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Formation of Reactive Oxygen Species by Atmospheric Particulate Matter

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Air Pollution & Health Effects

Air pollution leads to
4.2 million premature death per year worldwide
(Global Burden of Diseases)

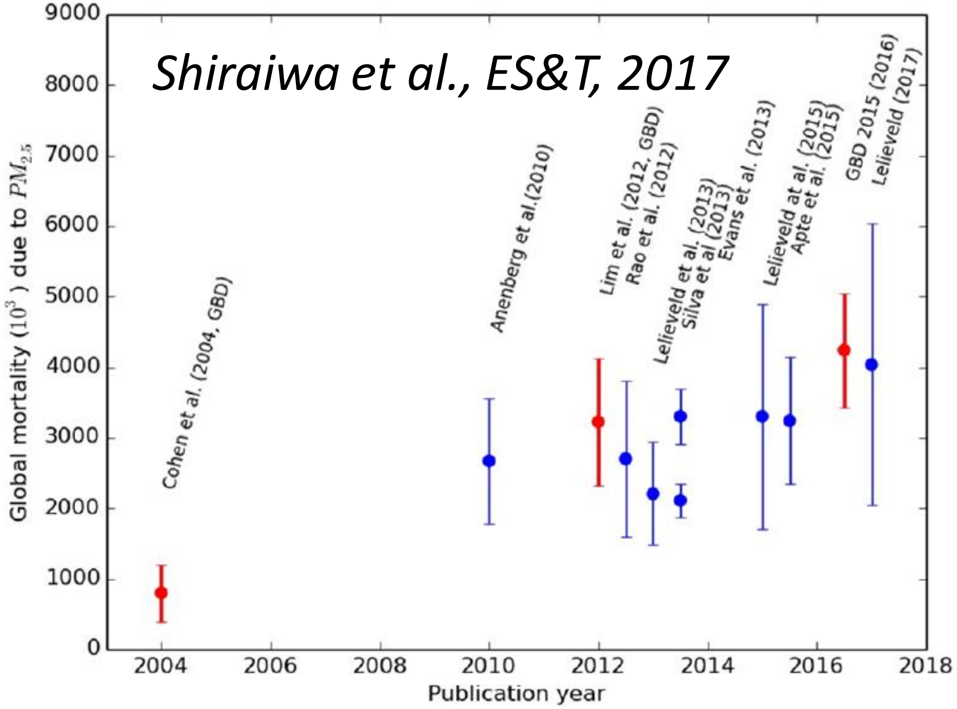
“Are we creating a hazardous atmosphere?”

Ozone background level increased from ~10 -20 ppb to 30 – 40 ppb

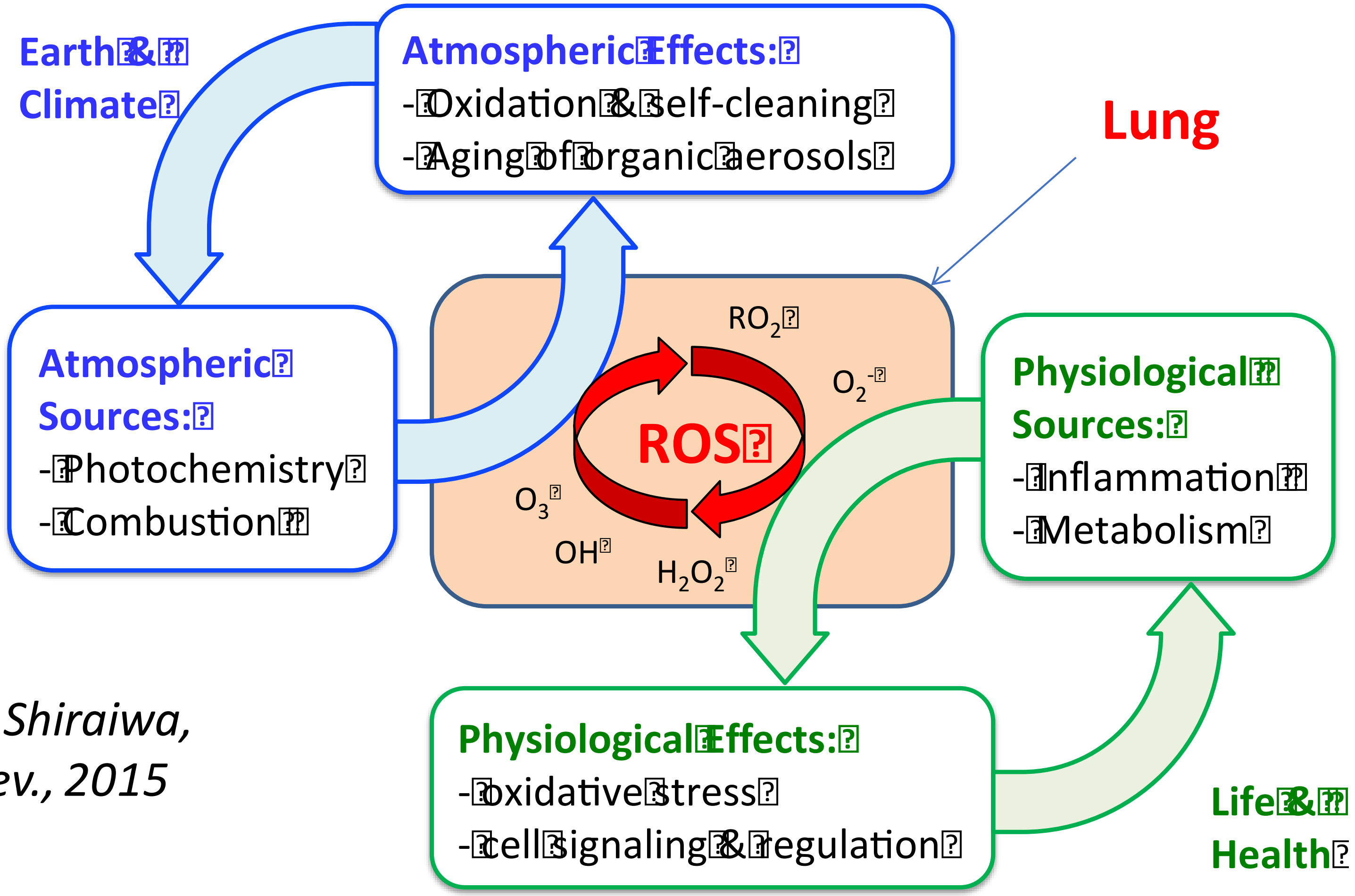
Particulate Matter (PM2.5):

~1-10 µg m^{-3} (pristine) vs.

~100 - 2000 µg m^{-3} (polluted)



Motivation: Air Pollution is a threat to human health,
but the underlying chemistry at the atmosphere-biosphere interface are poorly understood.
Reactive Oxygen Species (ROS) play a central role.

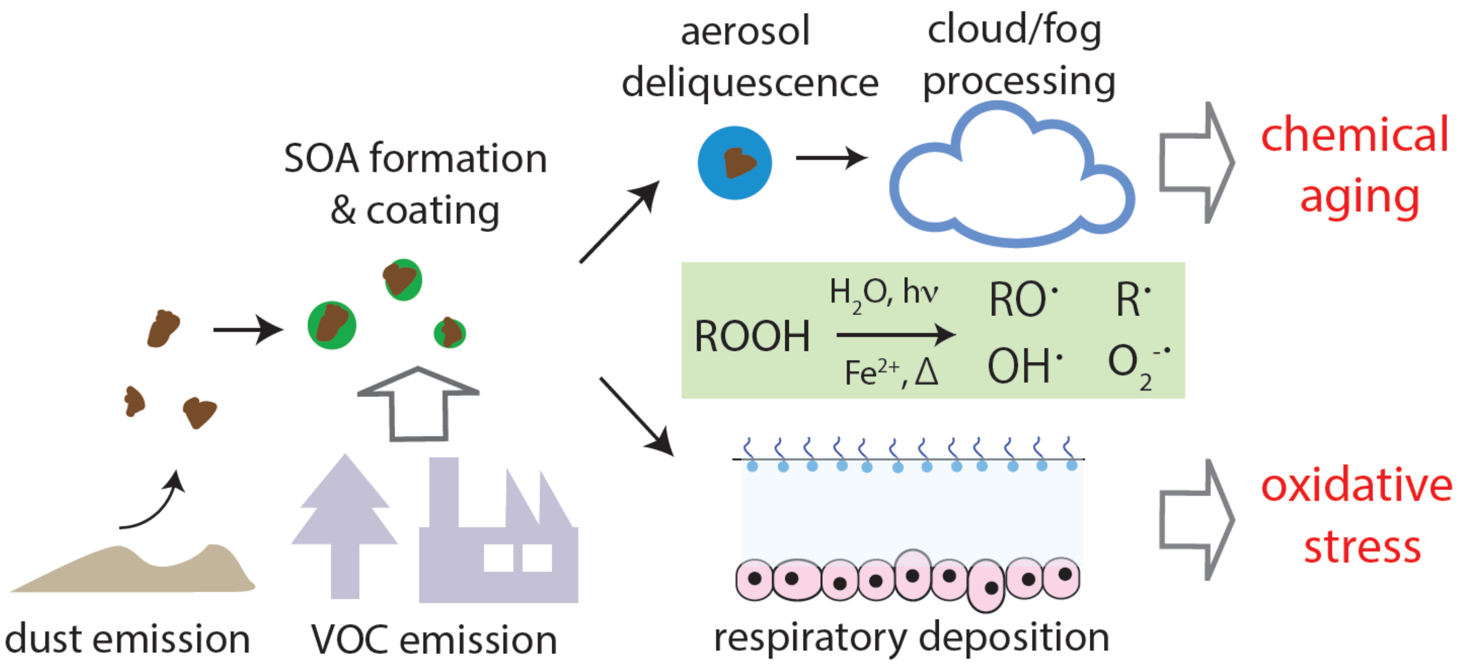


Pöschl & Shiraiwa, Chem. Rev., 2015

Goal: Quantitative understanding of ROS multiphase chemistry for better assessment & handling of air quality and public health

