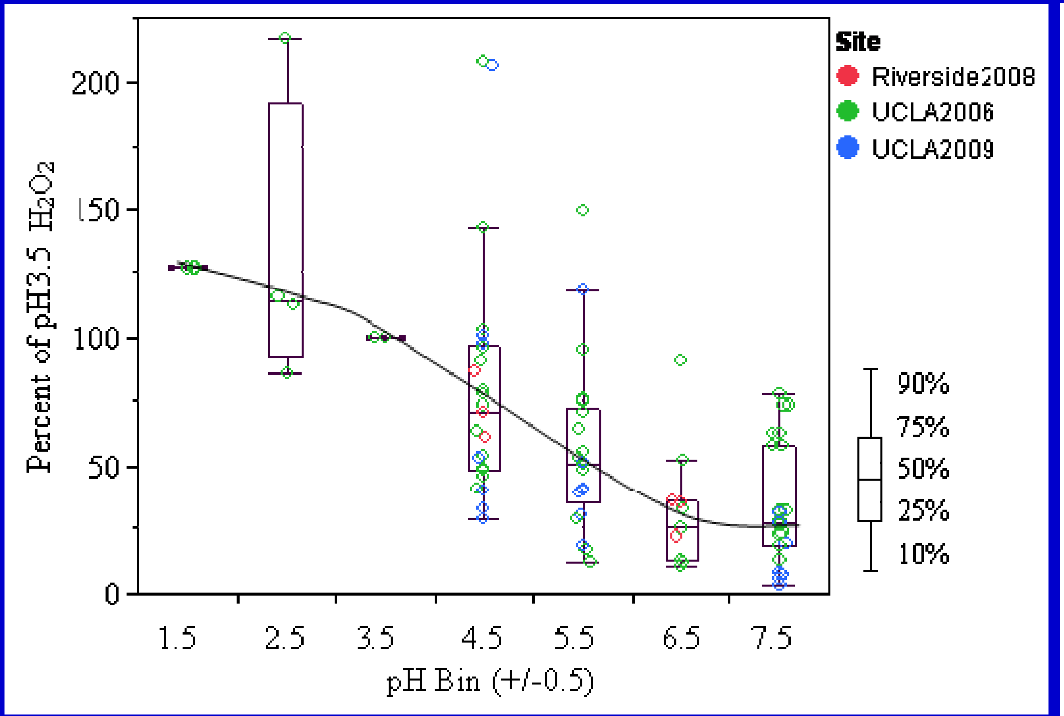


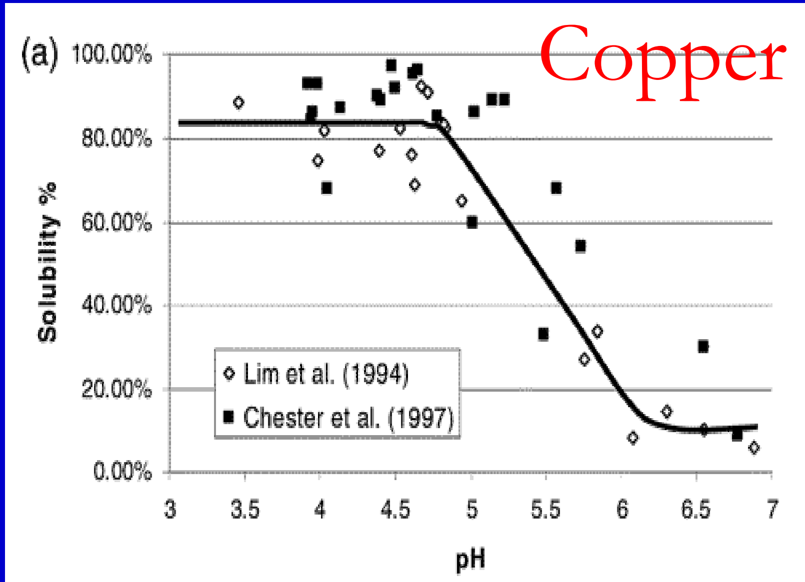


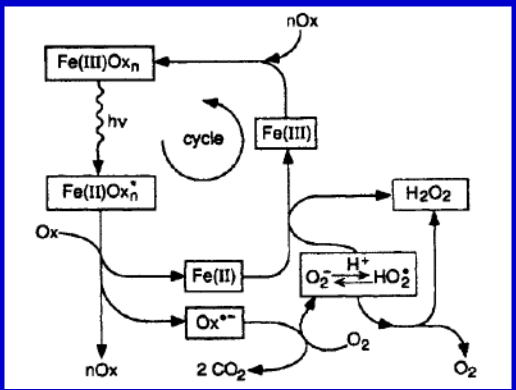
Correlation with hydrogen peroxide

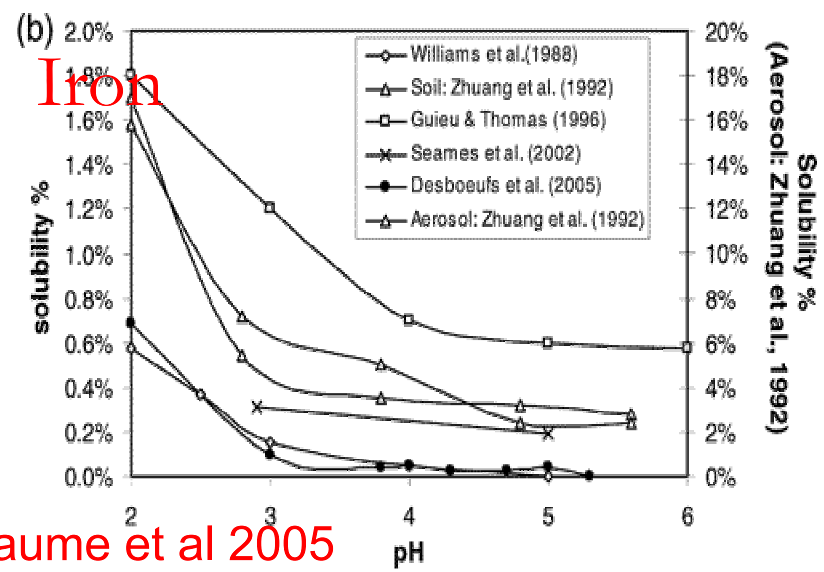
	UCR, 2005			CRCAES, 2008		
	R	p	N	R	p	N
Fe	**0.66****	0.00	33	**0.67****	0.00	27
Zn	0.51	0.08	13	**0.60****	0.00	24
Cu	0.40	0.06	22	0.47*	0.01	26
Al	.	.	.	0.44*	0.02	27
Si	.	.	.	0.43*	0.02	27

