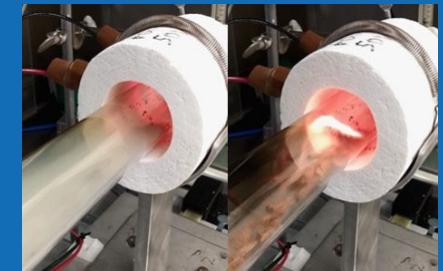




Comparative Toxicity of Biomass Smoke from Different Fuels and Combustion Conditions

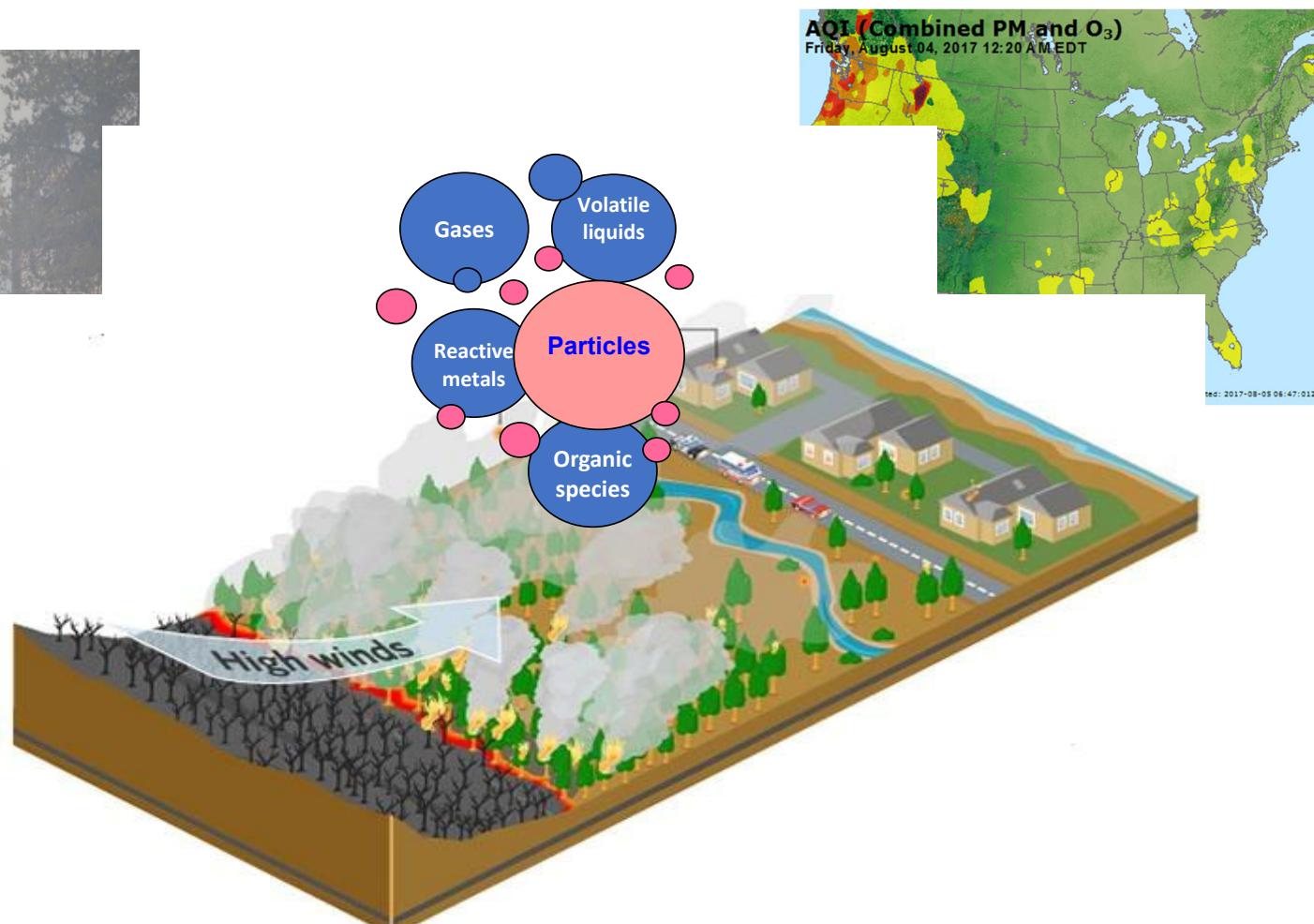
M Ian Gilmour Ph.D, DABT

Public Health & Integrated Toxicology Division
Center for Public Health and Environmental Assessment



Inhalation and Respiratory Specialty Section Webinar
December 13th 2019

Where There is Smoke There are Health Impacts!



Emissions by Chemical Class for Particle and Vapor Constituents in Woodsmoke

Chemical	Particle-phase (mg/kg wood burned)	Vapor-phase (mg/kg wood burned)
Carbon monoxide	---	130,000
Alkanes (C2-C7)	0.47 - 570	1.01 - 300
Alkenes (C2-C7)	0.58 - 280	92 - 1300
Polycyclic aromatic hydrocarbons (PAHs) and substituted PAHs	5.1 - 32,000	43.4 - 355
Methane	---	4100
Total nonmethane hydrocarbons C2-C7	[Included in vapor phase]	390 - 4000
Unresolved complex mixture (UCM)	300 - 1,130,000	---
Alkanols	0.24 - 5400	120 - 9200
Carboxylic acids	6200 - 755,000	2.4
Aldehydes and ketones	[Included in vapor phase]	0.94 - 4450*
Alkyl esters	0.37 - 4450	---
Methoxylated phenolic compounds	28 - 1000	1200 - 1500
Other substituted aromatic compounds	5.0 - 120,000	110 - 3600
Sugar derivatives	1.4 - 12600	---
Coumarins and flavonoids	0.71 - 12	---
Phytosteroids	1.7 - 34.0	---
Resin acids and terpenoids	1.7 - 41,000	21 - 430
Unresolved compounds	1.2 - 120	20 - 600

* Only aldehydes reported.

L.P. Naeher et al, Inhalation Toxicology 2007

Source-Based Inhalation Toxicology Studies at LRRI *

	Irritation & Inflammation	Allergies & Asthma	Respiratory Defenses	Respiratory & Cardiac Functions	Cancer
Diesel exhaust	*	*	*	*	*
Wood Smoke	*	*	*	*	*
Gasoline exhaust	*	*	*	*	*
Coal emissions	*	*	*	*	*
Cooking fumes	*	*	*	*	*
Road dust	*	*	*	*	*
Tobacco smoke	*	*	*	*	*

- Study of each atmosphere creates a “layer” in the combined database
- Multiple animal models address a range of health concerns

4 Exposure Levels = 6 hr/day, 7 days/wk for up to 6 months

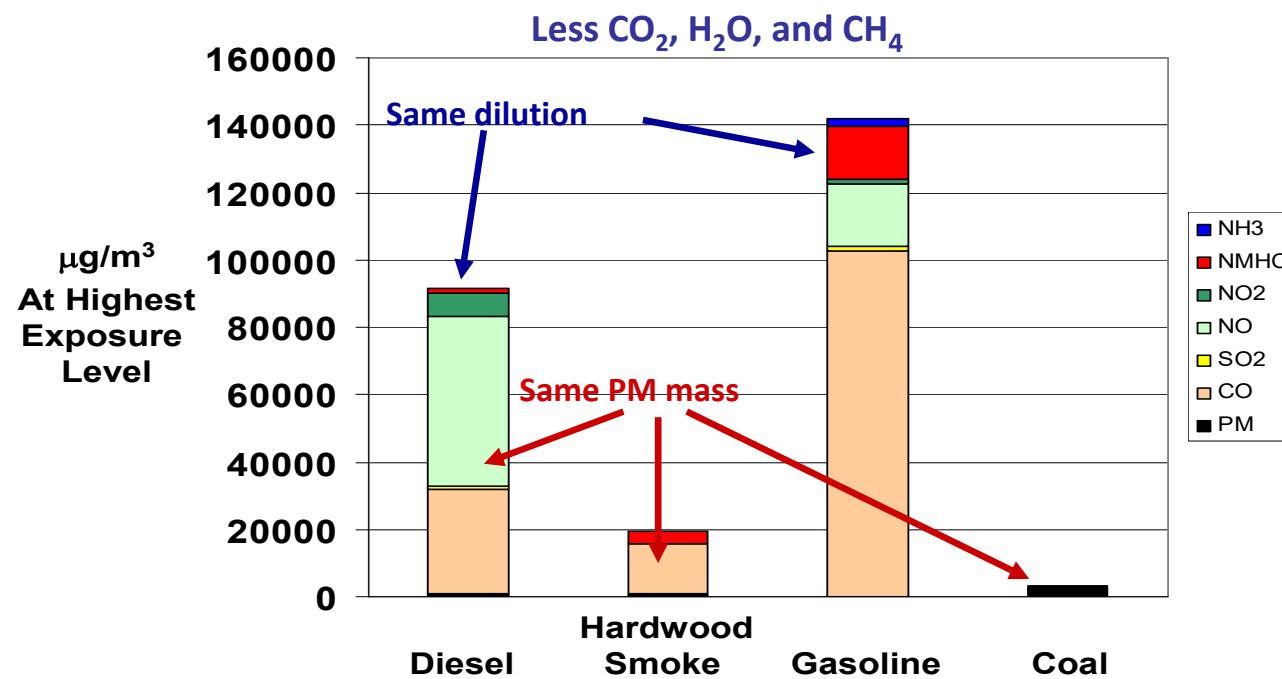
* Lovelace Respiratory Research Institute (LRRI) – National Environmental Respiratory Center