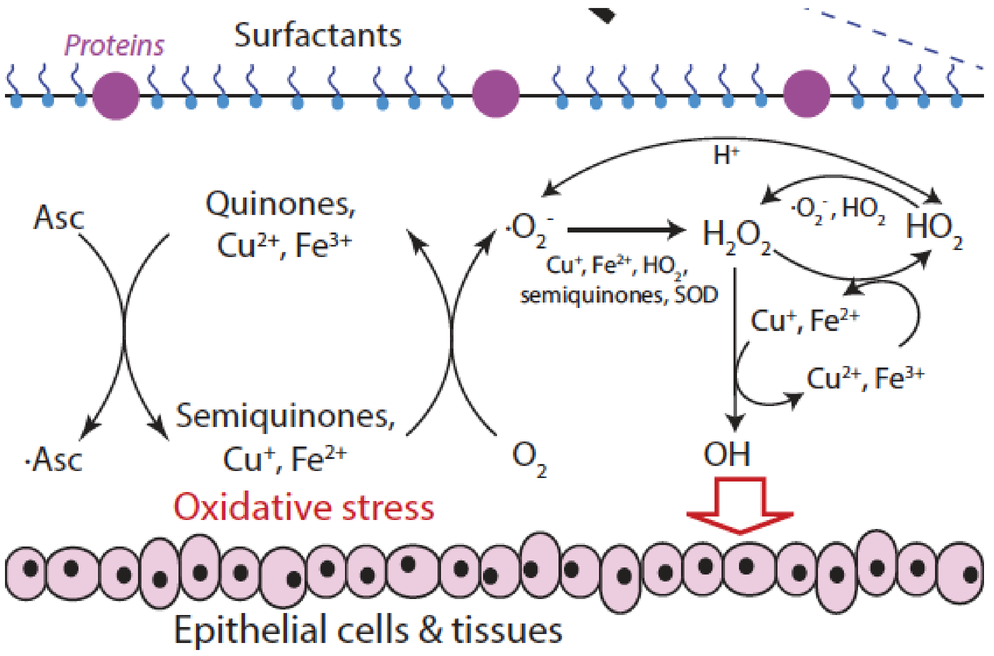
ROS Formation by Atmospheric Particulate Matter

SOA decomposition

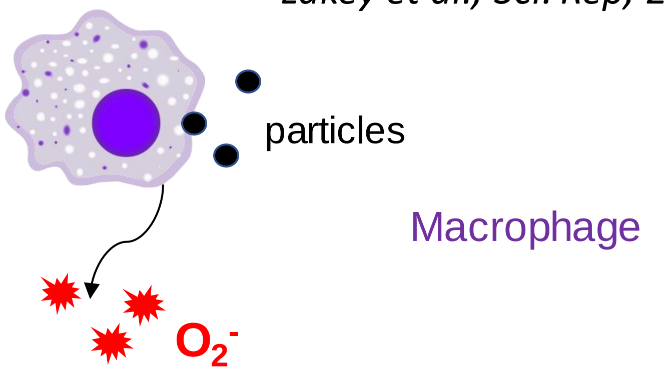


Tong et al., 2016; 2017

Redox reactions in lung fluid



Lakey et al., Sci. Rep, 2016



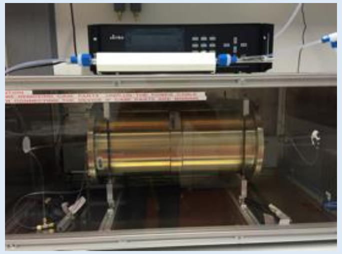
Atmospheric PM contain **reactive or redox-active compounds**

- organic hydroperoxides (HOMs, ELVOCs), alcohols, ketones
- quinones, environmentally persistent free radicals (EPFRs)
- transition metals (Fe, Cu)
- humic like substances

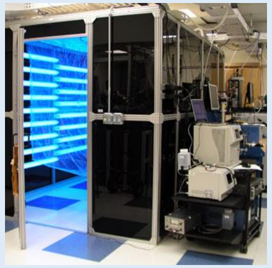
OH formation by SOA decomposition

Tong et al., Atmos. Chem. Phys., 2016

SOA Generation, Sampling



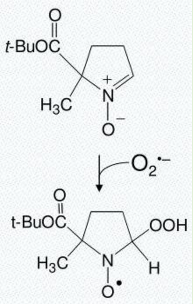
PAM chamber



reaction chamber

ROS Measurements

Electron
Paramagnetic
Resonance

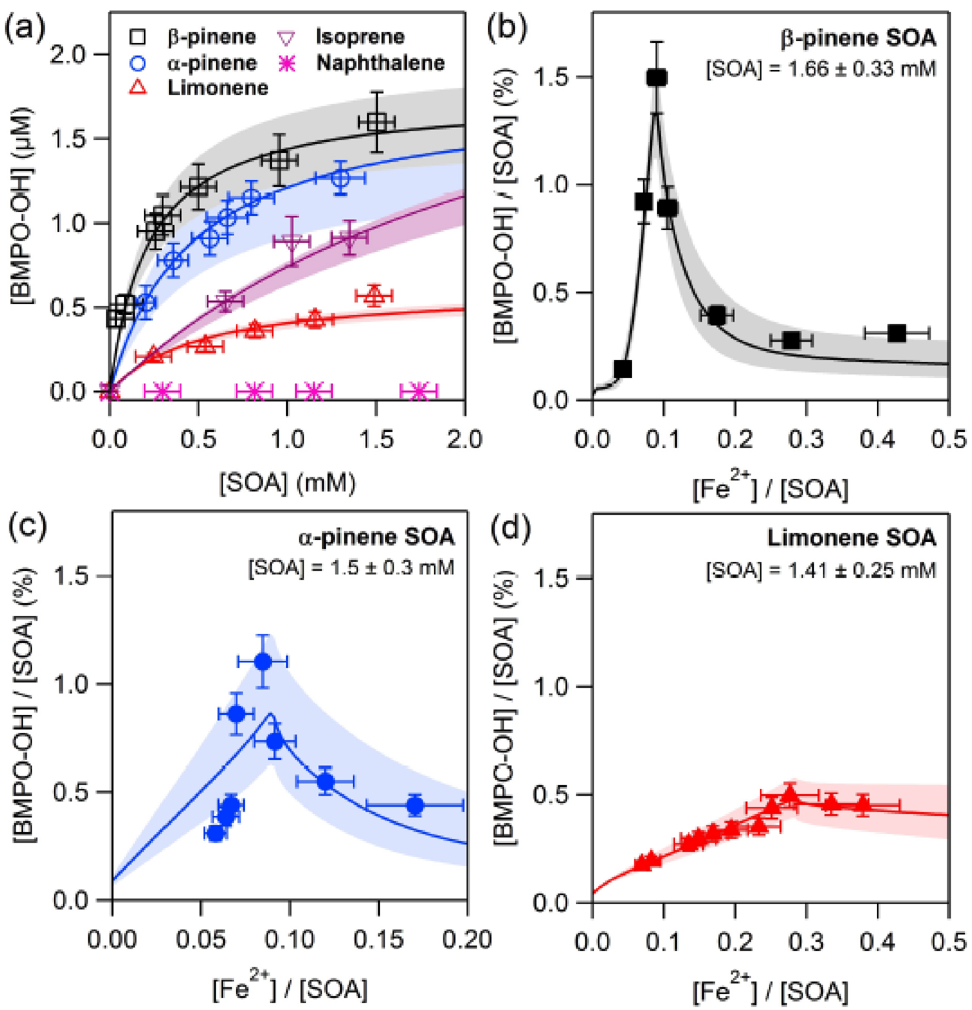


Spin trapping to detect short-lived radicals

Kinetic Modeling

- ROOH/ROH chemistry
- Fenton-like chemistry
- HOx coupling reactions
- BMPO trapping/decay

Monte Carlo Genetic Algorithm for fitting/error eval. (Berkemeier et al.)



Fenton-like reactions

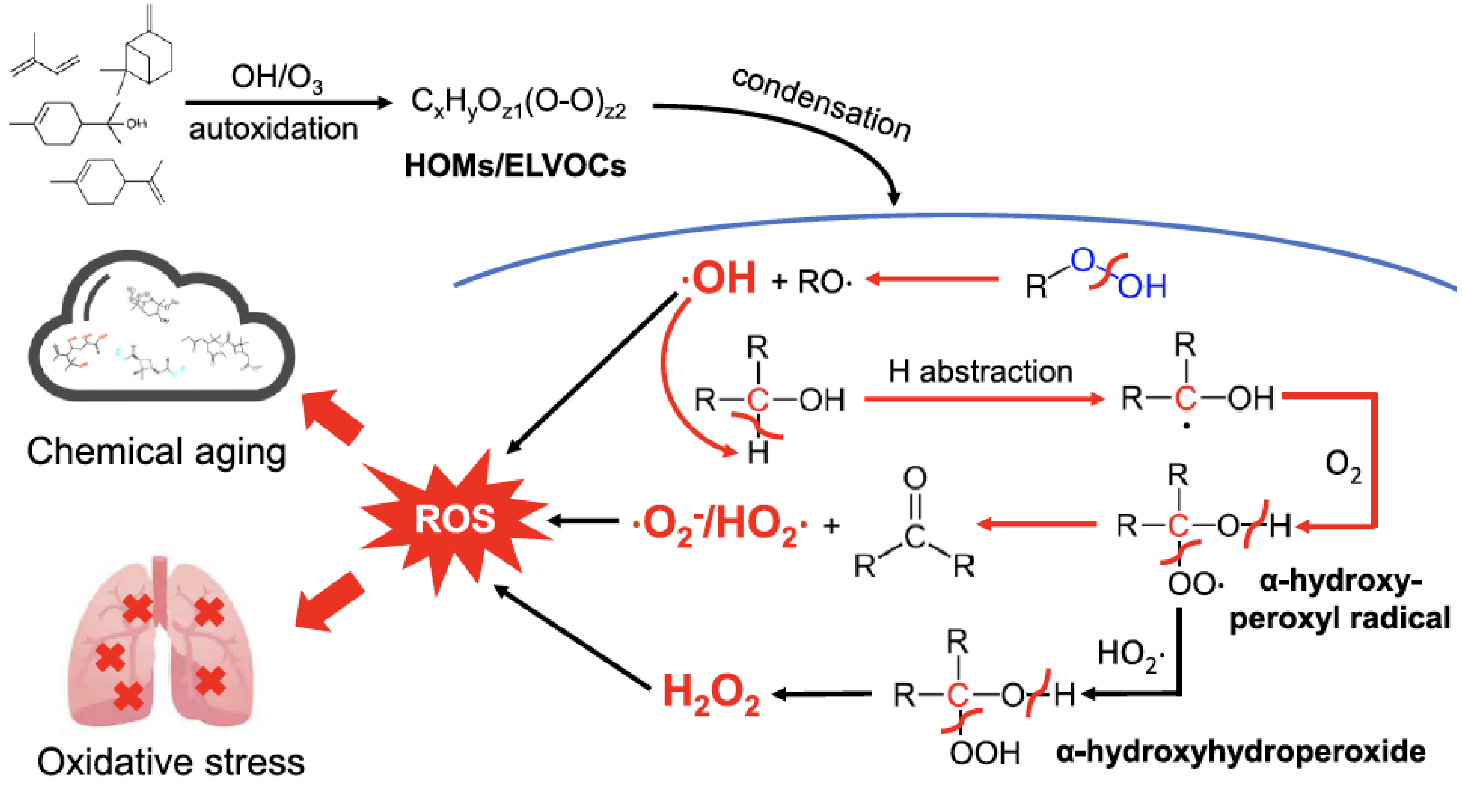
$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$