The pH Dependence is also consistent with a role for metals in Coarse mode H_2O_2 production









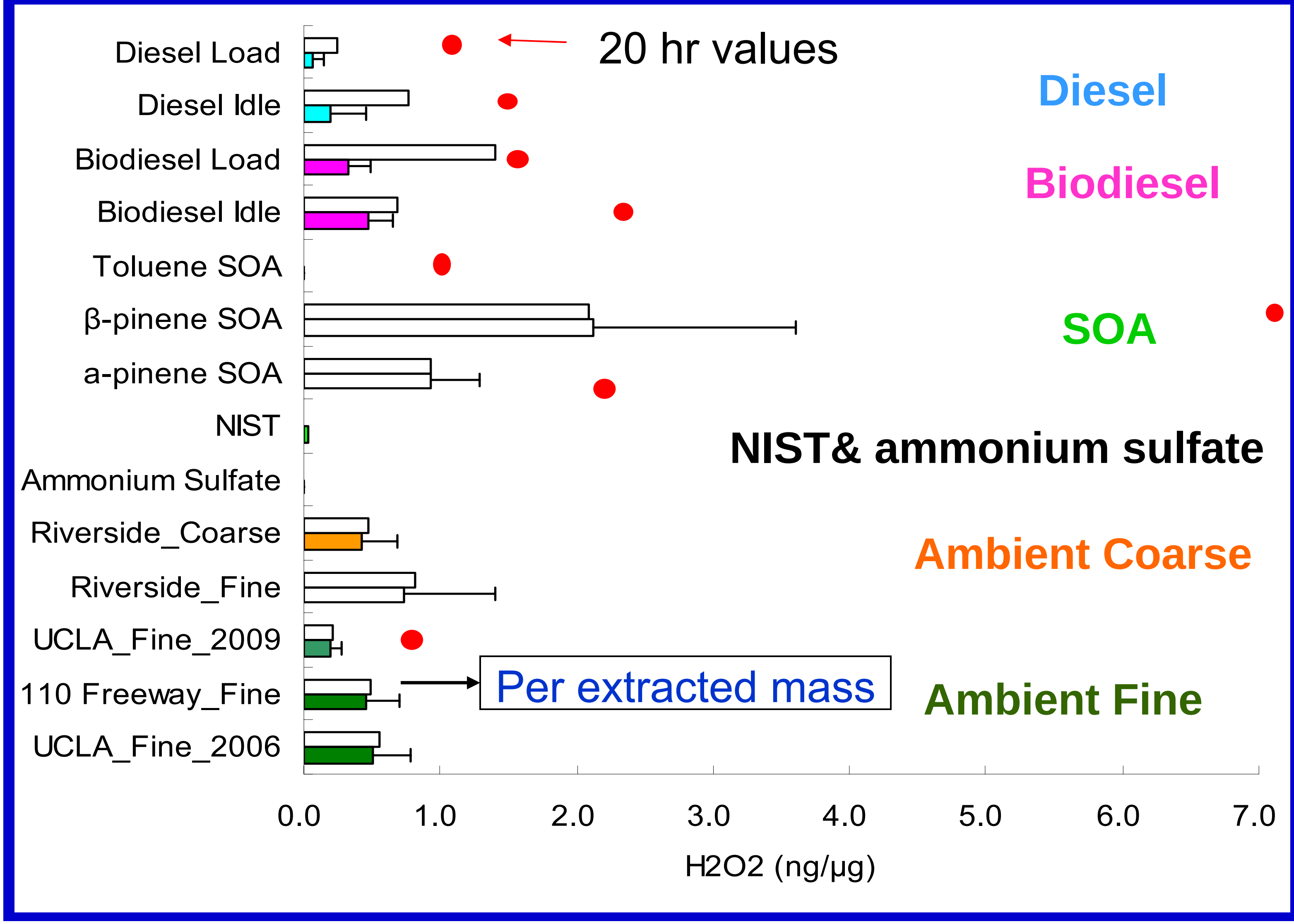
Deguillaume et al 2005

The Metals and H_2O_2 are About the Same Concentration, Especially When We Consider the (Unknown) Speciation/Availability of Metals

	Type	(nmol/ m^3)	H_2O_2	Fe	Cu	Zn
2005	Coarse	Mean	1.00	2.05	0.90	0.56
		Median	0.97	1.60	0.16	0.52
2008	Coarse	Mean	0.50	1.58	0.42	0.68
		Median	0.44	1.44	0.22	0.42