Mauderly and Colleagues. Inhalation Tox, 26(11), 2014

Courtesy, Dr J McDonald



Conclusion from NERC

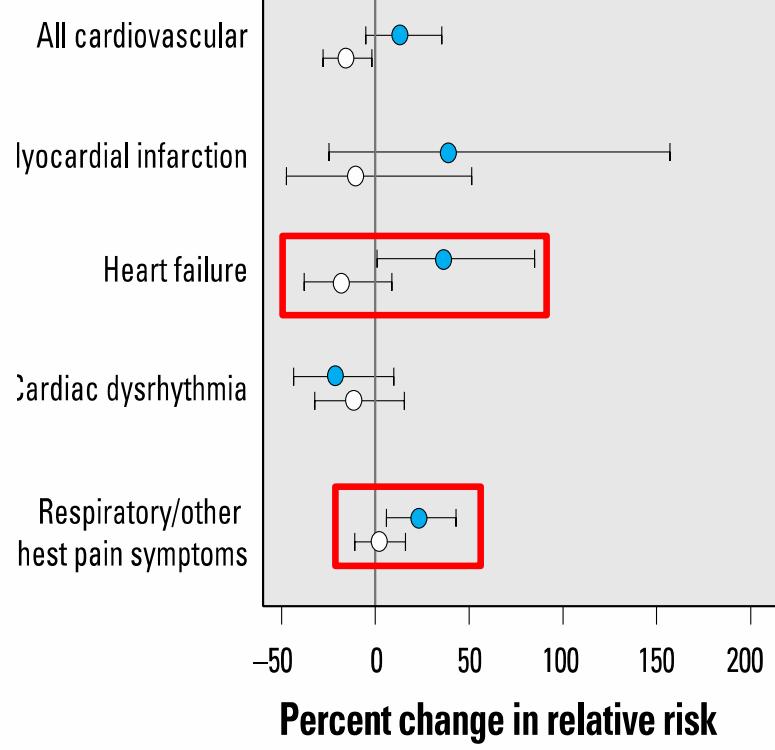
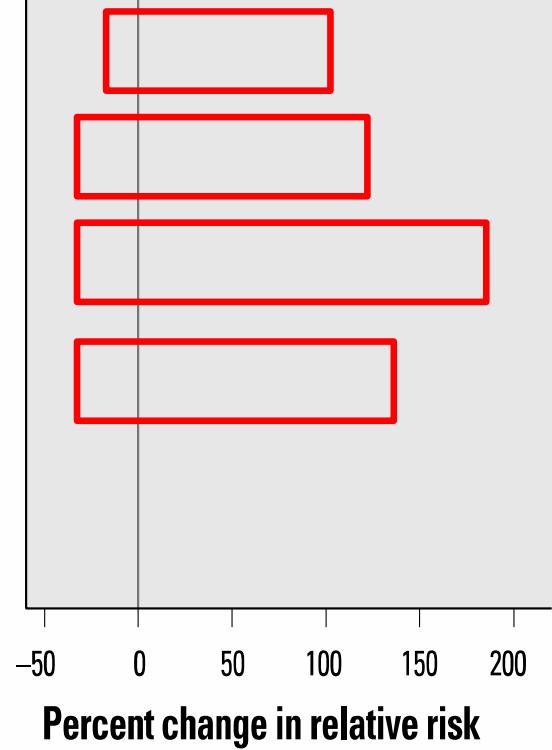


Diesel significantly affected the most parameters - coal the fewest DE \geq GE > HWS >> C