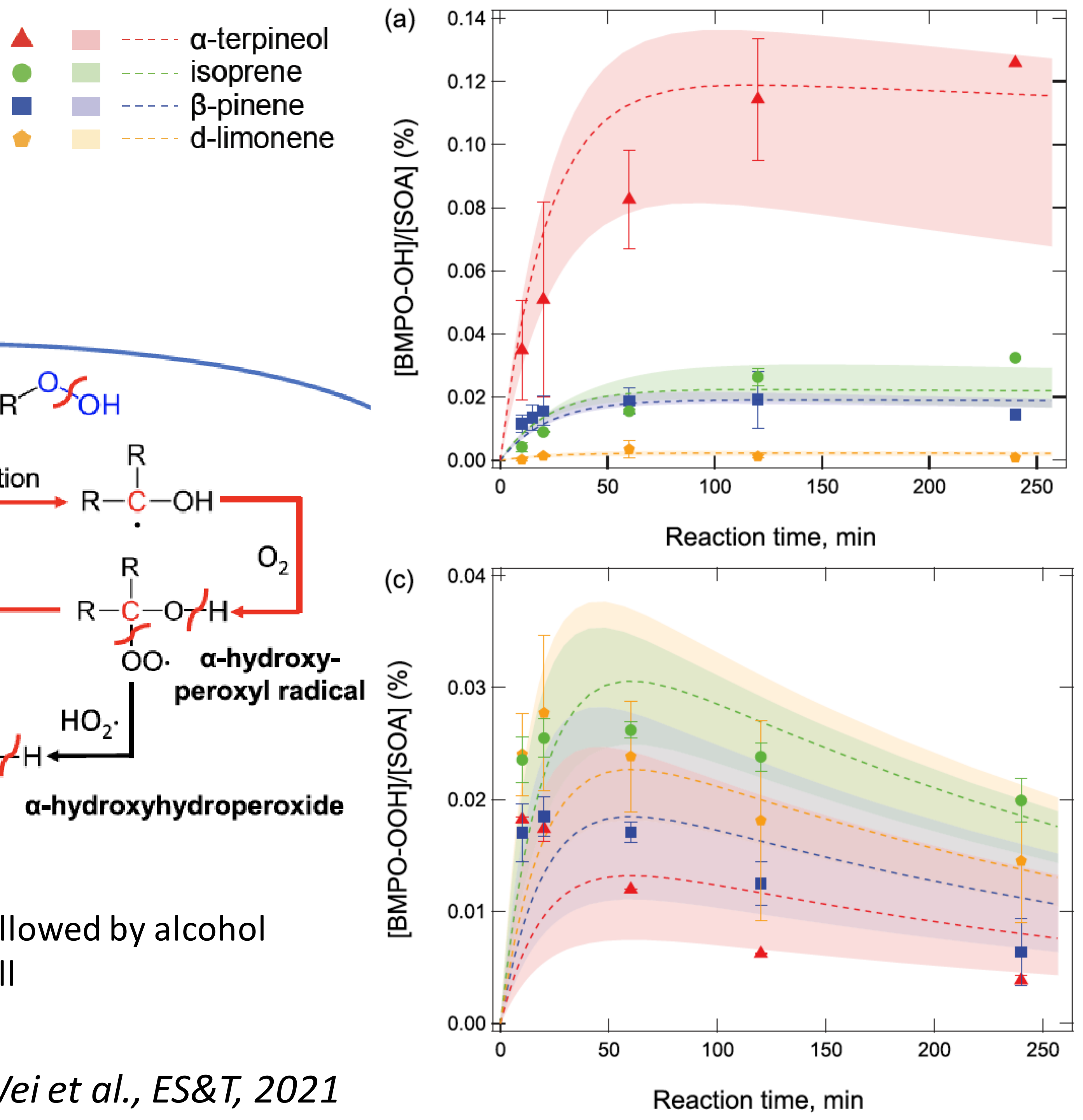
$$ROOH + Fe^{2+} \rightarrow RO^{\bullet} + OH^{-} + Fe^{3+}$$

$$ROOH + Fe^{2+} \rightarrow RO^{-} + {}^{\bullet}OH + Fe^{3+}$$

Goldstein et al., 1999

OH/O_2^- formation by biogenic SOA

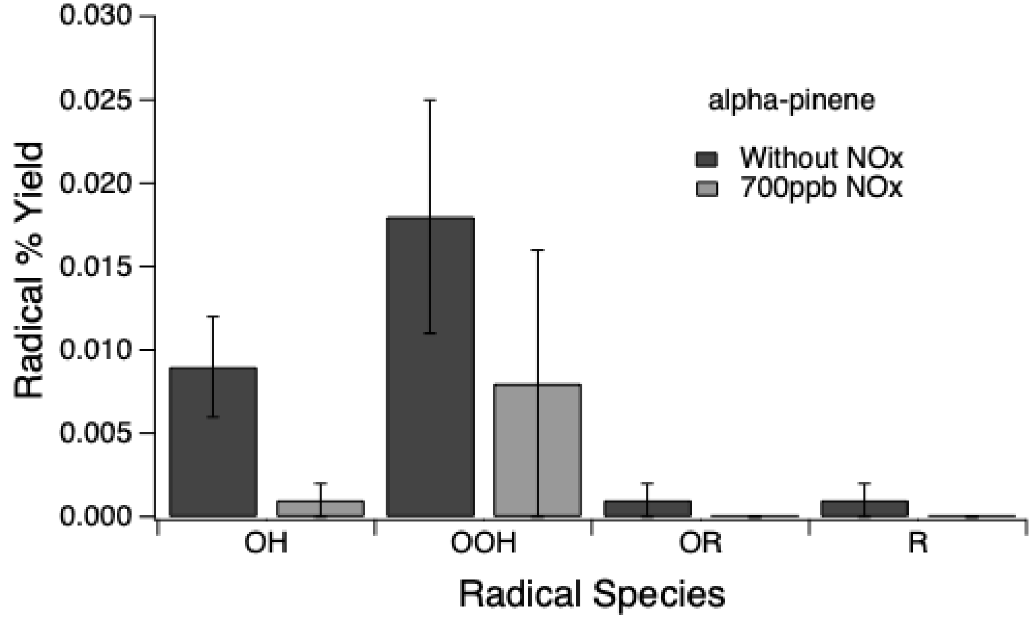


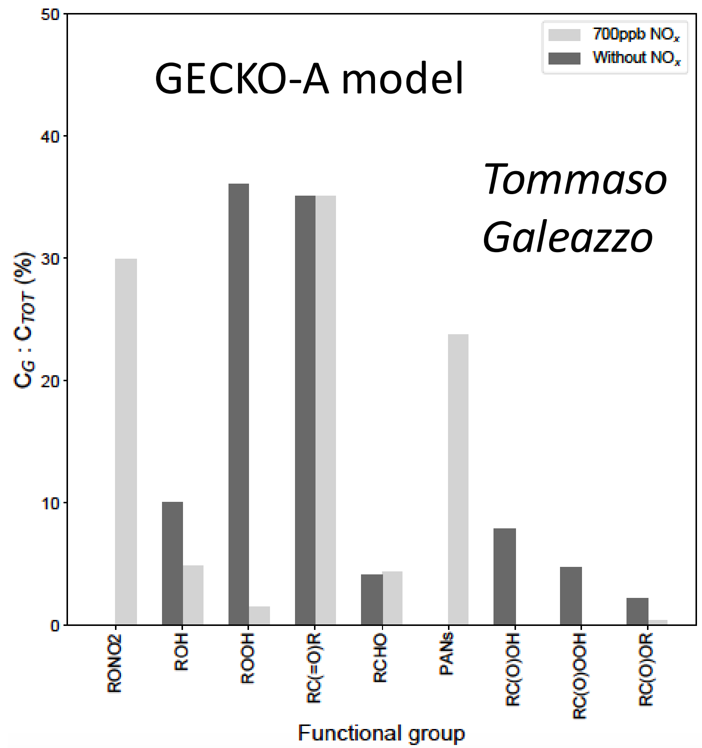


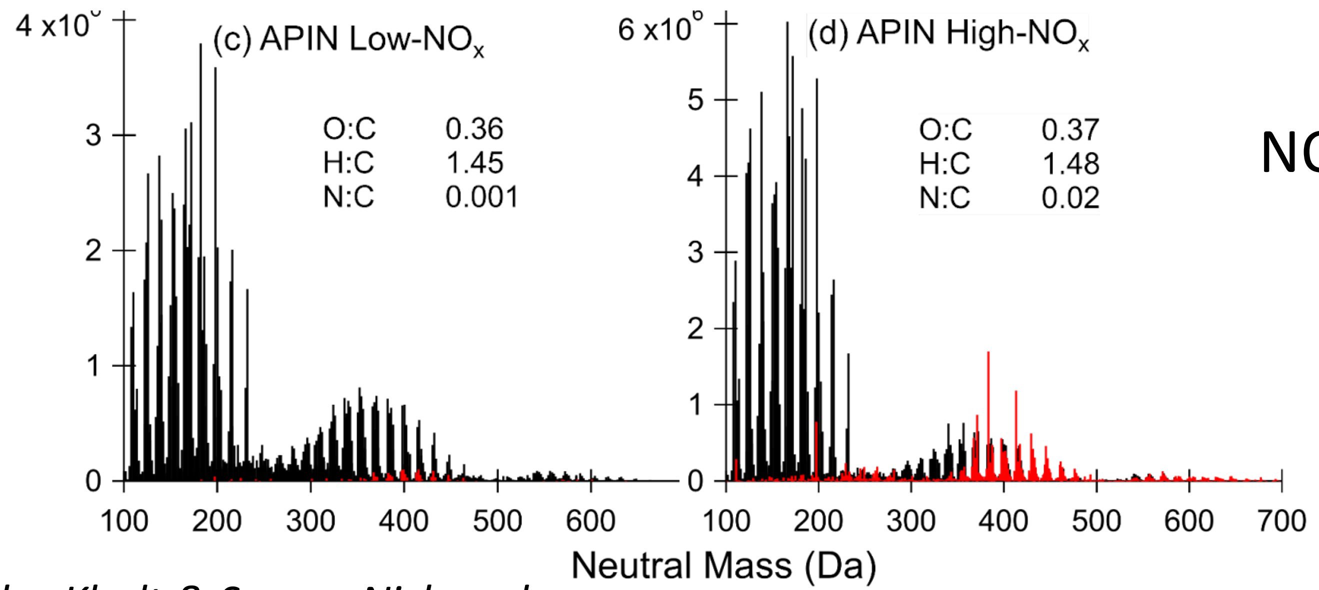
Kinetic modeling considering ROOH decomposition followed by alcohol oxidation explains the observed OH/O_2^- formation well