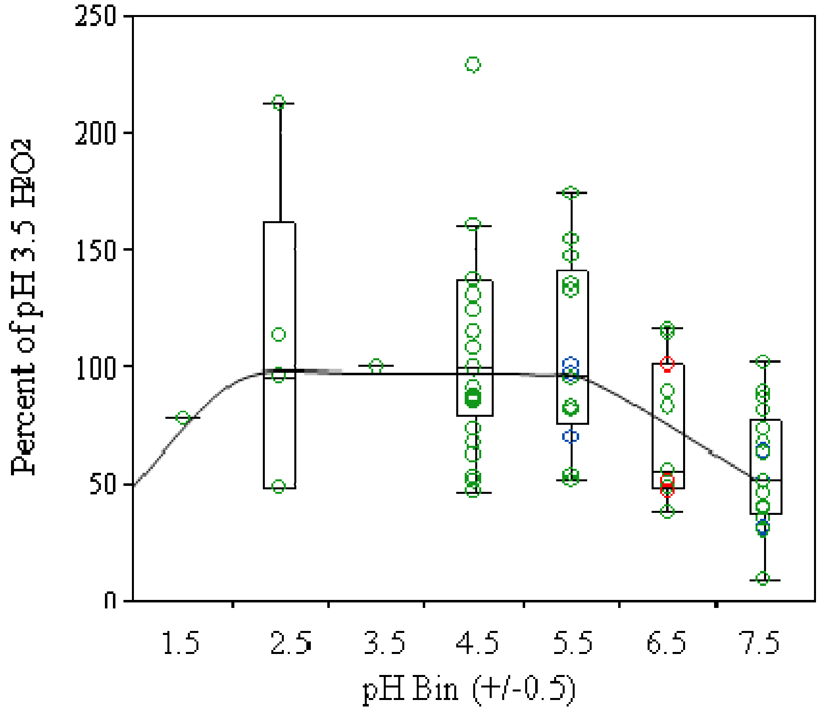
Fine Particles: Mixed Source

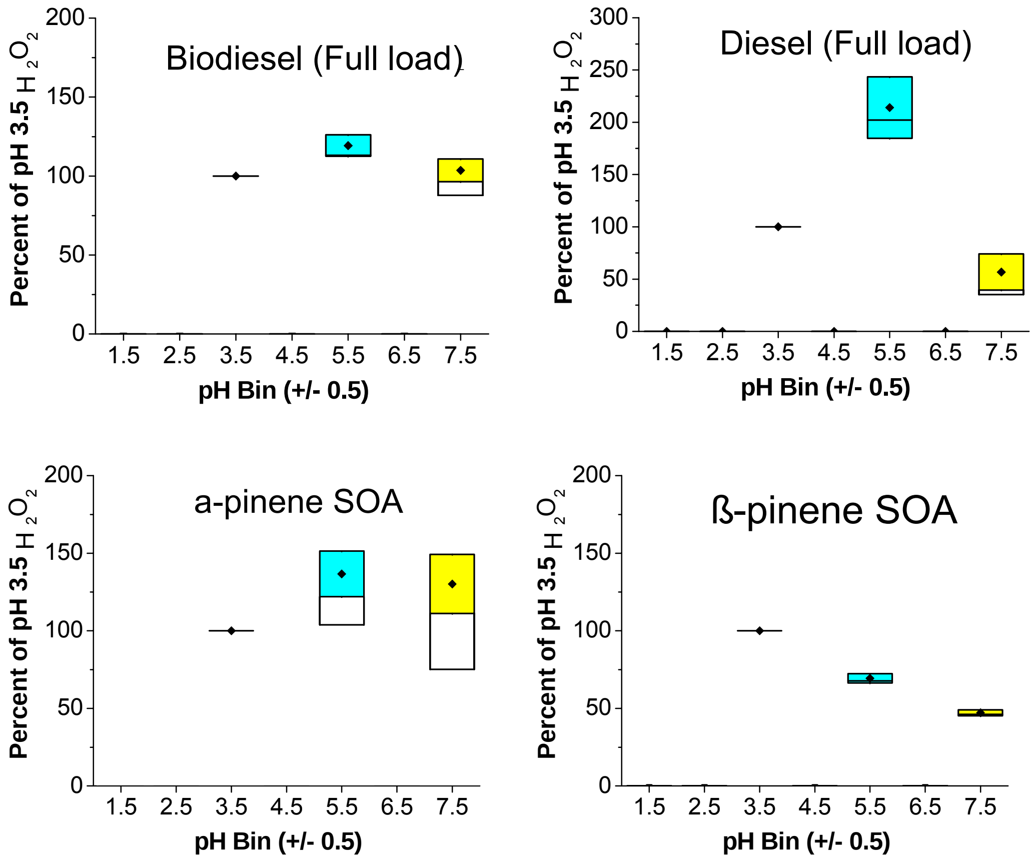
H_2O_2 Generation Varies by Source Aerosol