Gas phase components had a significant contribution

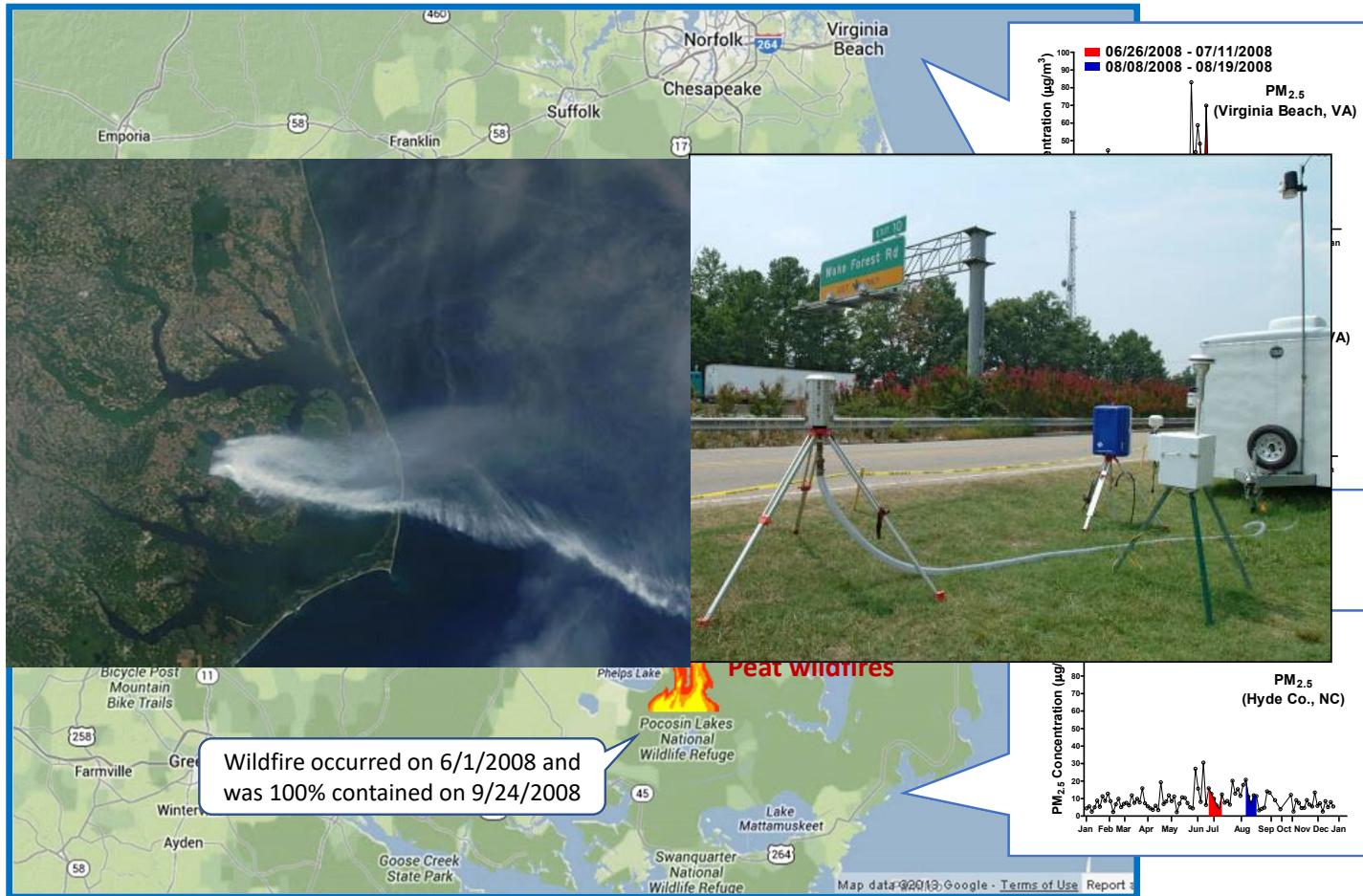


Courtesy, Dr J McDonald
Mauderly, Inhalation Tox, 26(11), 2014

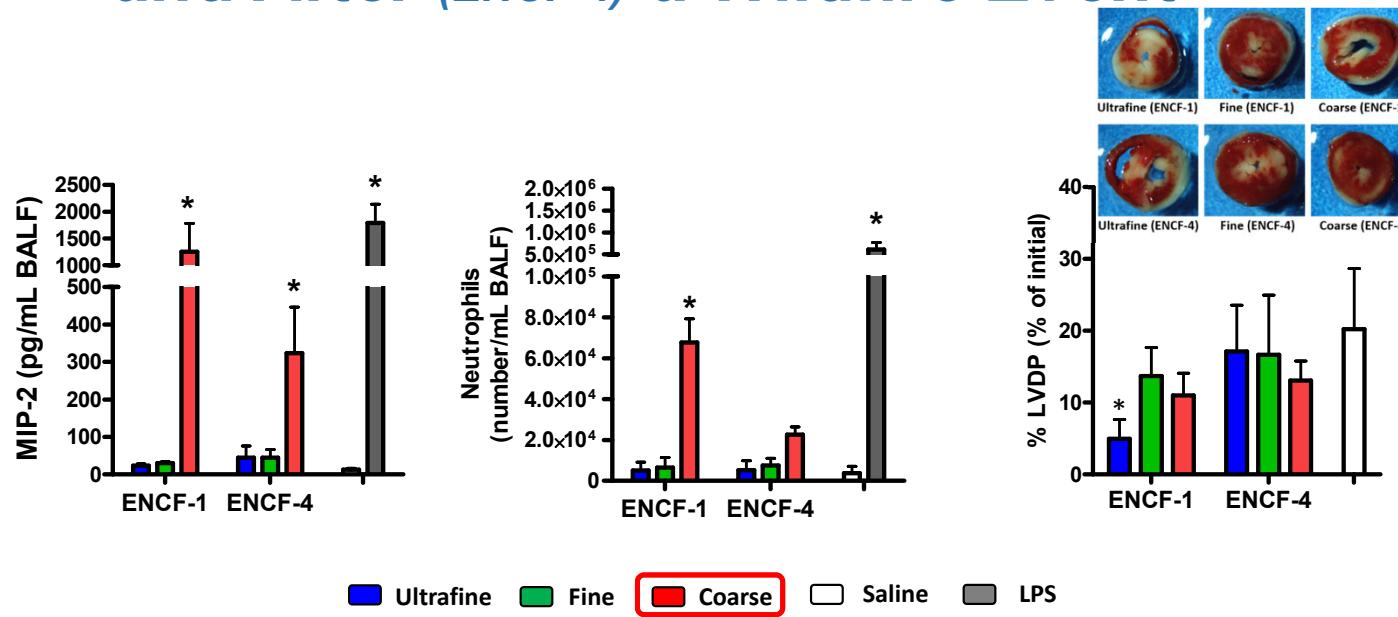


Percent change in cumulative RR by discharge diagnosis category for exposed and referent counties in NC during 3-day period of high exposure compared with the entire 6-week study period.

Location of Chemvol PM Sampler and Monitoring Data for (ENCF-1 and ENCF-4)

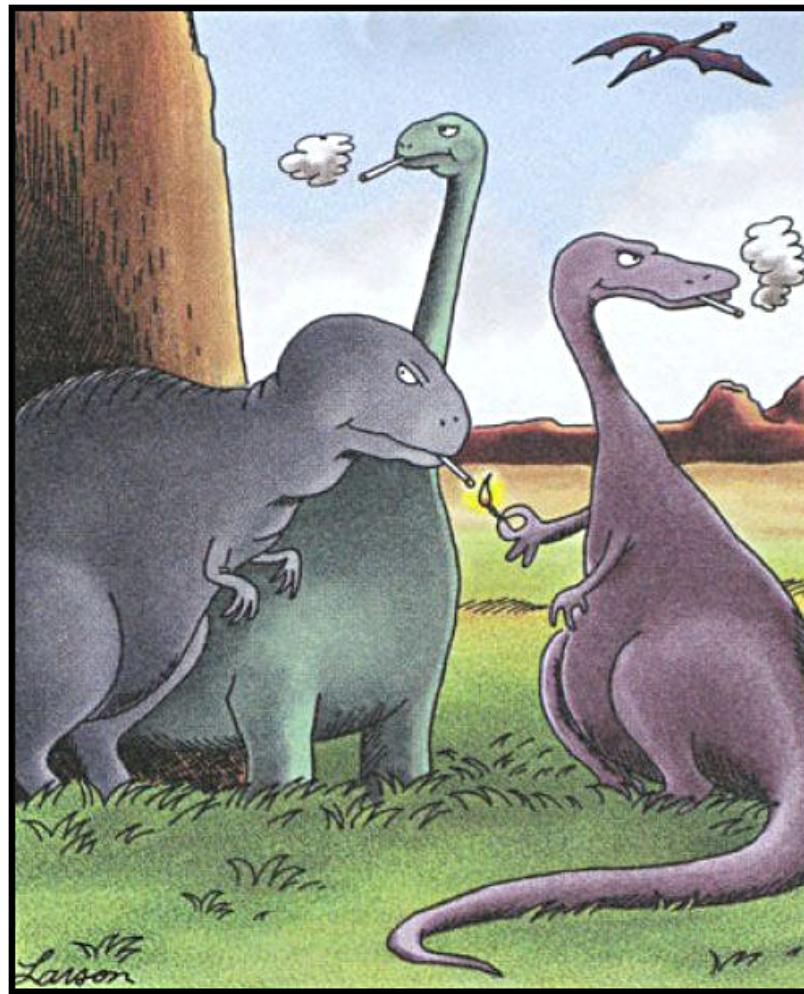


Comparative Toxicity of PM During (ENCF-1) and After (ENCF-4) a Wildfire Event



Exposure to the coarse PM significantly increased the levels of cytokines (IL-6, TNF- α , and MIP-2) and neutrophils in BALF of mice and this was higher with ENCF-1.

Exposure to the ultrafine PM from ENCF-1 significantly decreased cardiac function (left ventricular developed pressure) in mice compared to all other samples.



The real reason dinosaurs became extinct

All Smoke Is Not Created Equally!



← Fuel type
Combustion
phase



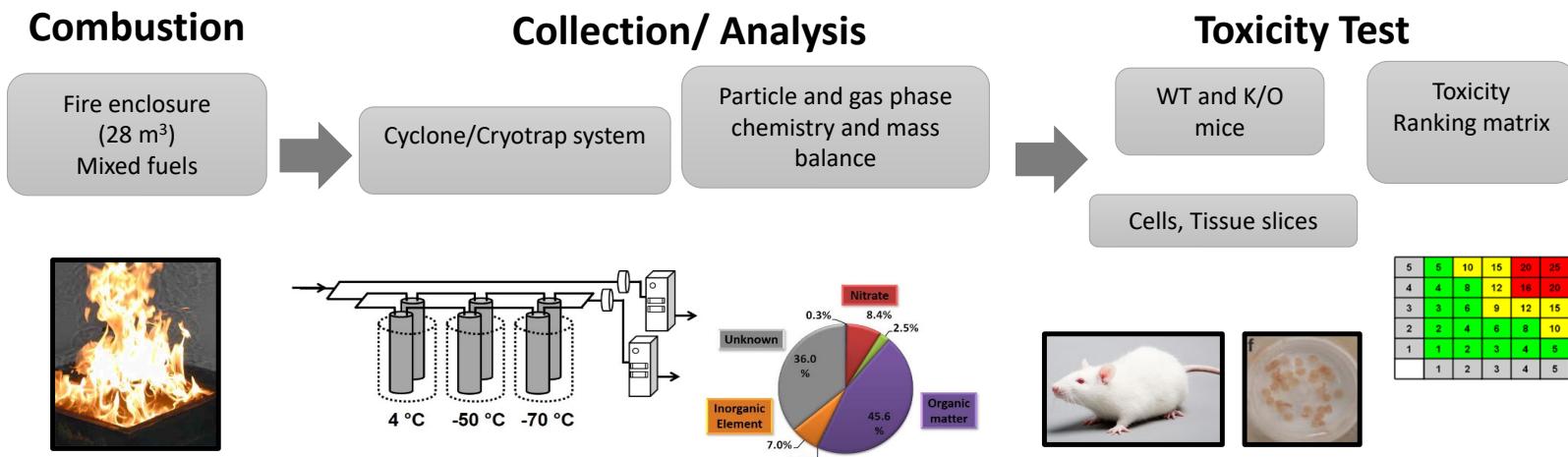
← Combustion
phase



Laboratory Generated Smoke Collection and Analysis with Subsequent Toxicity Testing

Objective:

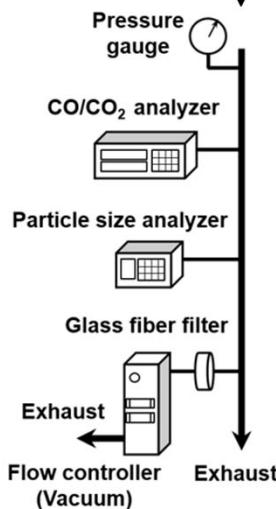
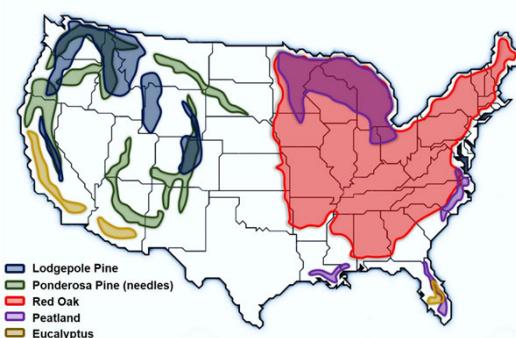
Compare the relative cardiopulmonary toxicity and mutagenicity of coarse and fine/ultrafine emissions from four distinct fuel types (pine, oak, peat, and a mixed pine and deciduous Southeastern forest biomass) obtained from both smoldering and active flame phases.