Wei et al., ES&T, 2021

NOx effects on ROS formation by SOA







Alex Klodt & Sergey Nizkorodov

NOx changes the fate of peroxy radicals RO_2

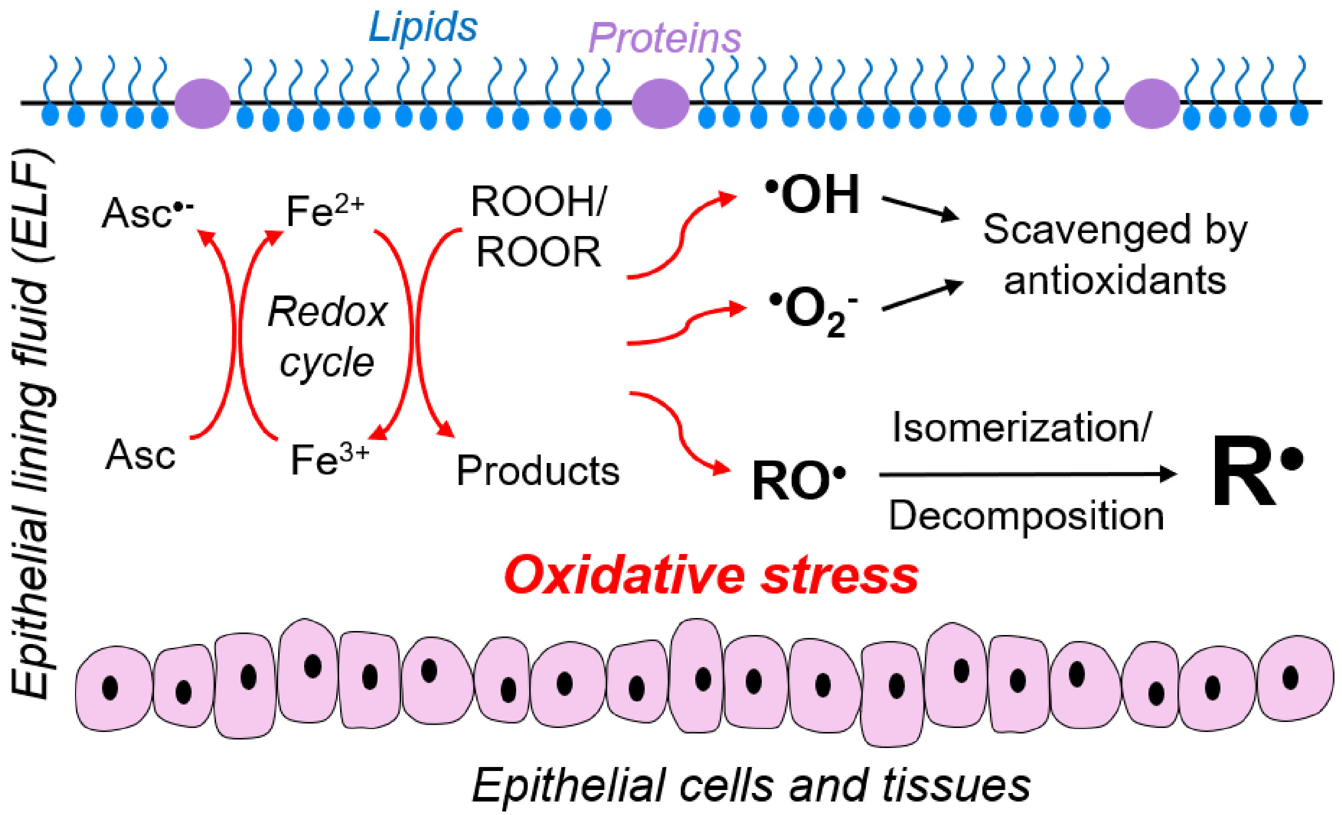
$$RO_2 + HO_2 \rightarrow ROOH$$

$$RO_2 + NO_2 \rightarrow ROONO_2$$

$$RO_2 + NO \rightarrow RONO_2$$

Edwards et al., J. Phys. Chem. A, 2022

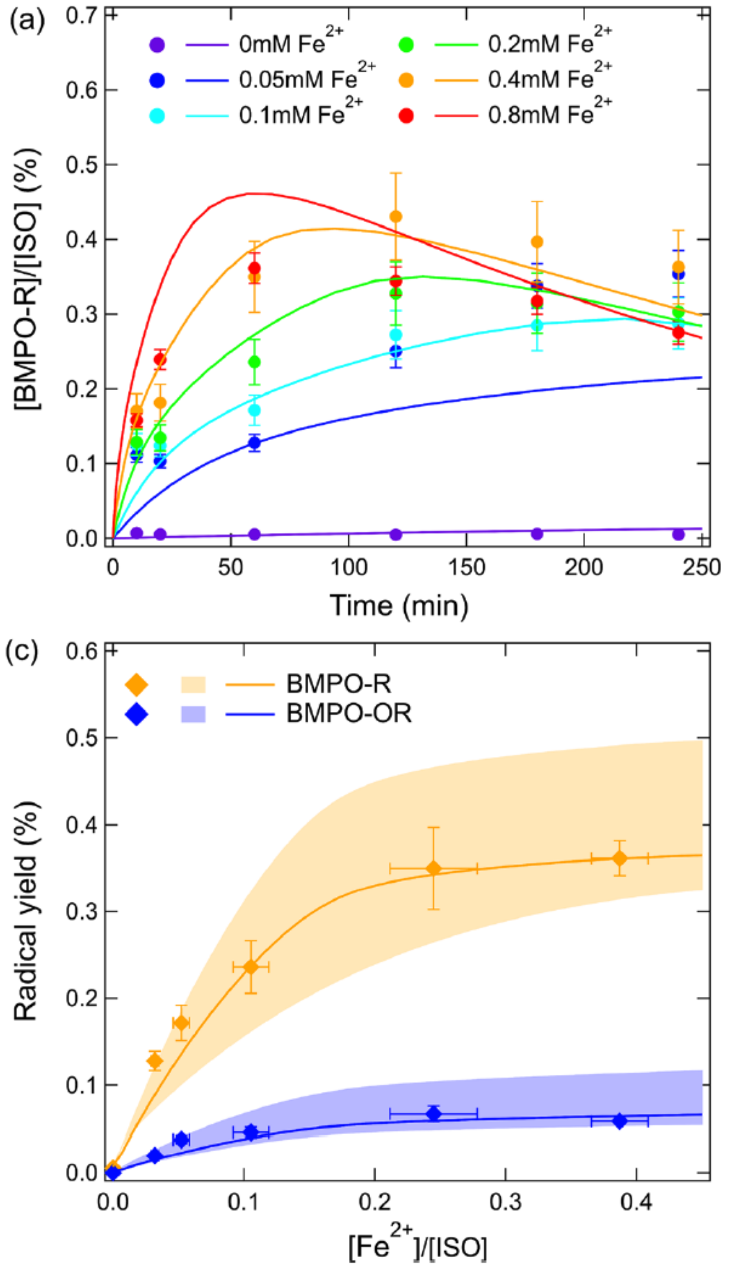
Dominant Organic Radical Formation in Epithelial Lining Fluid



$$ROOR' + Fe^{2+} \rightarrow RO^{\bullet} + R'O^{-} + Fe^{3+} \qquad (R9)$$

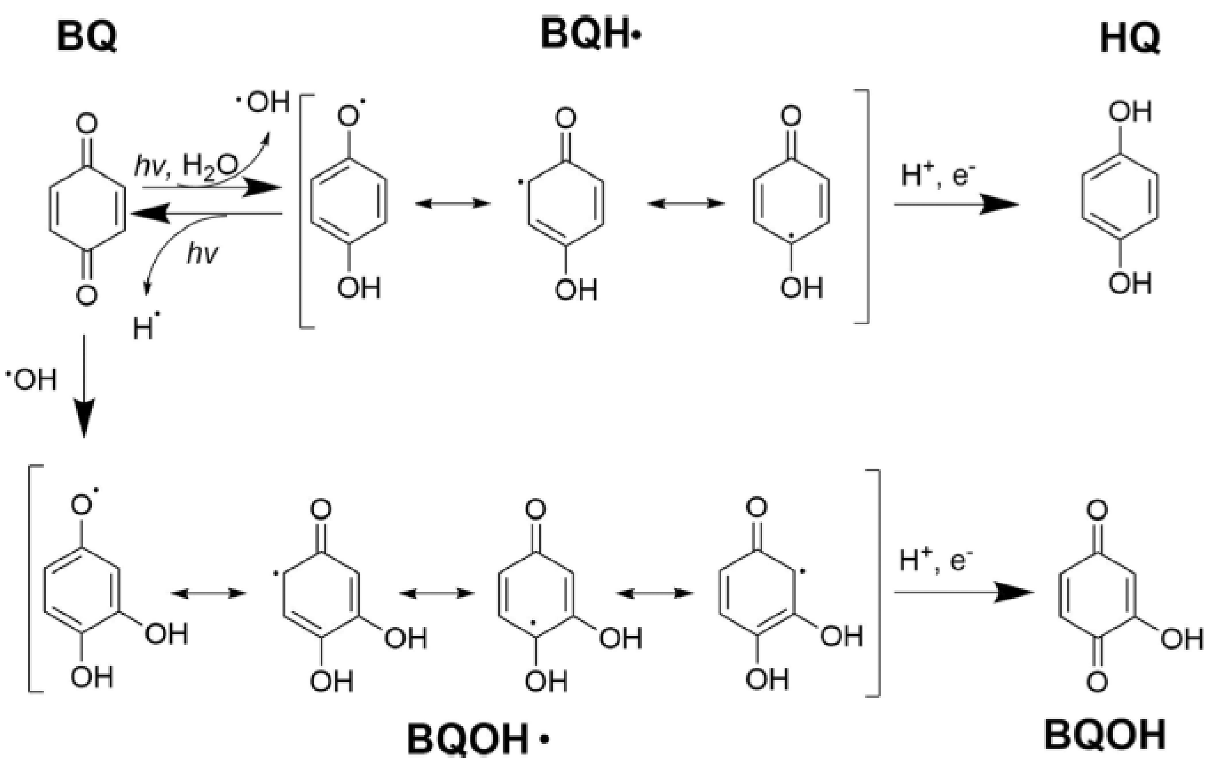
$$RO^{\bullet} + H_2O \rightarrow {}^{\bullet}R'OH + H_2O \qquad (R12)$$