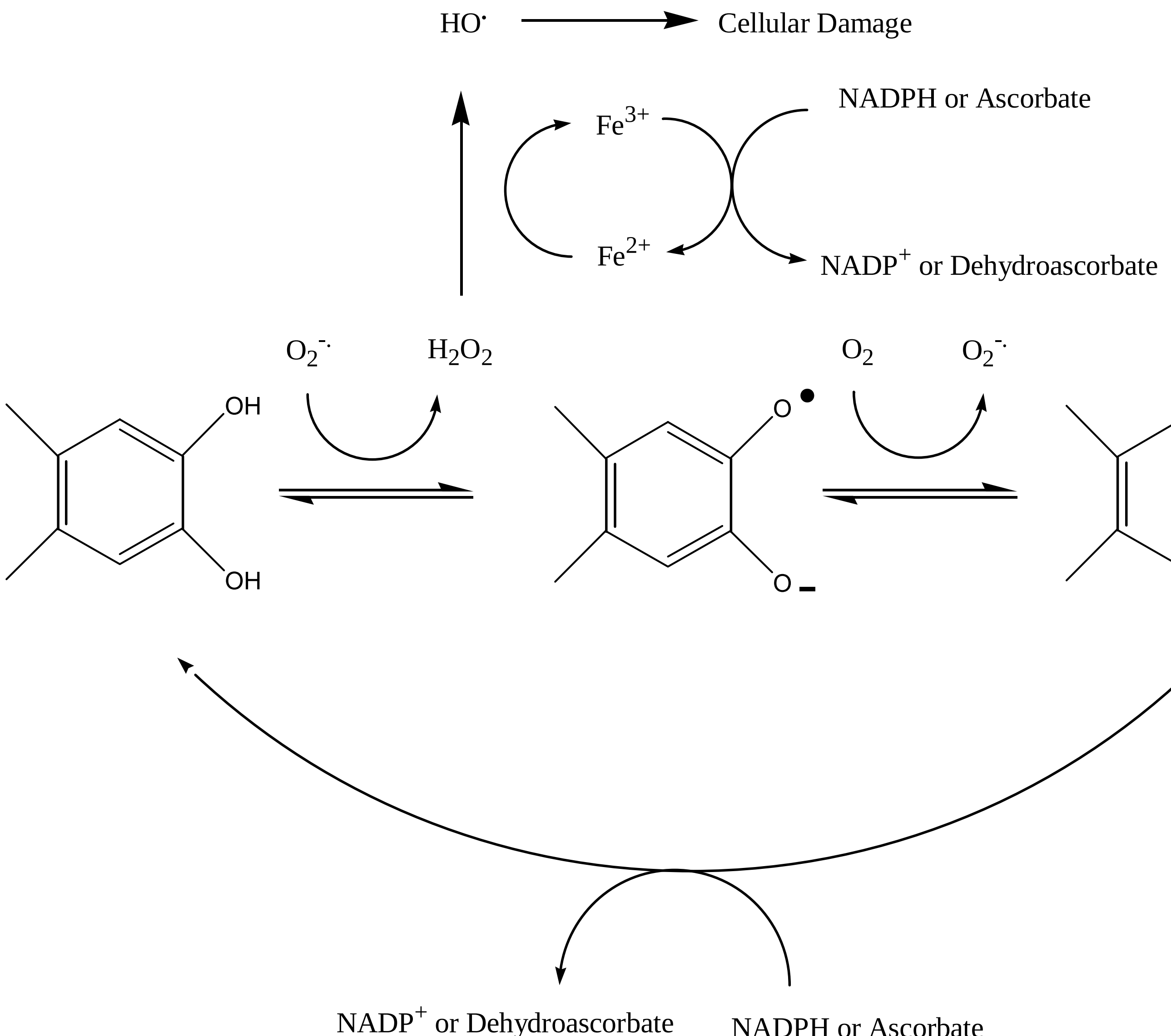
The pH dependence is very different for the fine mode. It appears to be consistent with a contribution from organics.