Biomass Combustion and Smoke Sampling System



Yong Ho Kim



Tube Furnace System

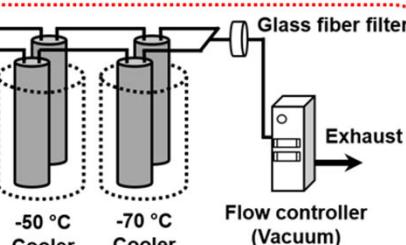


Biomass fuel

Direction of ring
furnace movement

Quartz tube

Air

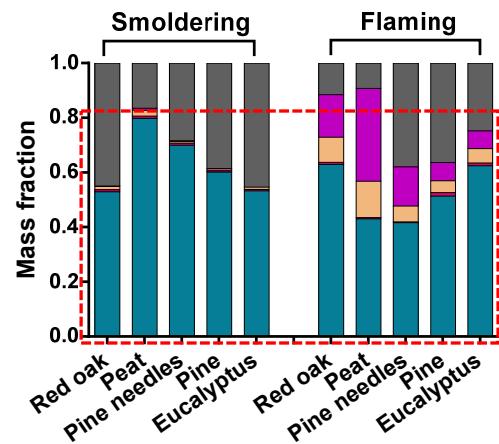


Multi-Stage Cryotrap System

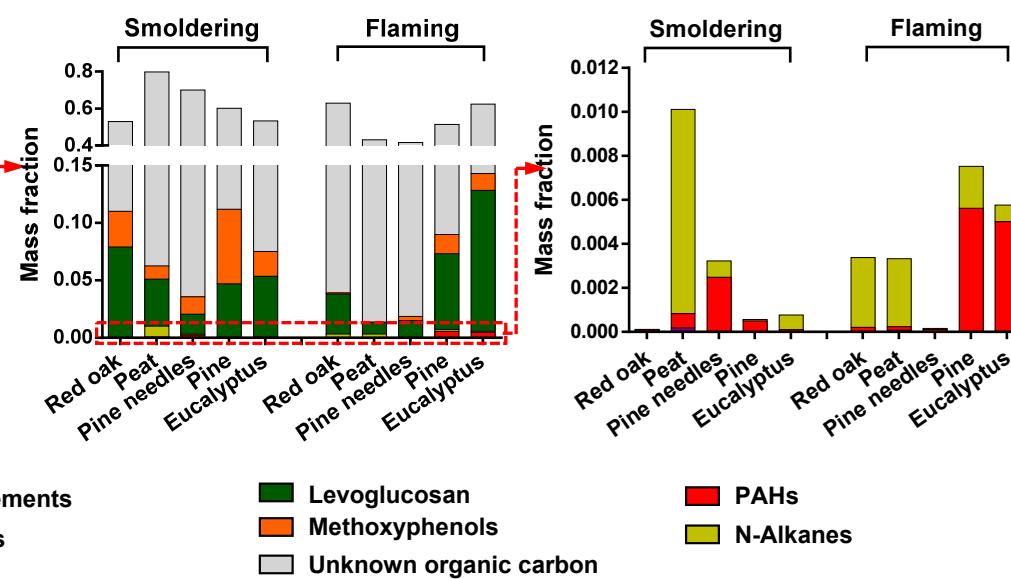
- The tube furnace is able to sustain stable flaming or smoldering phase consistently for 60 min.
- The cryotrap system is able to collect PM and semi-volatile compounds.

Chemical Components in Biomass Smoke Condensate

Major chemical compounds

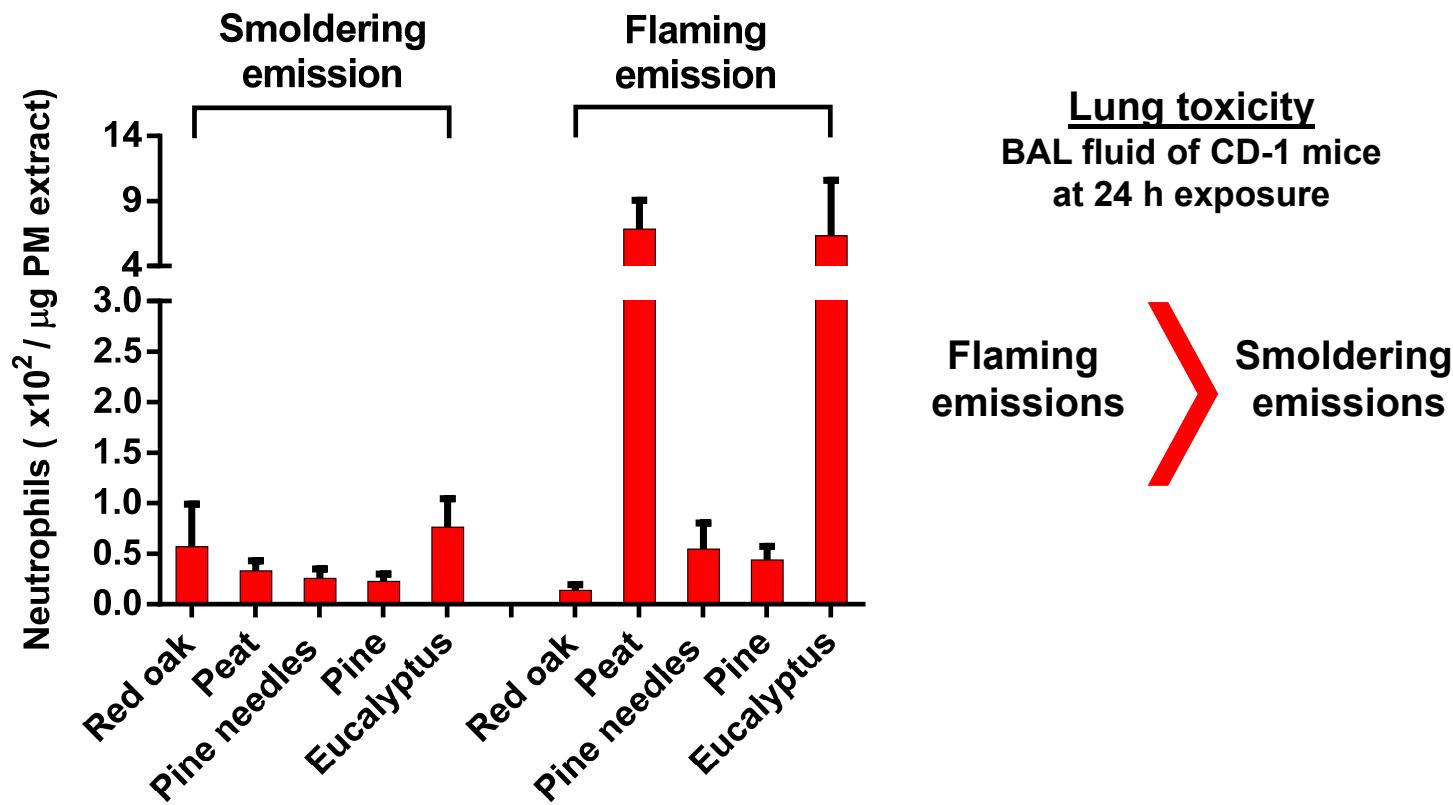


Semi-volatile organic compounds



- Chemical properties of biomass smoke varied depending on fuel types and combustion phases.
- Inorganic elements (e.g., heavy metals) and PAHs were higher in the flaming smoke PM.

Lung Toxicity of the Biomass Smoke Condensates Based on Equal Mass



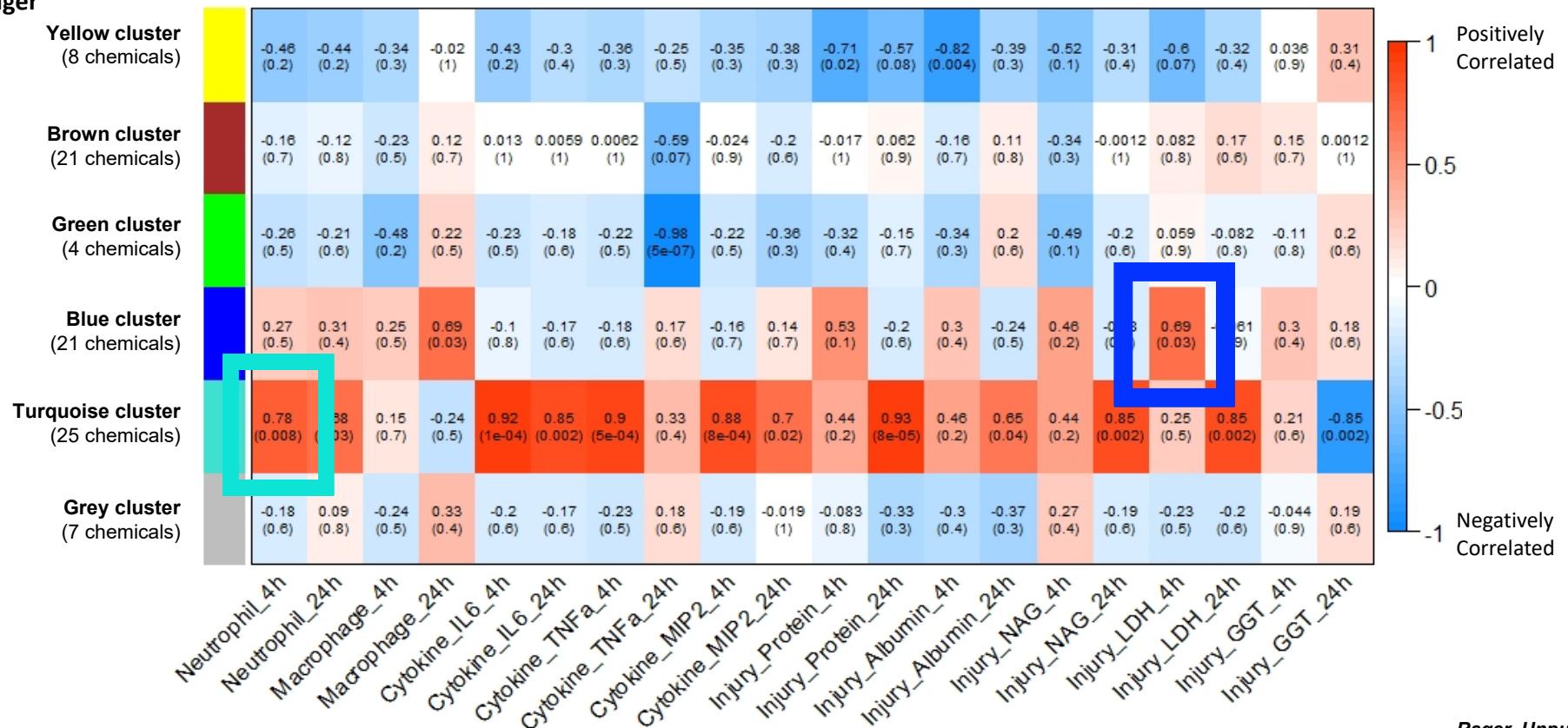
Lung toxicity
BAL fluid of CD-1 mice
at 24 h exposure