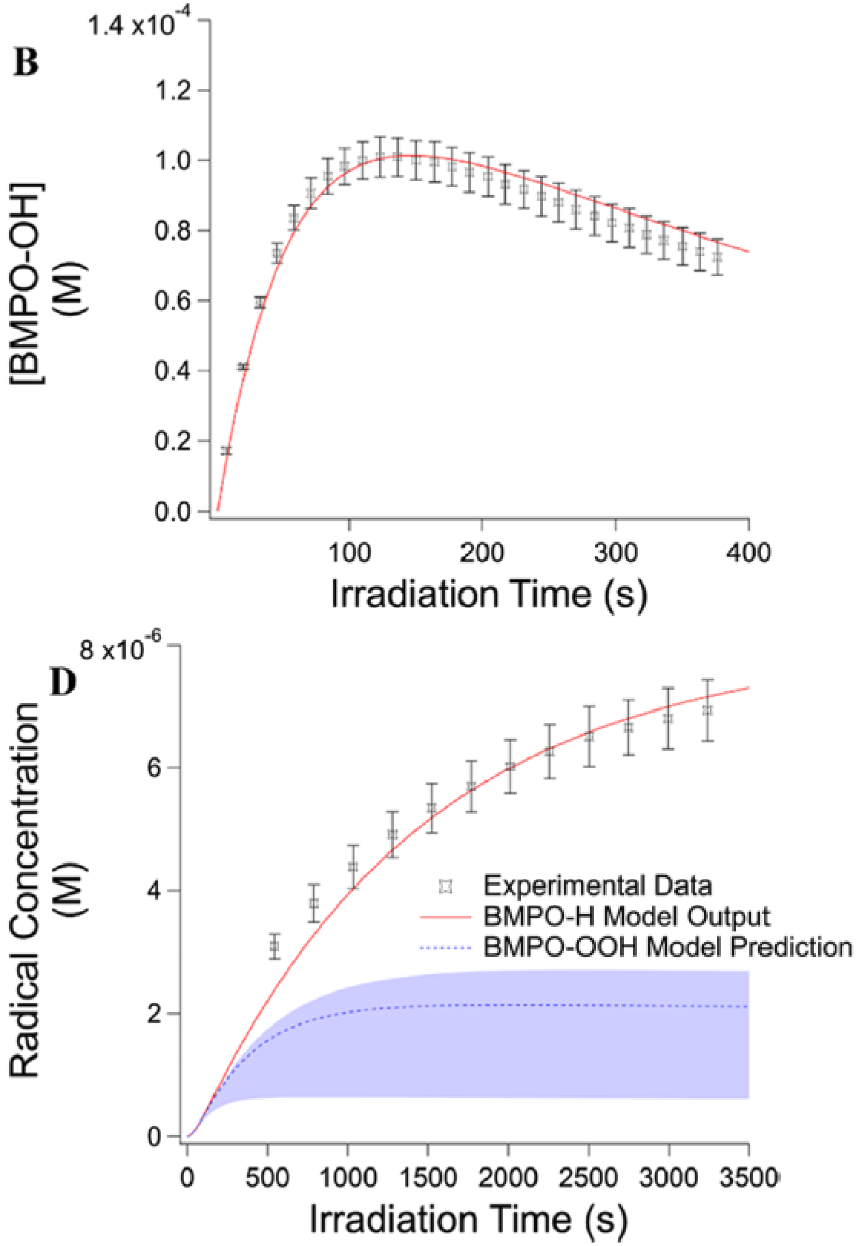
$$RO^{\bullet} \rightarrow R''^{\bullet} + carbonyls \qquad (R13)$$



Wei et al., ES&T, 2022 (Ellen Gonter Award for Jinlai Wei)

Photoenhanced Radical Formation in Levoglucosan/Benzoquinone





- Dominant formation of •OH, by triplet-state benzoquinone with H_2O
- H• were observed, generated by photochemical decomposition of semiquinone radicals.
- Substantial formation of C- and O-centered organic radicals

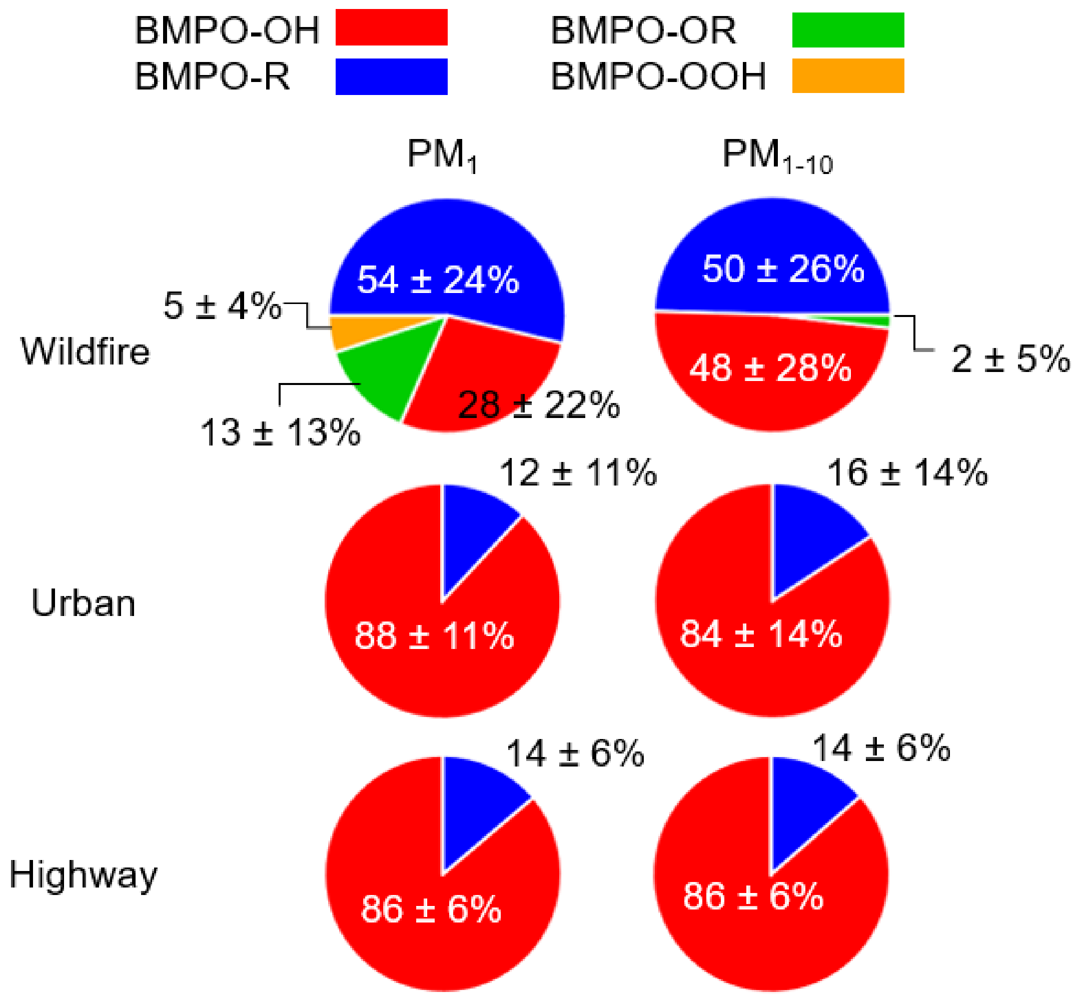
Gerritz et al., J. Phys. Chem. A, 2023

Ambient PM Sampling with high-volume sampler & MOUDI

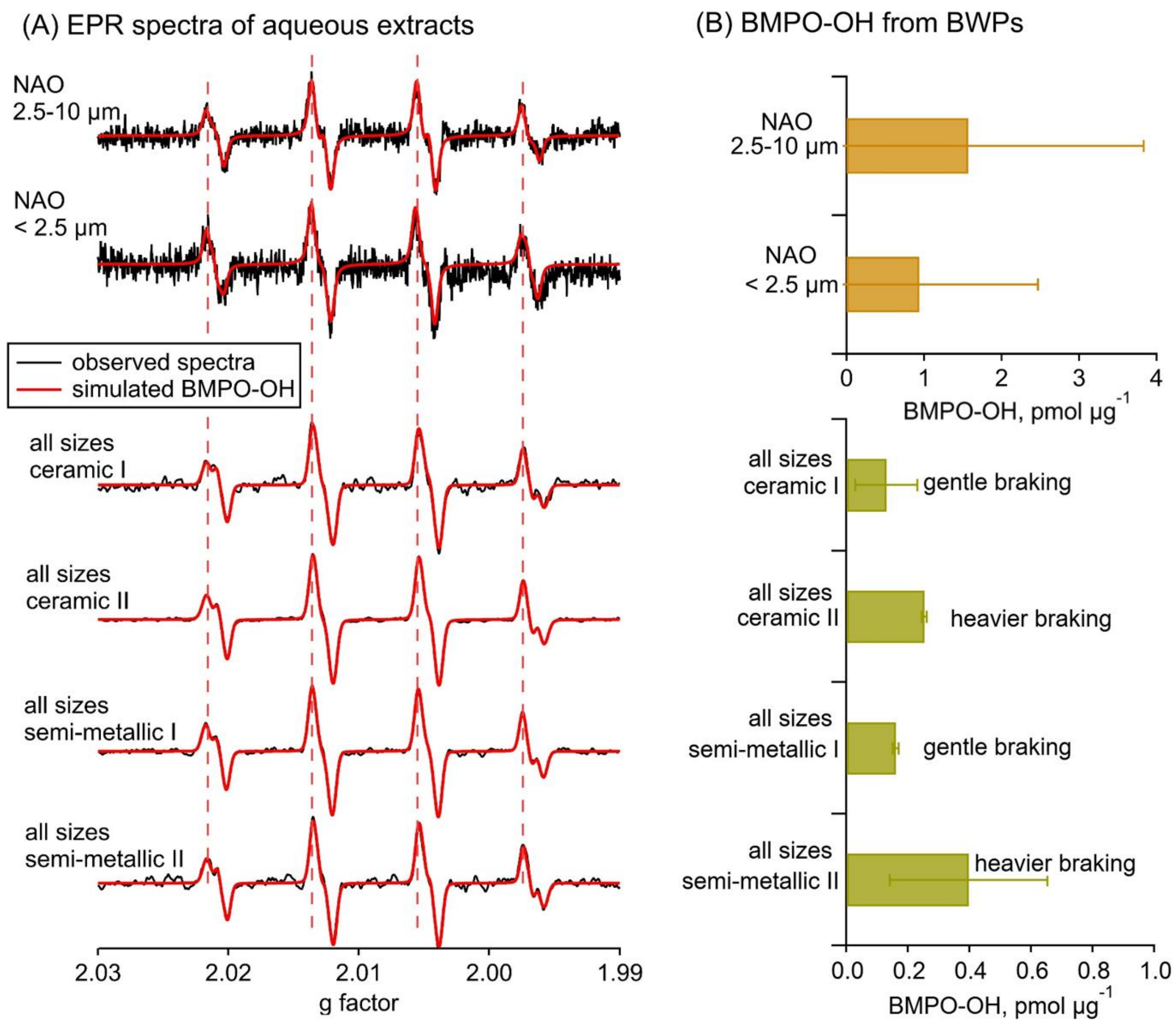
(A) Ambient collection of wildfires, highway, and urban PM

Winter 2022 in Fairbanks, Alaska
Cold/dark environments

EPR Measurements of **environmentally persistent free radicals (EPFRs)** & **ROS** in water