Fine Mode
Ambient Aerosol



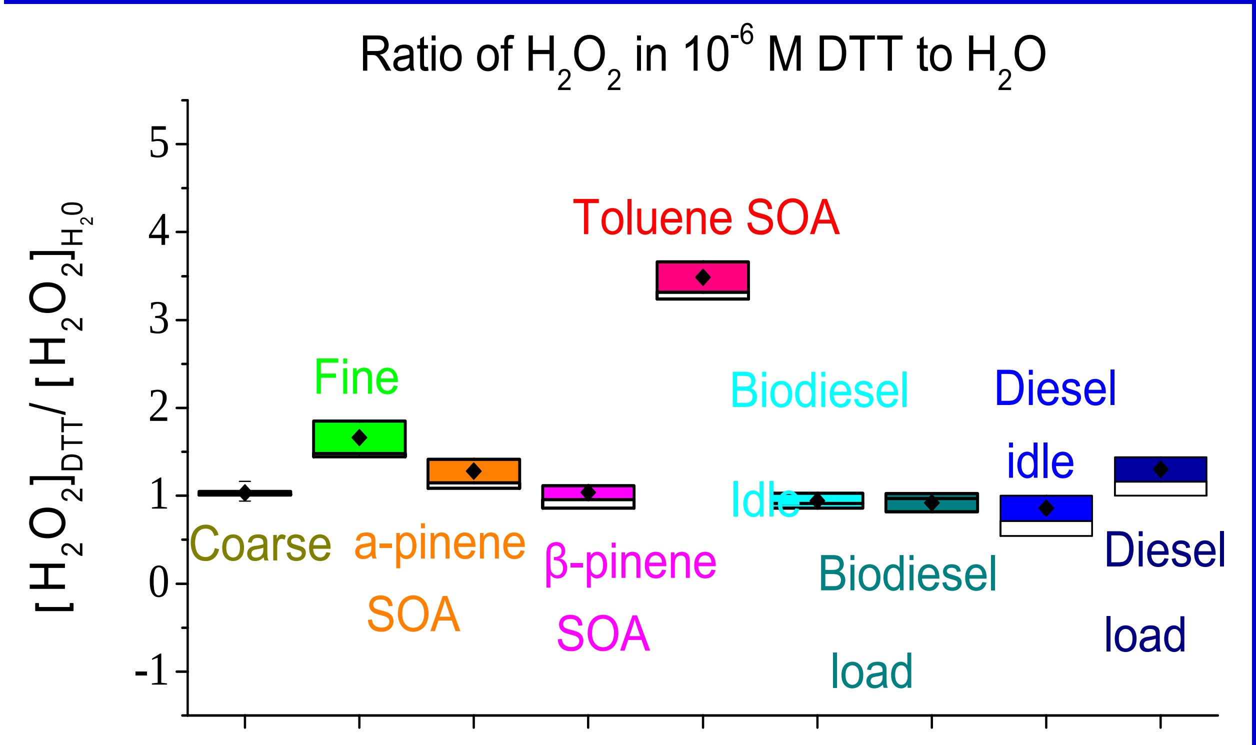


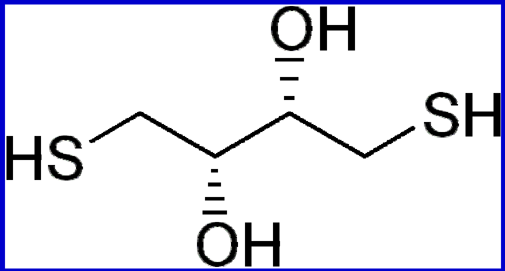
Quinone Chemistry? Needs and Electron Donor—Aerosol Quinone Concentrations are Small.



Source: A. Hasson

Evidence for the Contribution of Quinones in the Fine Mode: Increased Activity in the presence of Dithiothreitol





Q + DTT → $Q^{\bullet-}$ + DTT-thiyl

Q + DTT-thiyl → $Q^{\bullet-}$ + DTT-disulfide

$Q^{\bullet-} + O_2 \rightarrow Q + O_2^{\bullet-}$

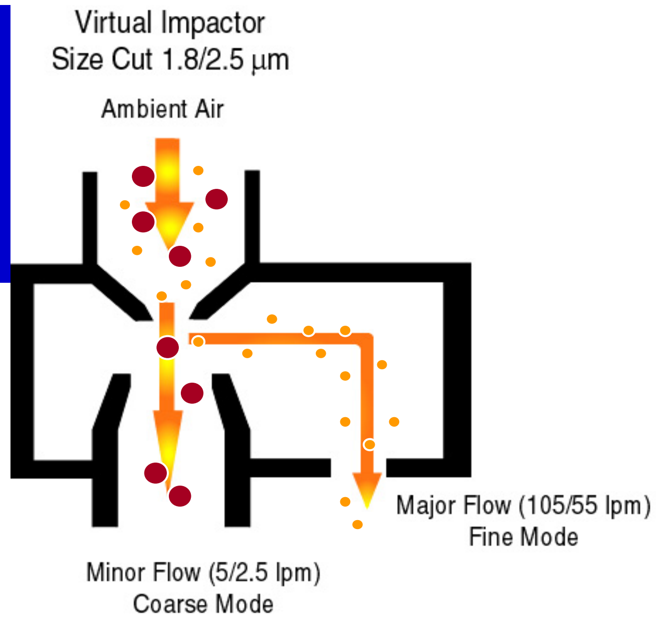
$O_2^{\cdot -} + H^+ \rightarrow HO_2 \rightarrow \rightarrow H_2O_2$