Flaming emissions Smoldering emissions



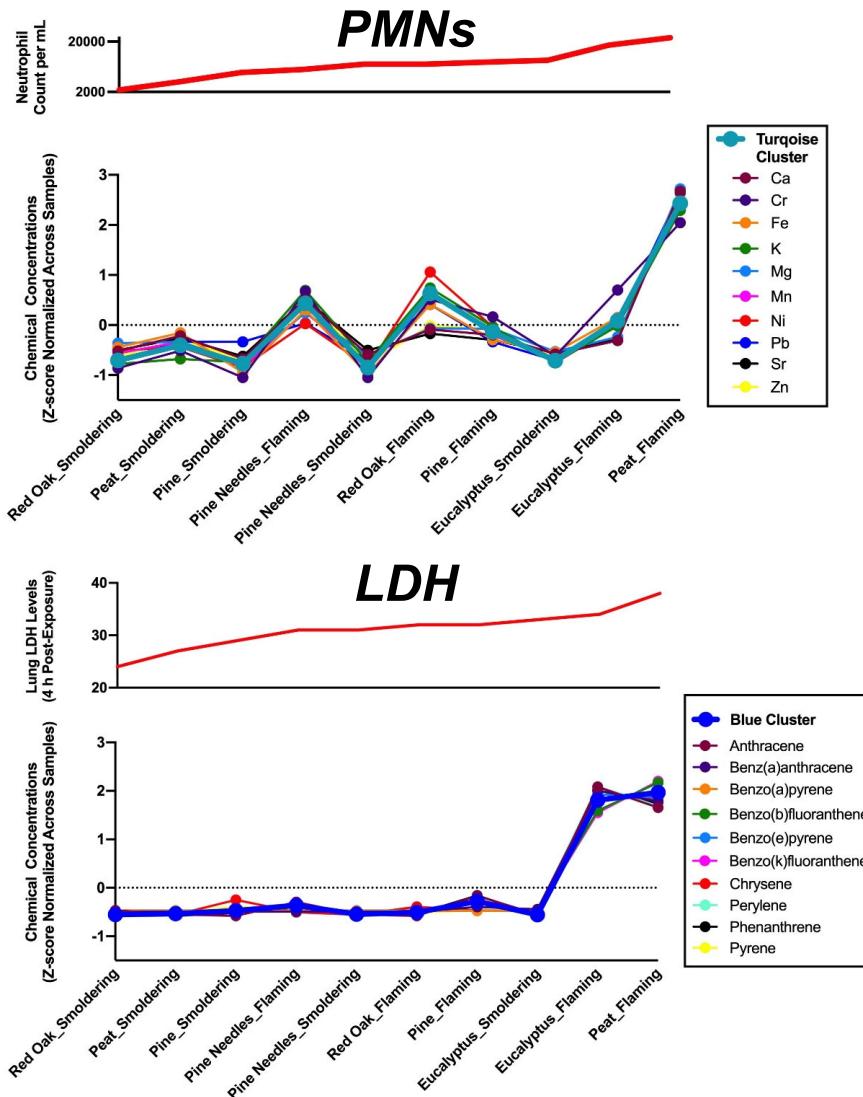
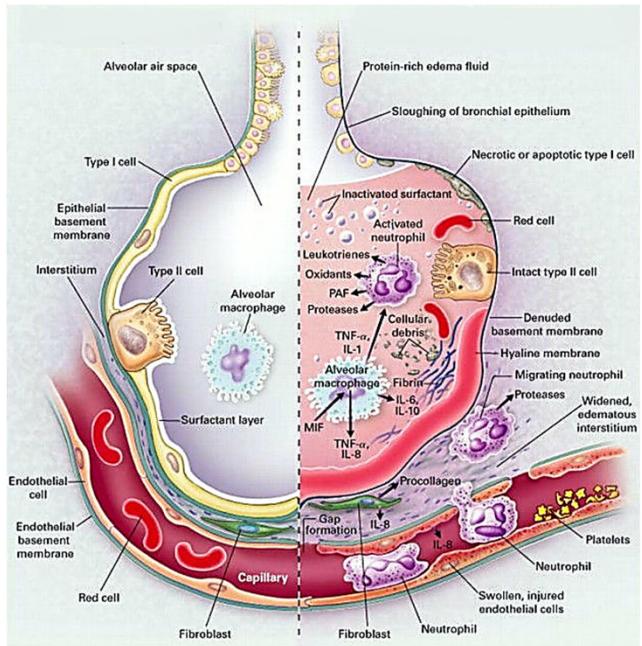
Bioinformatics Approach to Link Toxicity Responses with Chemical Clusters

Julia Rager



Rager. Unpublished

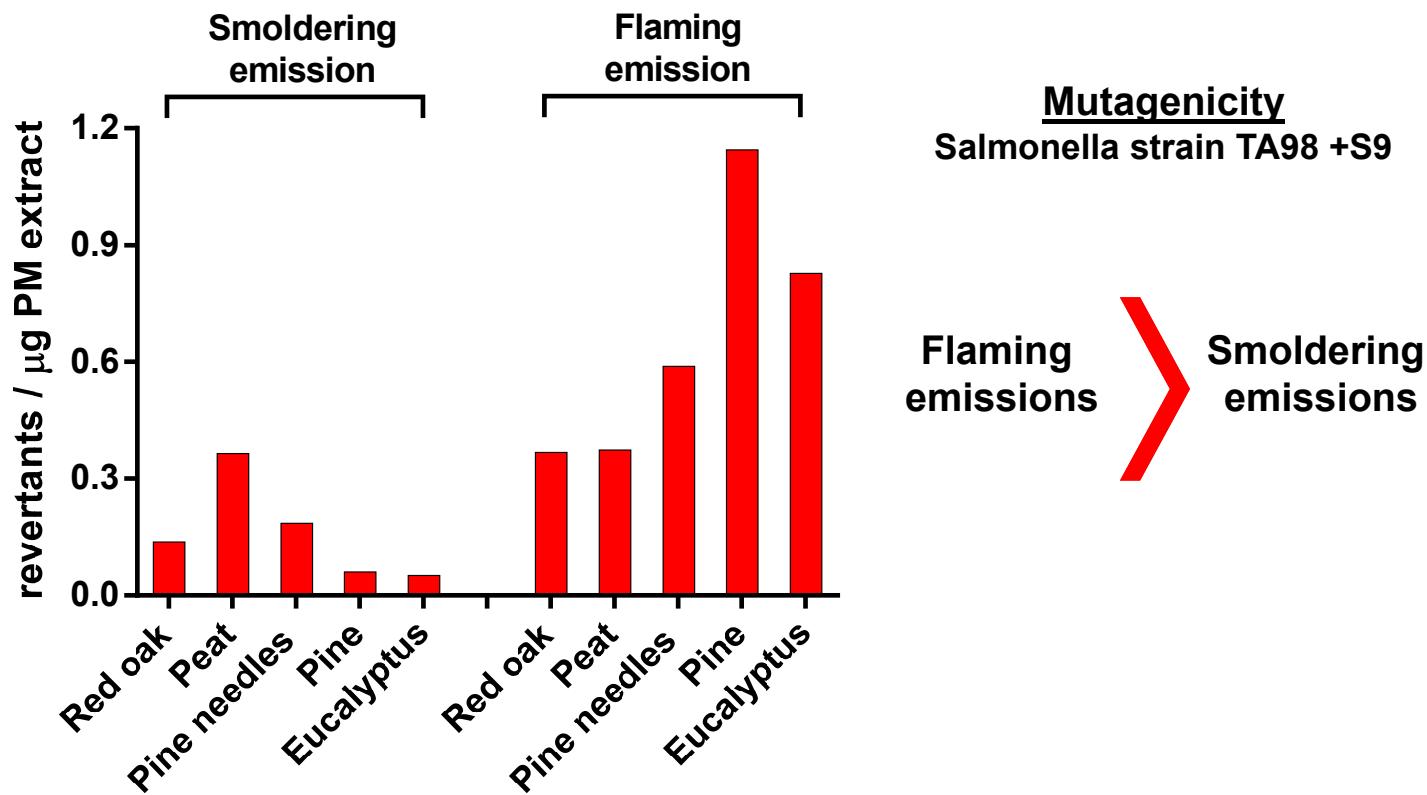
Top-Ranking Species Across Biomass Burns Associated with Neutrophil Inflammation (PMNs) and Lung Injury (LDH)