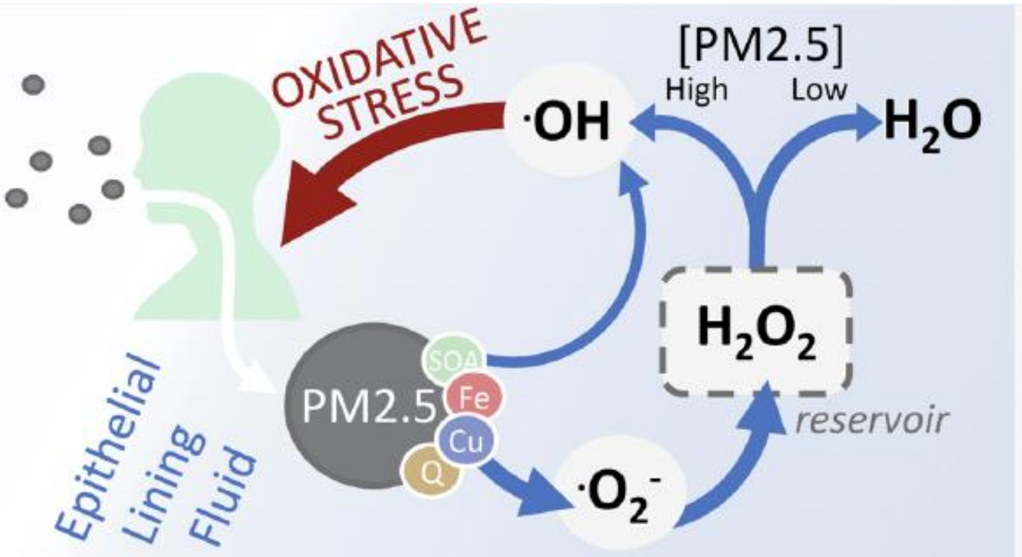
Hwang et al., ACS ESC, 2021; Fang et al., ESA, 2023



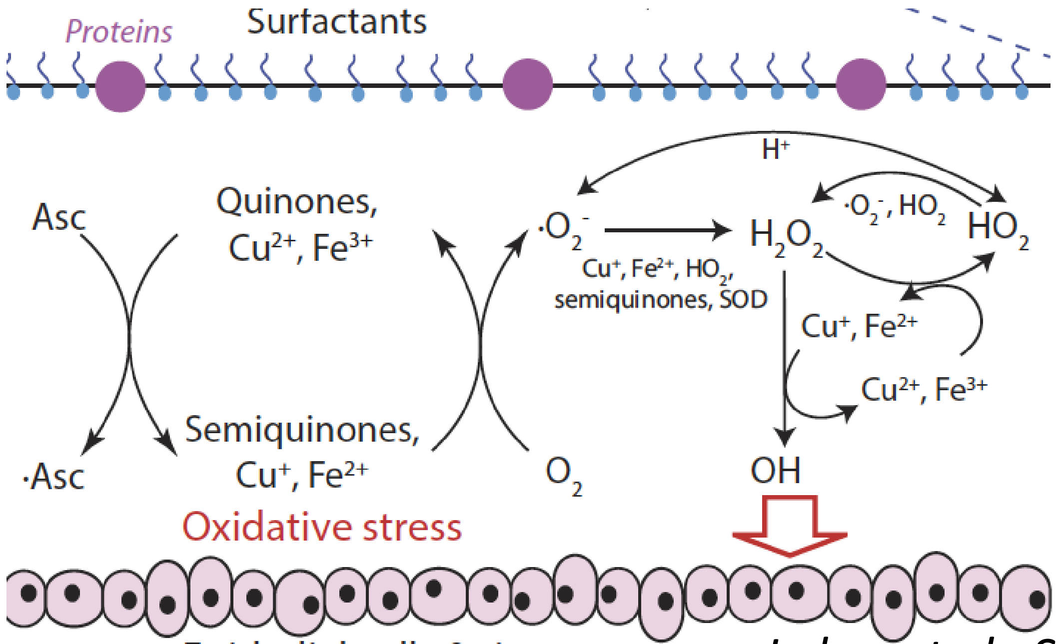
Fang et al., submitted

- Highway/urban PM form mainly OH·: sources from non-tailpipe emissions (**brake wear**)
- Wildfire PM generates various radicals including OH, $\cdot O_2^-$, organic radicals.

Modeling Chemical Exposure-Response Relationship



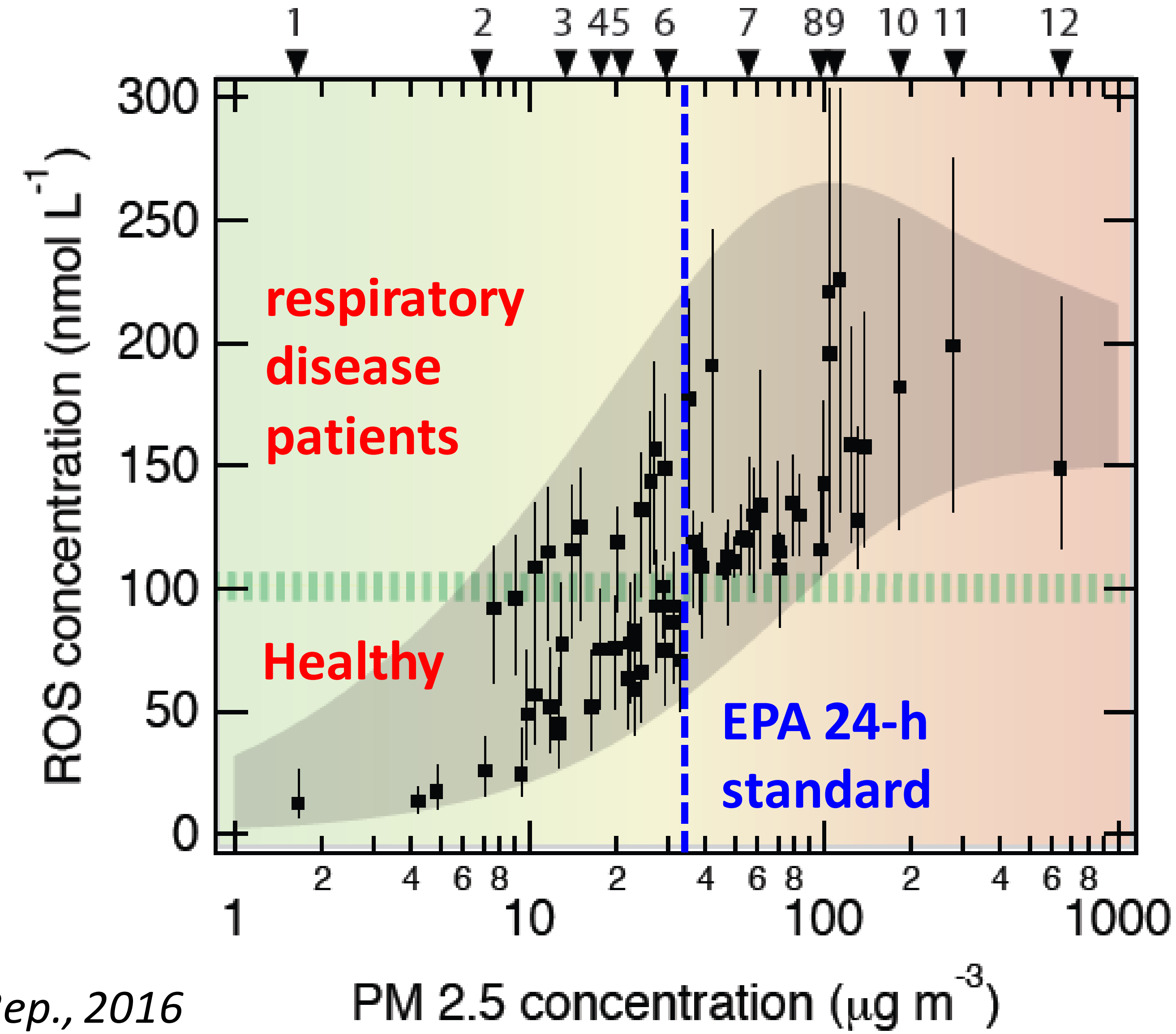
Lelieveld et al., ES&T, 2021



Lakey et al., Sci. Rep., 2016

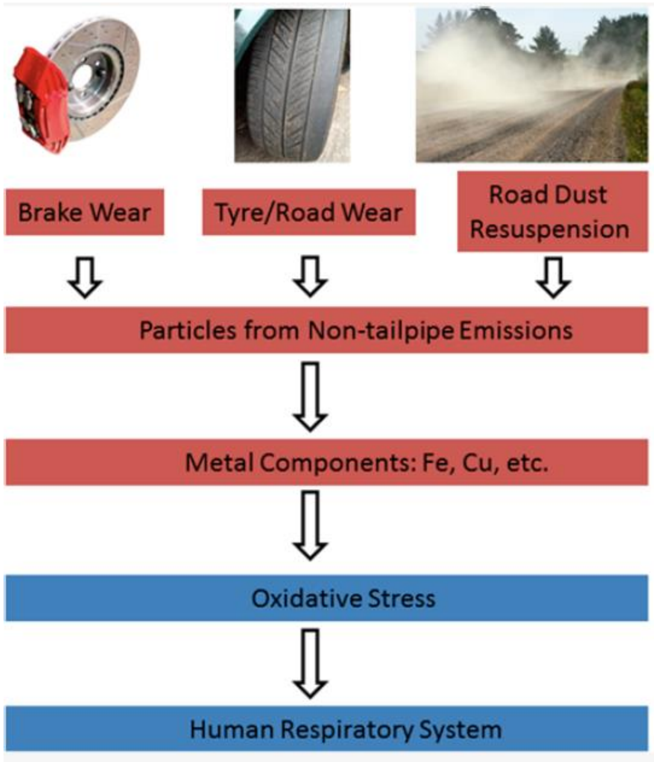
KM-SUB-ELF Model

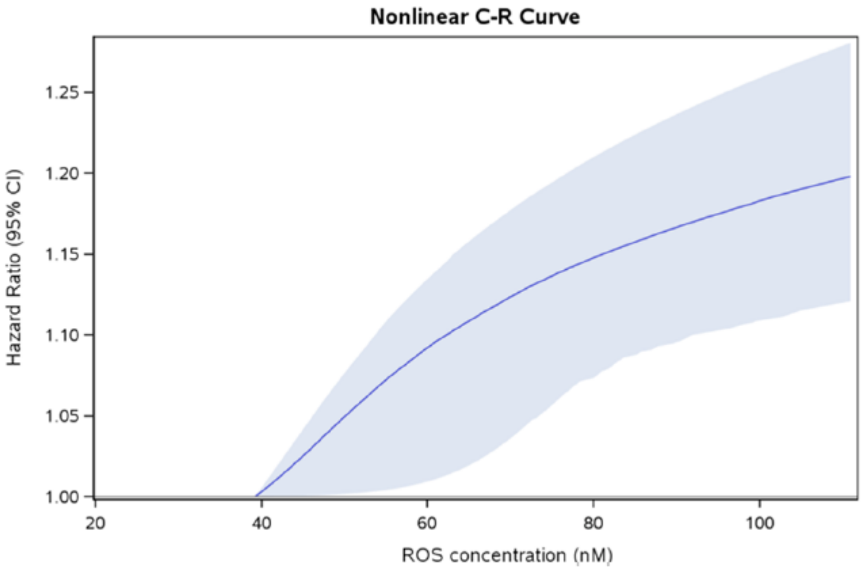
1. Amazon
2. Edinburgh
3. Toronto
4. Tokyo
5. Budapest
6. Hong Kong
7. Milan
8. Guangzhou
9. Pune
10. Beijing
11. New Delhi
12. Indonesia