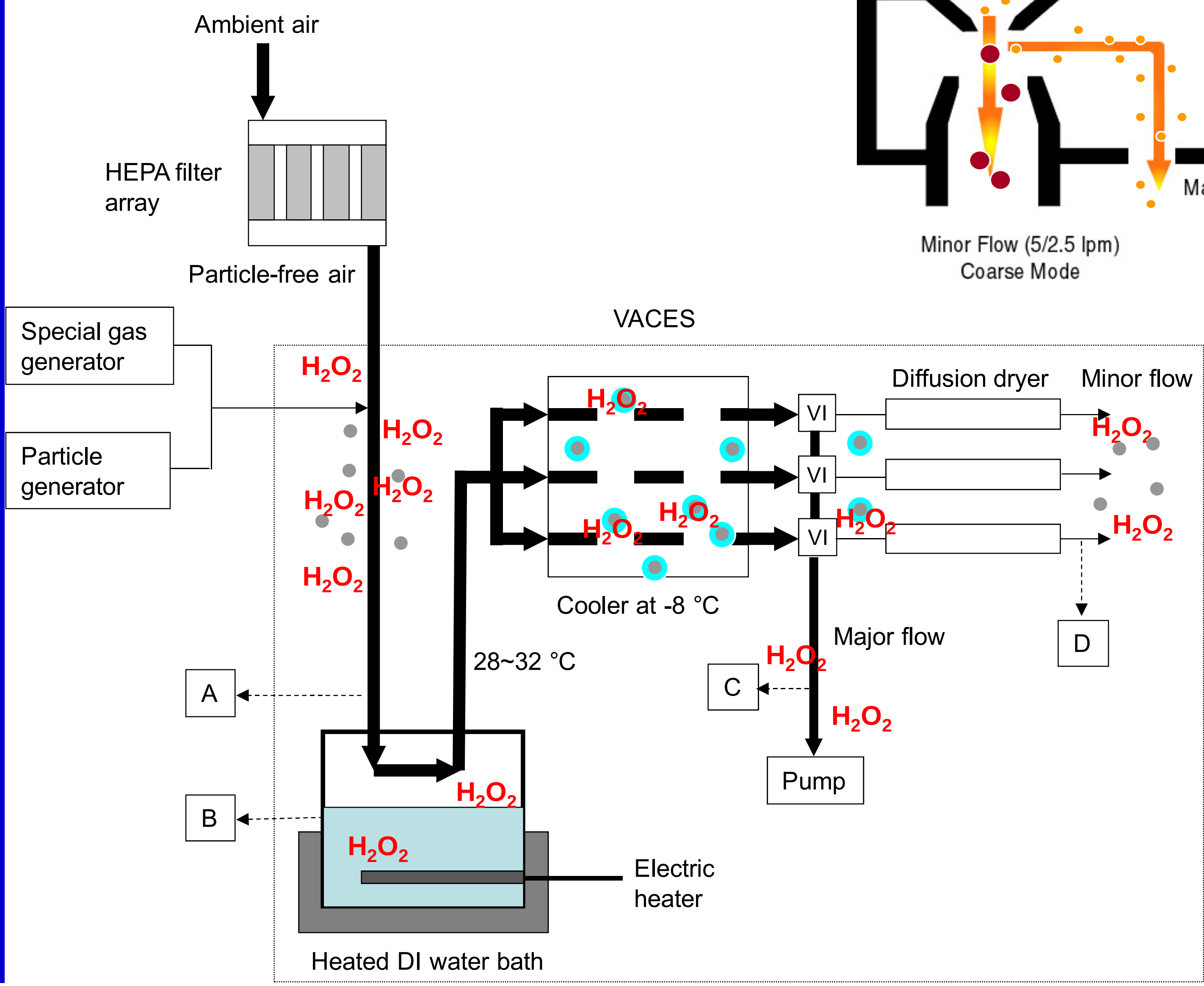
Conclusions

- **Particles generate high concentrations of H_2O_2 for many hours after they are removed from the atmosphere.**
- ***In vitro* and *in vivo* results point to significant cell damage from aerosol borne/generated H_2O_2.**
- **Aerosol borne ROS is variable day-to-day and location to location; source seems to be metal-mediated redox activity for larger particles, possibly organics, including quinones, for smaller particles.**

Behavior of Hydrogen Peroxide in the VACES

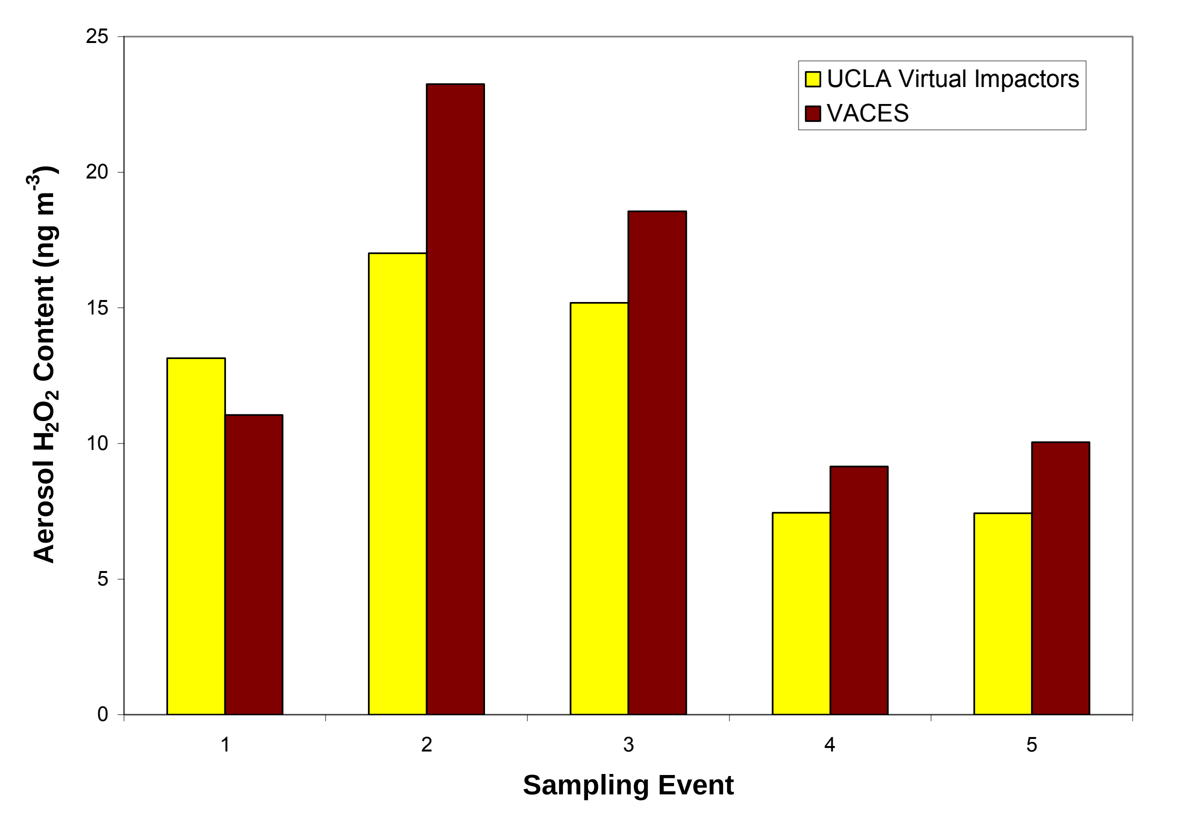
Virtual Aerosol Concentration Enrichment System Operation