Mutagenicity of the Biomass Smoke Condensates Based on Equal Mass



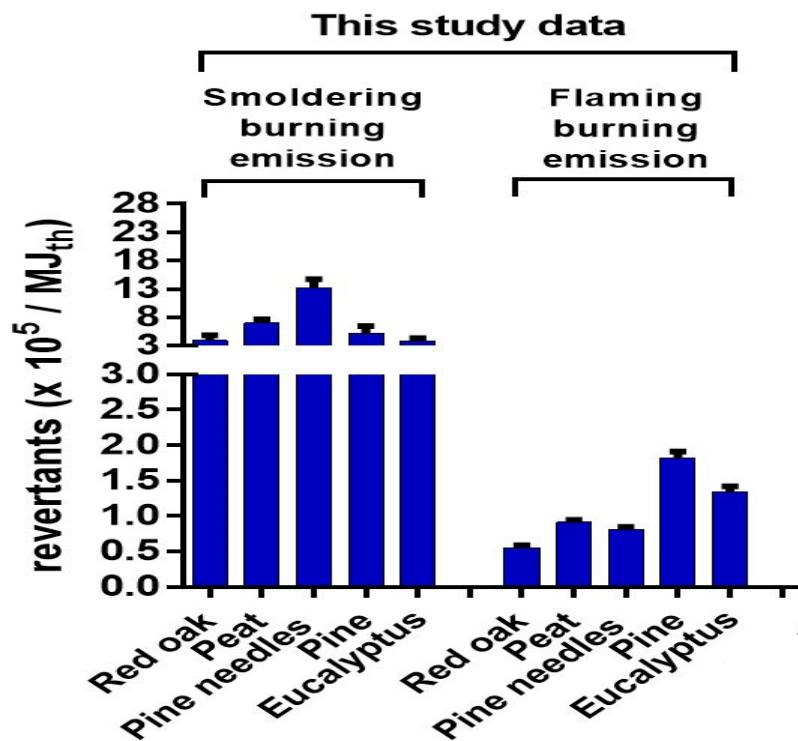
David DeMarini



Mutagenicity
Salmonella strain TA98 +S9

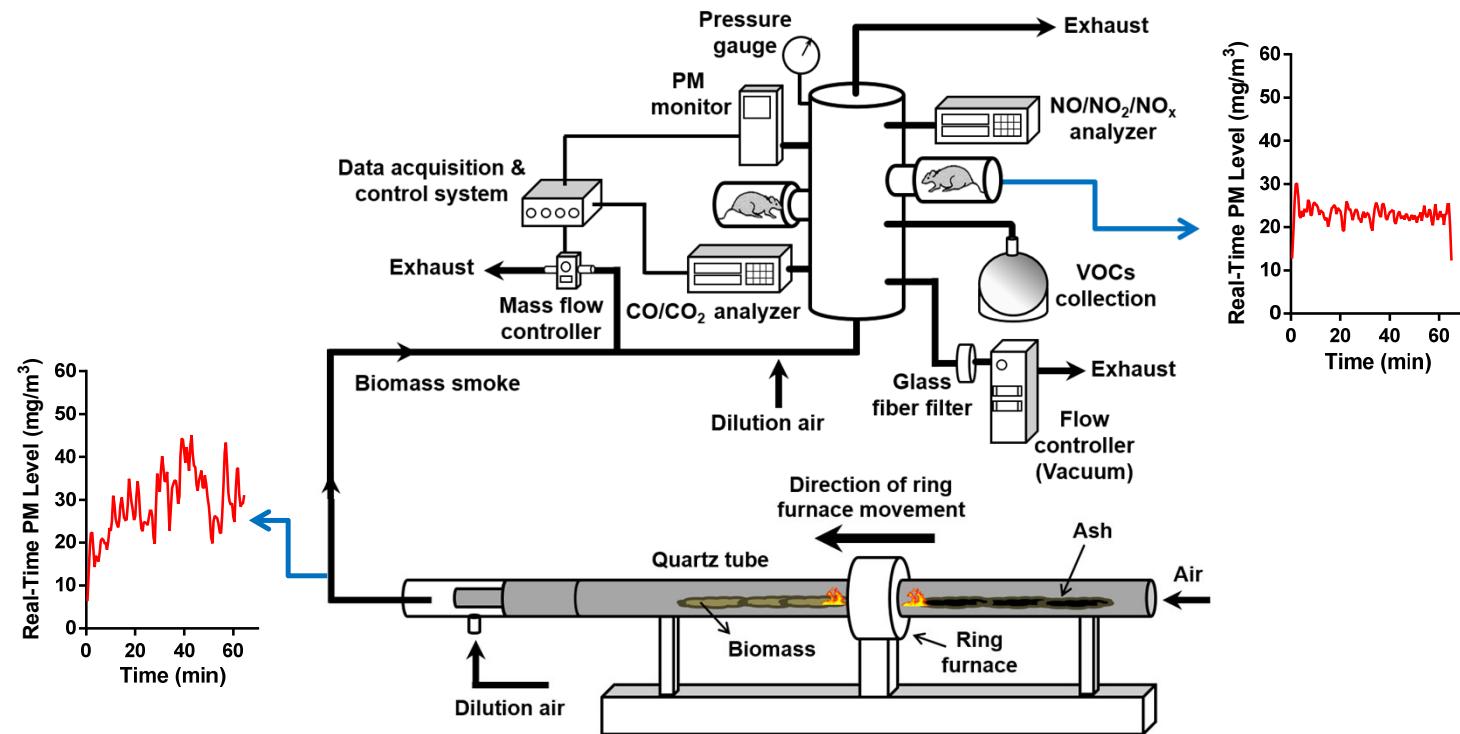
Flaming emissions → Smoldering emissions

Comparison of Mutagenicity Emission Factors (EFs) of Various Combustion Emissions

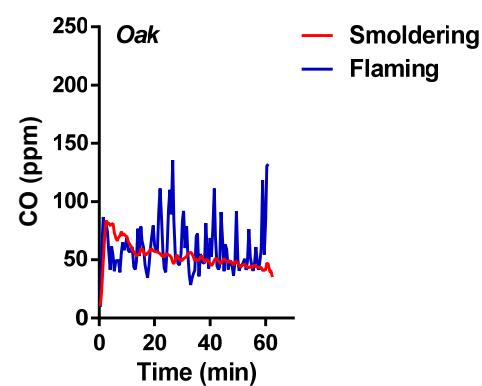
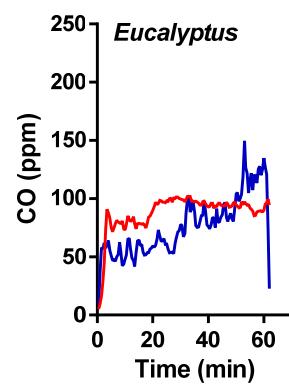
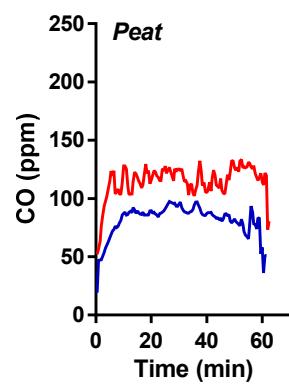


The mutagenicity EFs (rev/kg fuel; Figure 6C) were converted to rev/MJ_{th} using the values for the heat energy of each fuel (MJ_{th}/kg fuel). The mutagenicity EFs for wood burning cookstove emissions were 0.2, 1.2, and 2.4×10^5 rev/MJ_{th} for the force-draft stove, natural-draft stove, and three-stone fire, respectively, and the data were obtained from a previous report (Mutlu et al. 2016). The mutagenicity EFs for non-wood burning emissions were 0.4, 0.4, 2.5, and 22.7×10^5 rev/MJ_{th} for the municipal waste, diesel exhaust, agricultural plastic, and tire, respectively, and the data were obtained from previous reports (DeMarini et al. 1994; Linak et al. 1989; Mutlu et al. 2015; Watts et al. 1992).