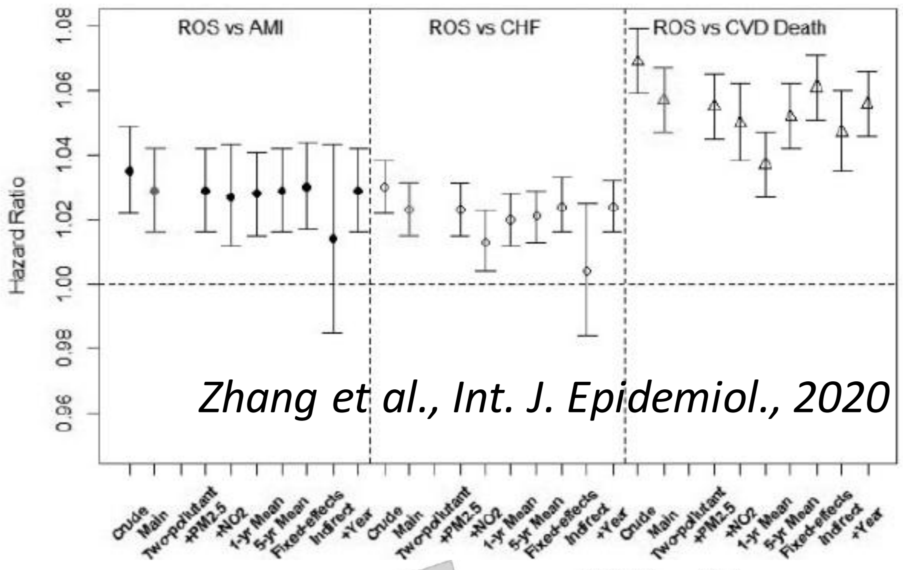
Applications of KM-SUB-ELF to Epidemiological Studies

In collaboration with ***Scott Weichenthal (McGill), Michael Jerrett (UCLA)***

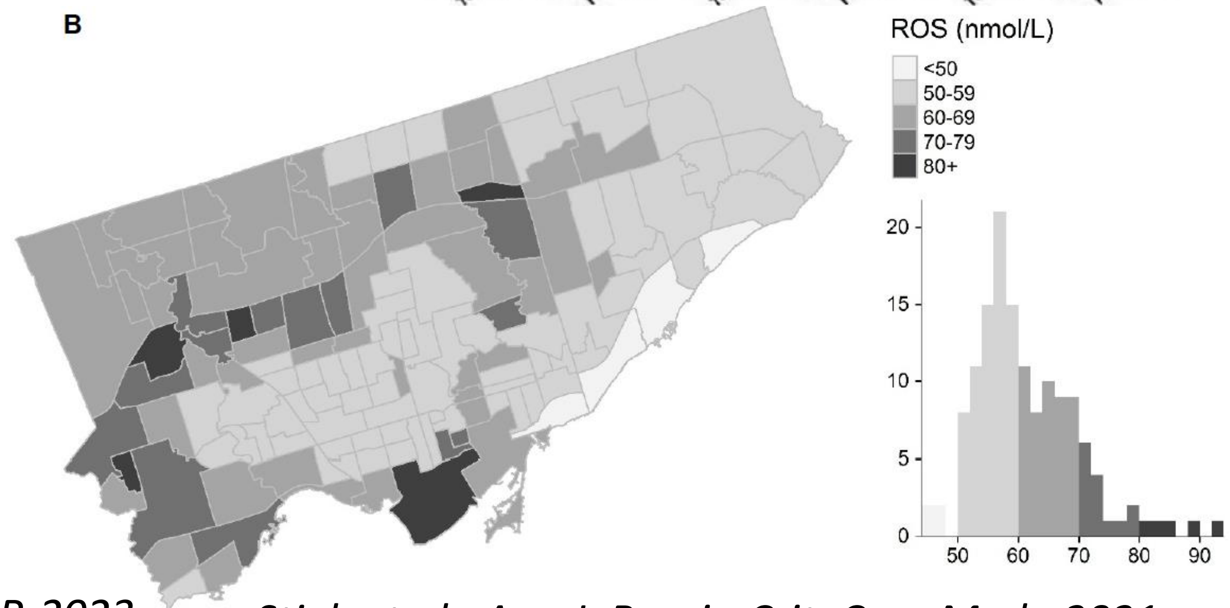




Zhang et al., EST, 2021



Zhang et al., Int. J. Epidemiol., 2020



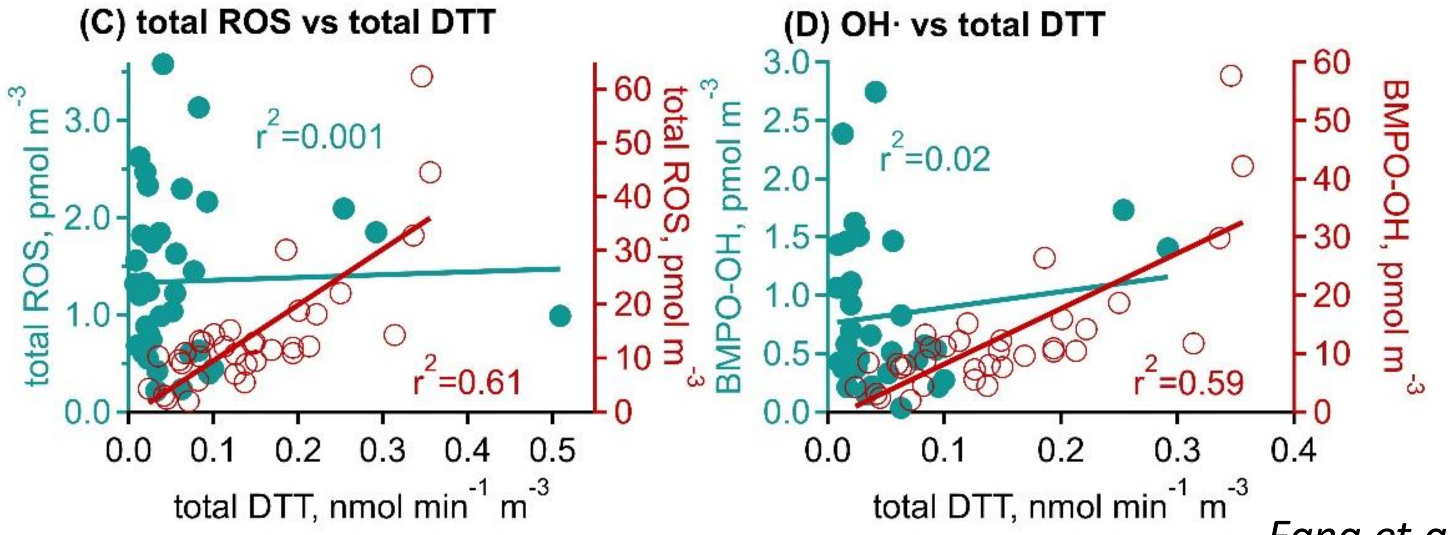
The observed associations were stronger for the estimated ROS than for iron and copper individually.

Oxidative stress in lung have strong associations with respiratory & cardiovascular diseases, adverse birth outcomes, allergenic diseases in children in L.A.

To et al., 2022 & Liu et al., 2022; Ripley et al., 2023, Meng et al., EHP, 2023

Stieb et al., Am. J. Respir. Crit. Care Med., 2021

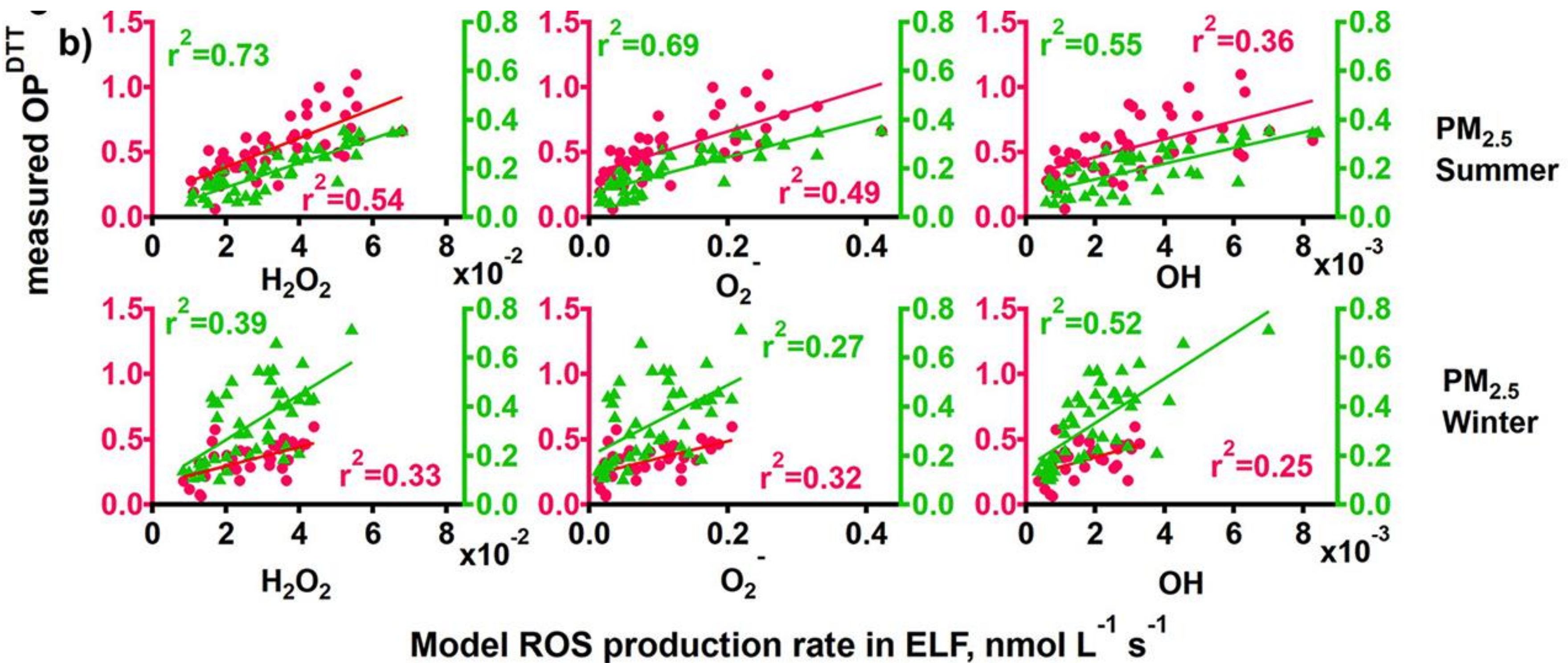
Oxidative Potential vs. ROS



- OP-DTT of highway/urban samples are correlated with ROS/OH
- no correlation is observed in wildfire PM

Fang et al., ESA, 2023

Road side oxidative potential (AA/DTT) measurements in Atlanta



PM oxidative potential may be a reasonable indicator of ROS at road site, but less so when affected by biomass burning.