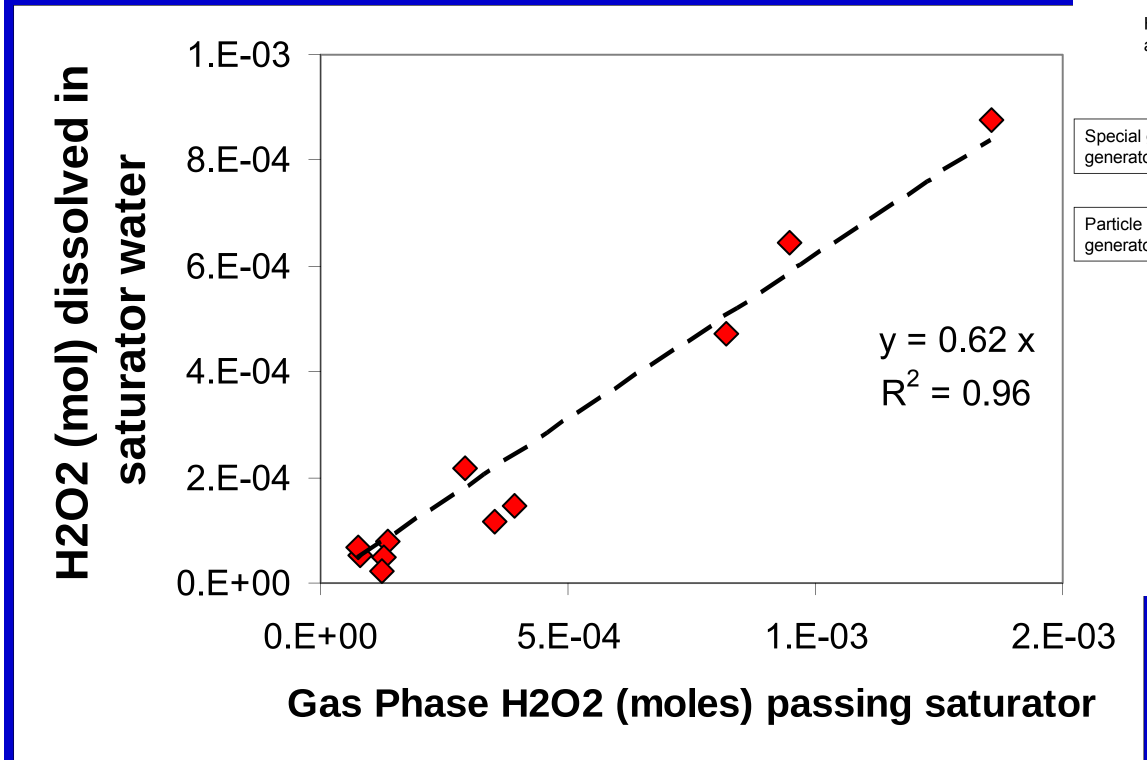
The VACES does not appreciably effect the Aerosol H_2O_2, because most of the H_2O_2 is generated by the Particles

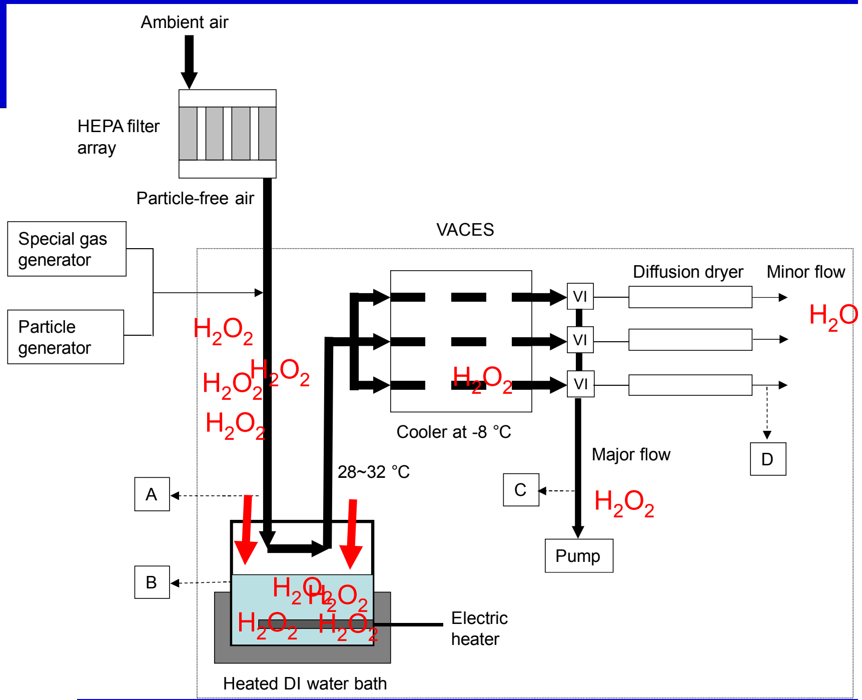
Comparison of H_2O_2 associated with particles with (dark red) and without (yellow) the VACES in line.