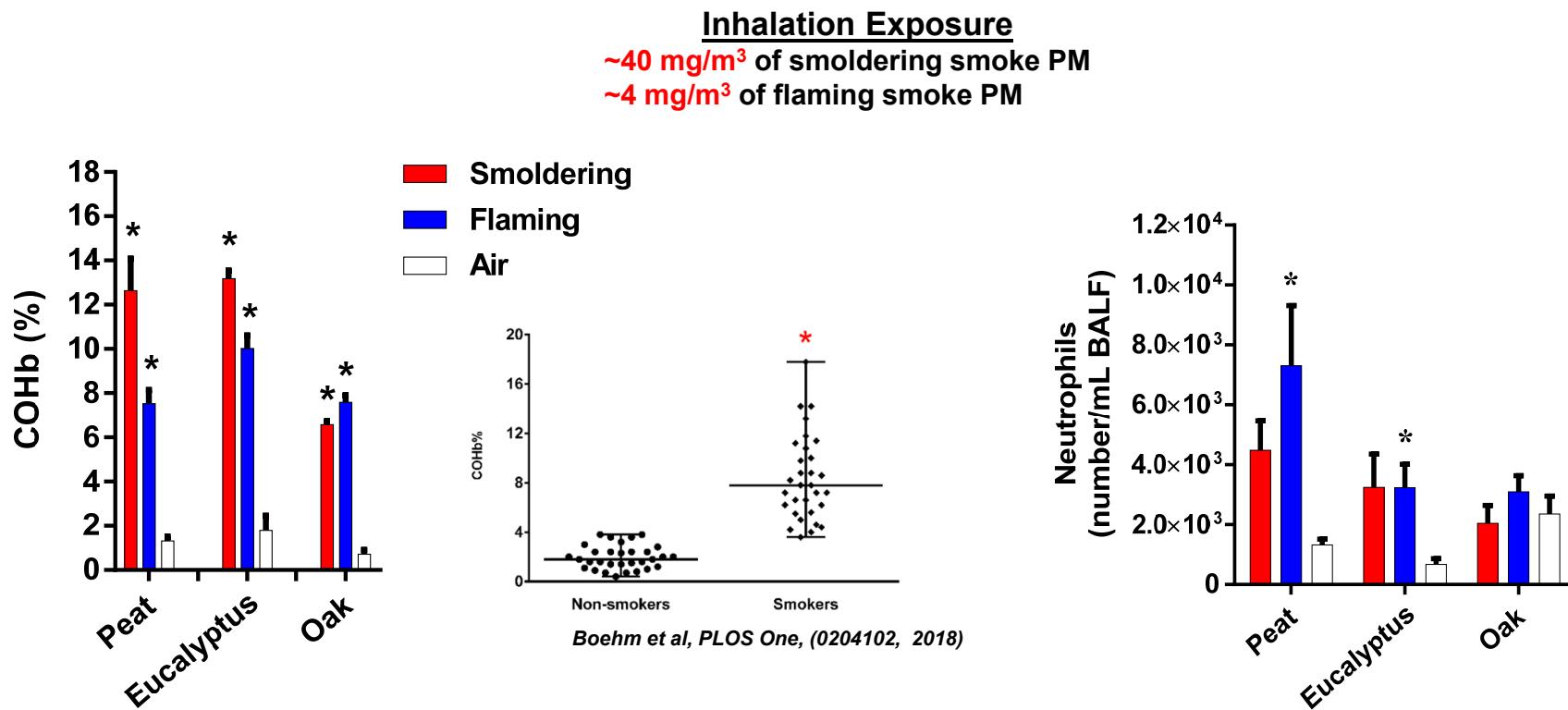
Creating Stable Biomass Emissions in a Computer-Controlled Inhalation Exposure System



Stable Biomass Smoke Atmospheres Created Through a Feedback Control Loop



Effect of Fuel and Combustion Conditions on Carboxyhemoglobin and Lung Inflammation



Carboxyhemoglobin mirrored CO exposure levels (mean is 5-8 % in smokers)

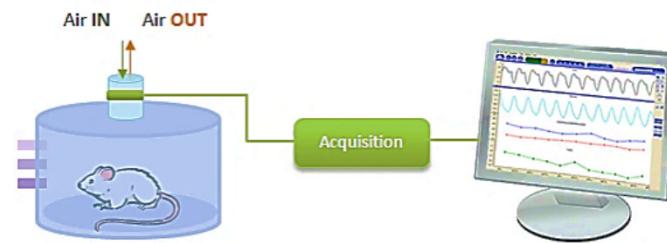
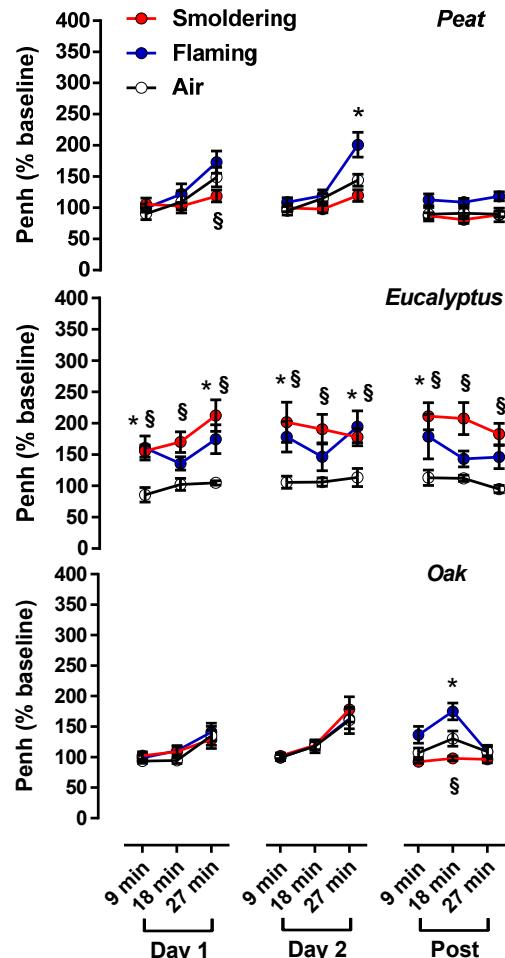
The flaming peat and eucalyptus were as potent as smoldering samples despite 10-fold lower PM concentration

Kim et al Arch Tox 93(6), 2019.

Lung Function Responses (*In Vivo*)



Steve Gavett

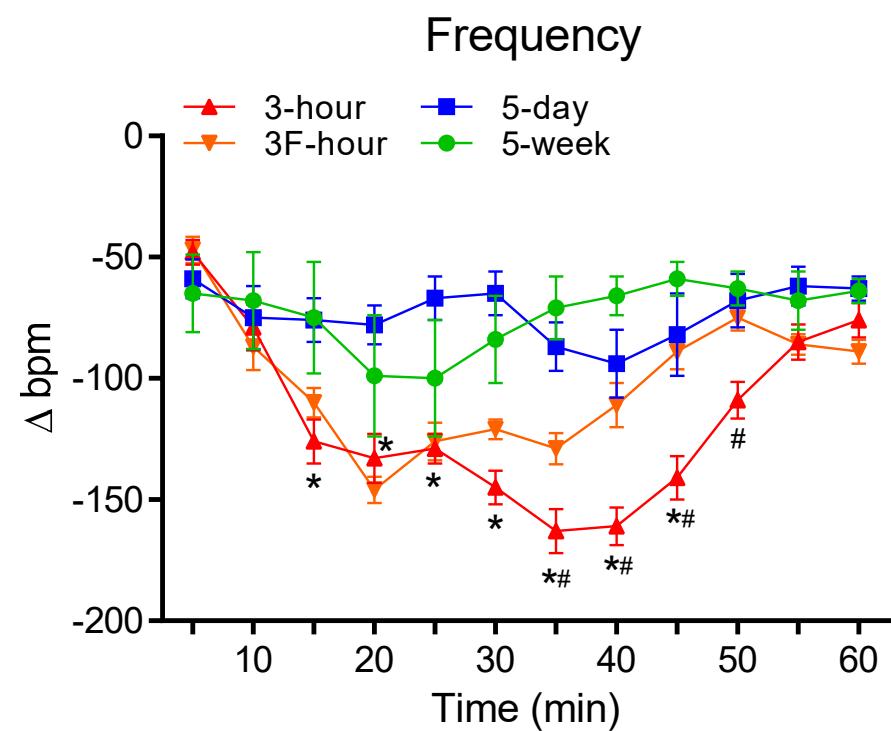
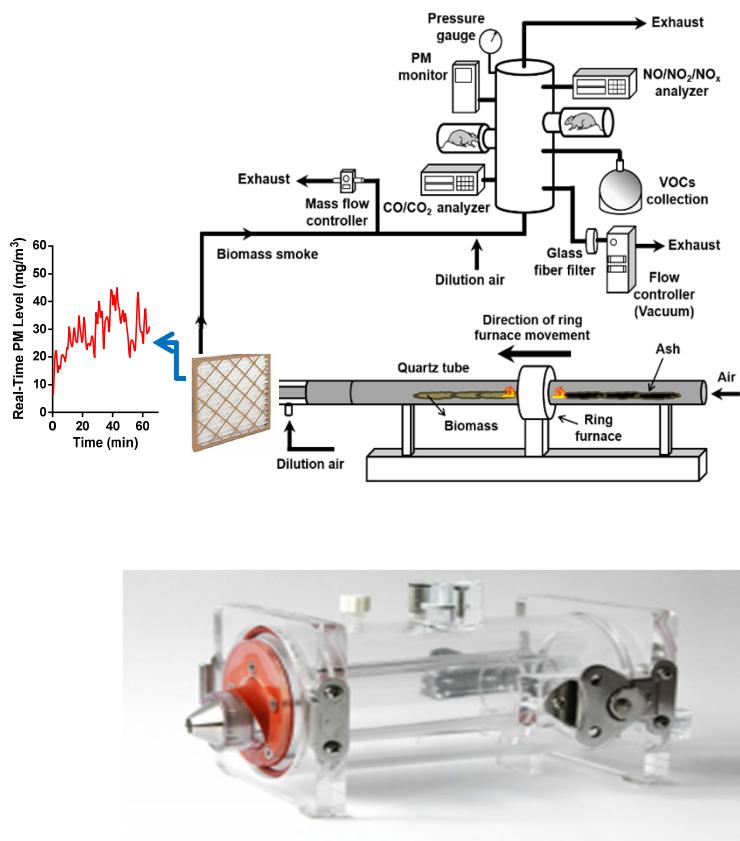


Mouse Ventilatory Function Analysis

Ventilatory function parameters were measured at 9 min intervals in the 30 min before exposure (baseline), right after exposures (Day 1 and Day 2), and 24 h after the second day exposure (Post), respectively.