Fang et al., ES&T, 2019

EPFRs vs. Oxidative Potential of OH formation in Lung Fluid

EPFRs are emitted by traffic and residential wood burning in Fairbanks

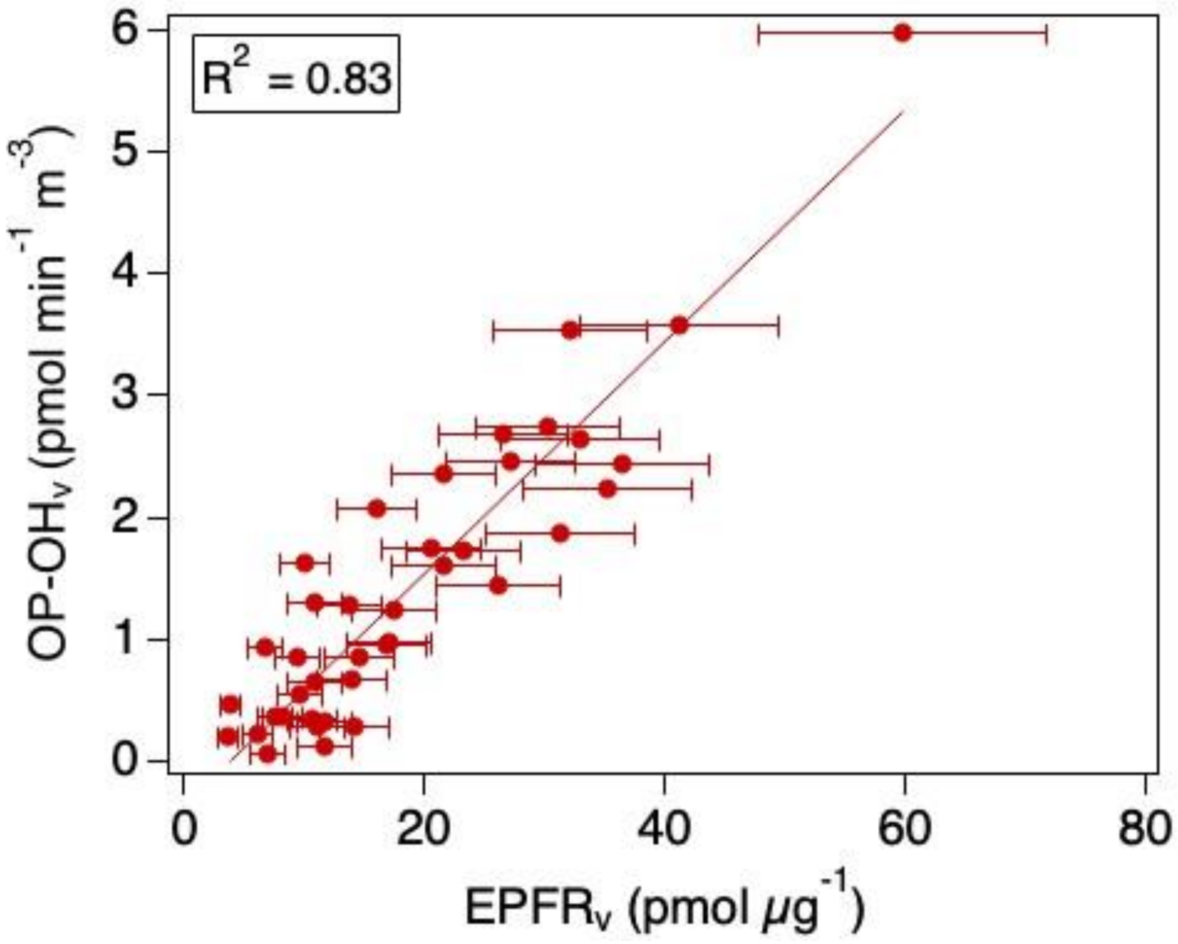
EPFR concentrations are equivalent to smoking ~0.4 - 1 cigarette daily

EPFR is known to be redox active (Dellinger et al.)

Weak correlation of EPFR vs. OP-DTT

Excellent correlation of EPFR vs. OP-OH

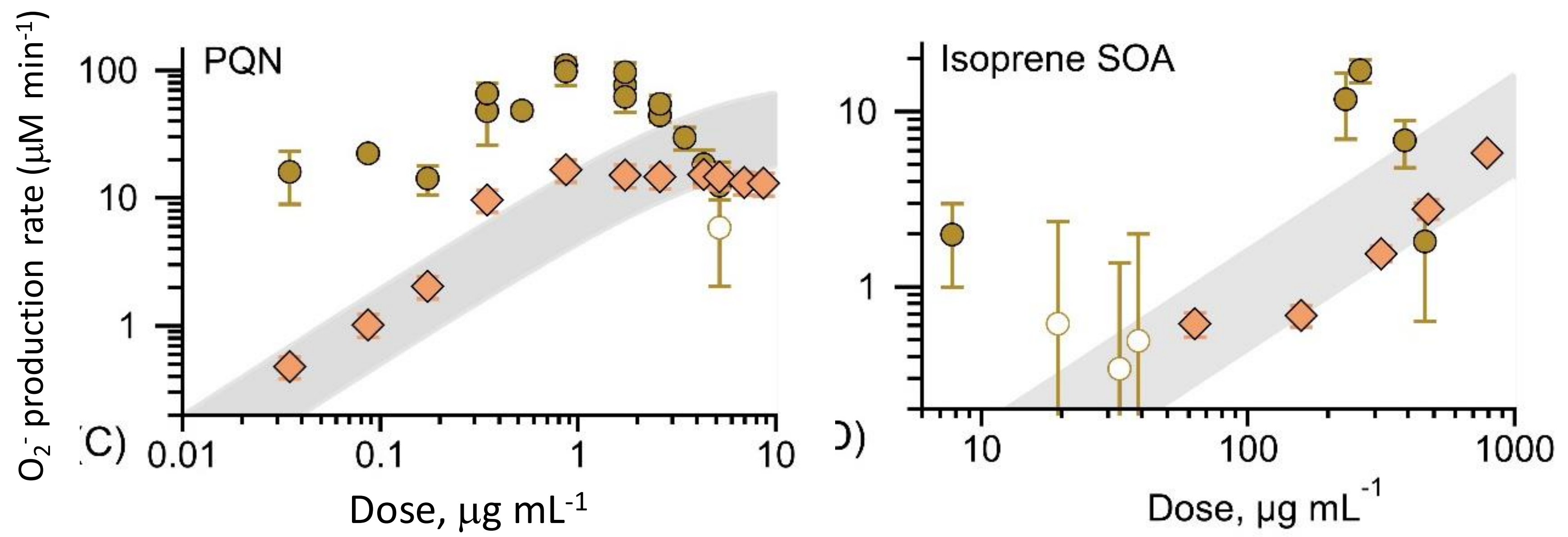
ALPACA campaign, OP-OH by Rodney Weber (GIT)

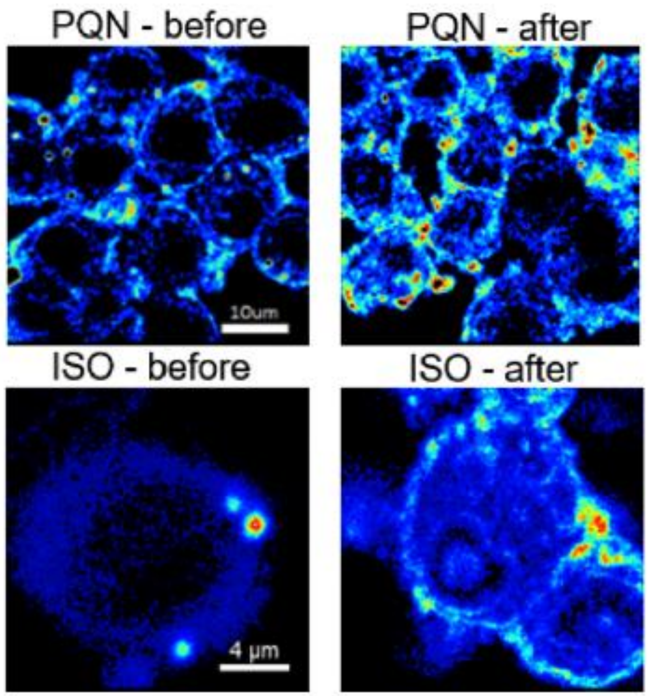


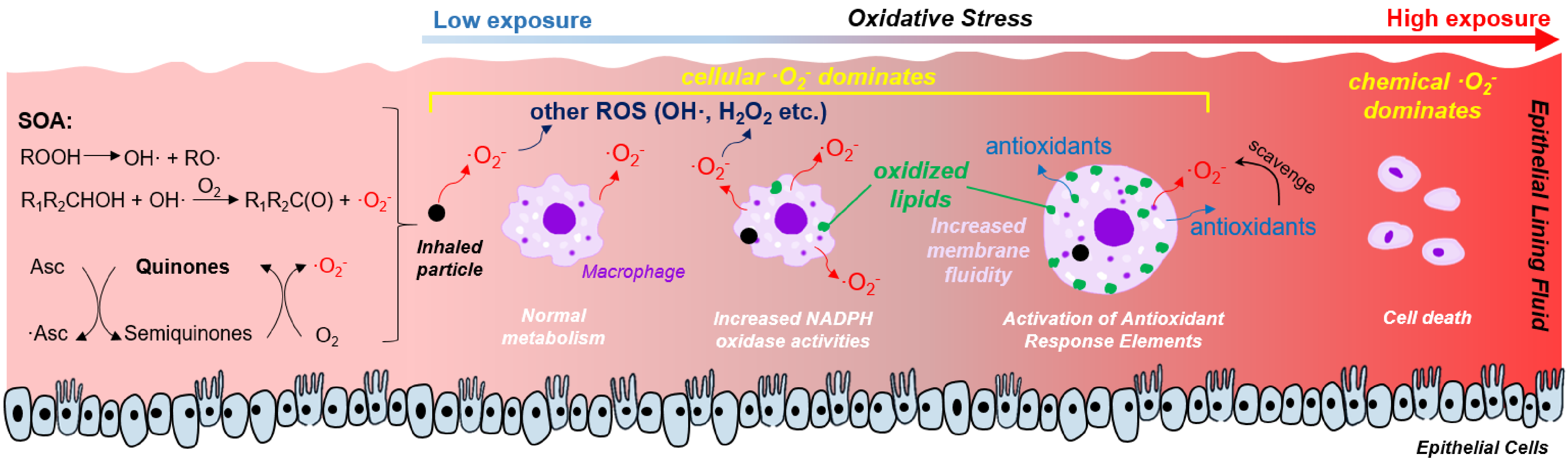
Edwards et al., to be submitted

Cellular vs. Chemical ROS

Fang et al., ES&T, 2022







Conclusions

- Atmospheric PM contains reactive and redox-active compounds, which can induce ROS formation in lung fluid to cause oxidative stress.

- Decomposition of organic hydroperoxides is a major ROS source in SOA, which can be promoted by photolysis and Fenton-like reactions.

- KM-SUB-ELF model can estimate ROS levels in lung fluid, which can be applied into epidemiological studies, showing strong associations with a variety of adverse health outcomes.

- Model needs to be improved: chemistry with other antioxidants, cellular processes, enzymes, synergistic effects by other pollutants, ….

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HEALTH EFFECTS INSTITUTE

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