Arellanes, Paulson, Fine and Sioutas et al., *Envir. Sci. Tech.* 2006

Hydrogen Peroxide is Taken Up by the Water Bath

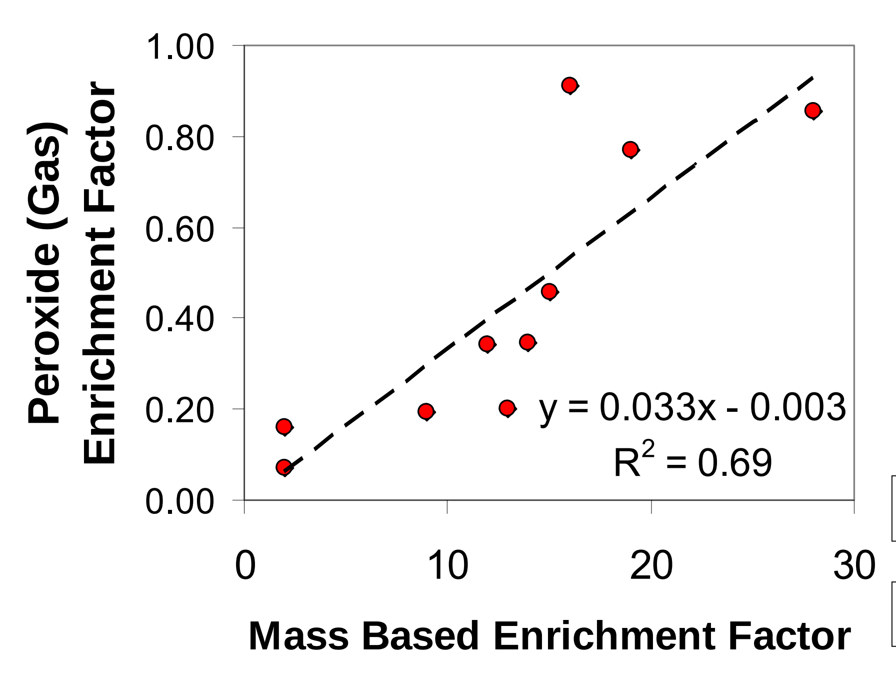




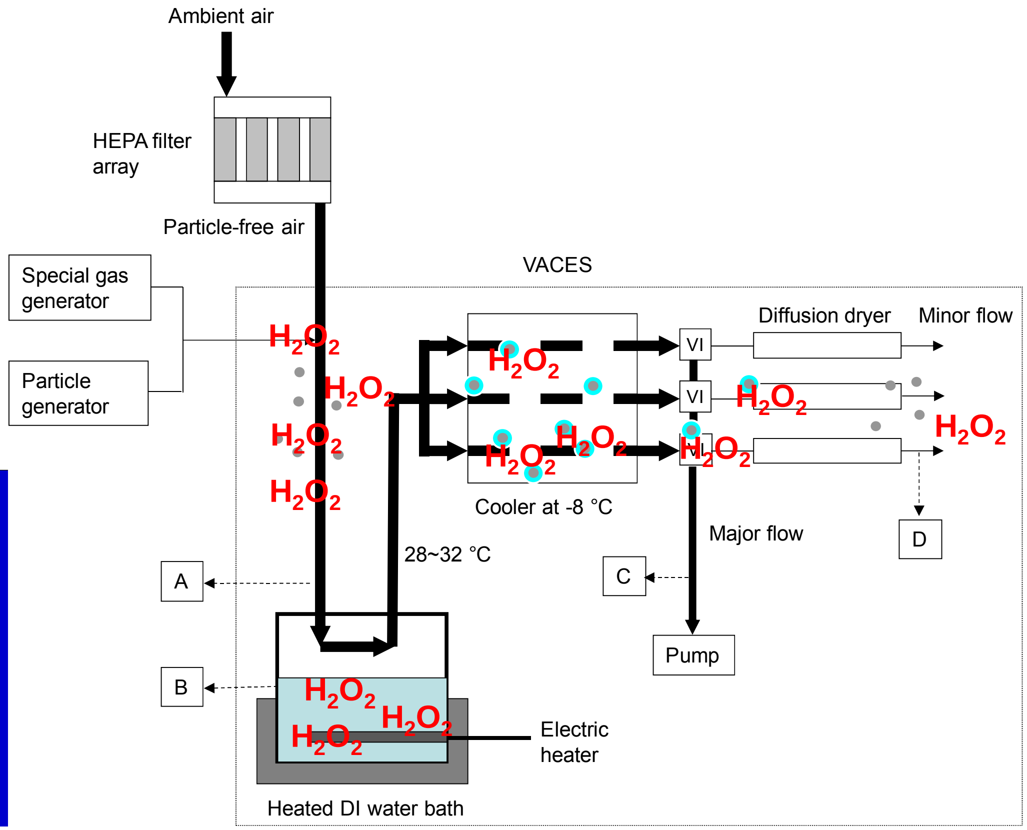
H_2O_2 is also elevated in other condensed water (liquid, ice) that collects in various places in the instrument.

Jung, Arellanes, Zhao, Paulson, Anastasio and Wexler, submitted to AS&T

The Effect of the VACES can be to Concentrate **OR** Enrich soluble **gasses**, depending on its Operating Conditions



The enrichment step concentrates soluble gasses; the water bath etc depletes them



Conclusions: VACES & soluble gasses

- **Soluble gasses are taken up in the water bath and other condensed phases**
- **Soluble gasses are concentrated by the particle enrichment step.**
- **Since the two processes act in opposite directions, the gas phase concentrations of soluble gasses are generally only moderately perturbed. Presumably due to the same combination of processes, nitric acid is fairly depleted by the VACES, and ammonia moderately enriched.**

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