- A significant increase in airflow obstruction (as measured by Penh) was observed in mice exposed to flaming peat (*), and smoldering eucalyptus (§) smoke immediately after each day of exposure.

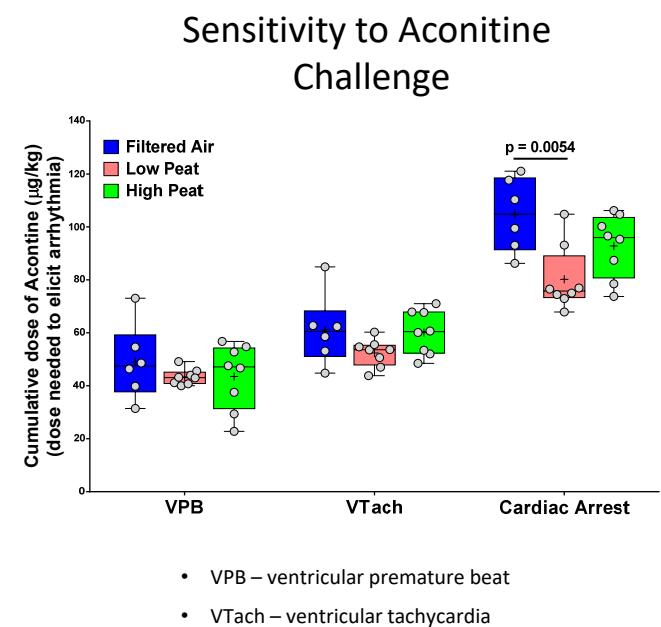
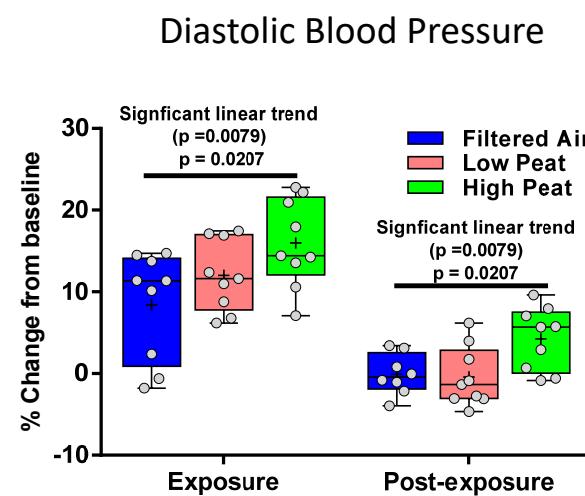
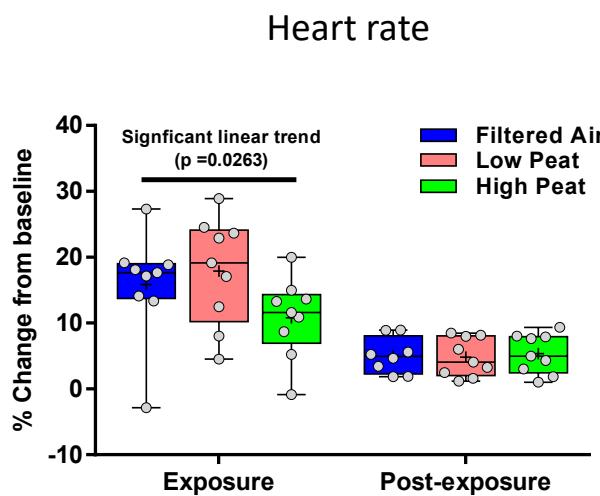
Inhalation Exposure Shows Greater Effects of 1-Day CxT vs. Longer CxT Exposure Protocol on Breathing Frequency, and Partial Benefit from Filtering the Smoke





Cardiovascular Impacts of Single Exposure to Low or High Smoldering Peat

Aimen Farraj



Farraj. Unpublished

Conclusions

The combustion system and associated methods provide stable and reproducible smoke atmospheres that can be used for emission testing and toxicity assays.

Fuel composition and combustion conditions influence the chemistry, toxicity and mutagenicity of biomass smoke with peat and eucalyptus smoke being more potent (on a PM mass basis) than e.g. oak.

Biomass smoke inhalation has significant effects on lung injury and inflammation, and decreases breathing frequency and heart rate, while increasing blood pressure and risk of cardiac disease.

Depending on the fuel type, filtration can partially but not completely abrogate pulmonary effects.

Where do we go from here?

Continue exploring effects of acute, intermittent and chronic exposures from various scenarios (including combustion of man-made materials) on health endpoints.

Utilize these and other toxicological approaches to identify most effective interventions (e.g. air purifiers, filtration, anti-oxidants etc).

Determine relative potency of fresh and “aged” biomass smoke against other sources: e.g. mobile sources, power plant emissions and urban “smog”.

Assess the effect of smoke exposure on higher throughput in vitro systems e.g. 3D human lung cell cultures at the air liquid interphase (ALI).

Perform mechanistic studies under both healthy and at-risk (e.g. asthma, diabetes, COPD, in utero) conditions.

Acknowledgements

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- Bill Preston
- Kasey Kovalcik

University of North Carolina

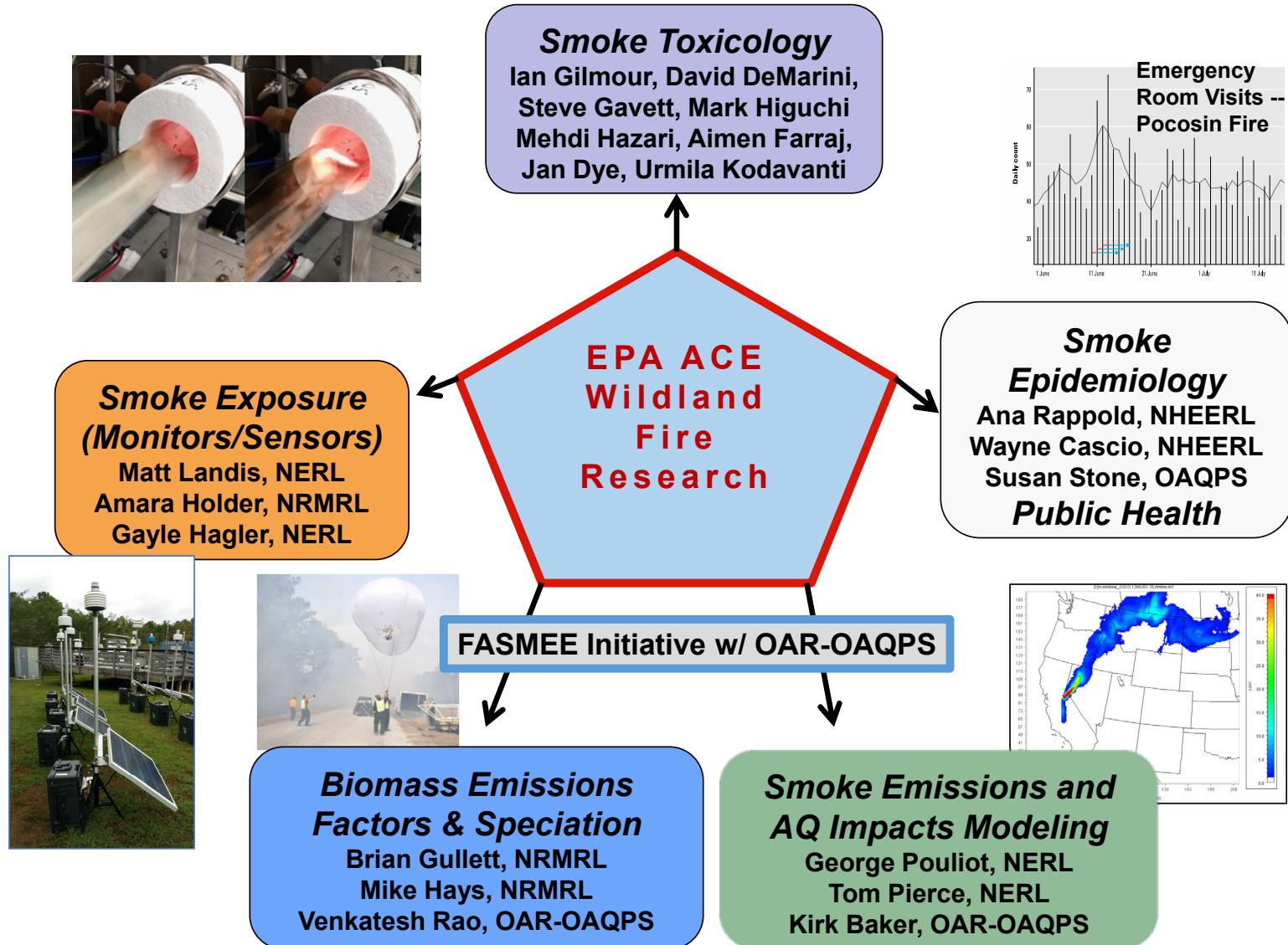
- Julia Rager

U.S. Forest Service / Missoula Fire Sciences Laboratory

- Shawn Urbanski

LRRI Albuquerque (slides)

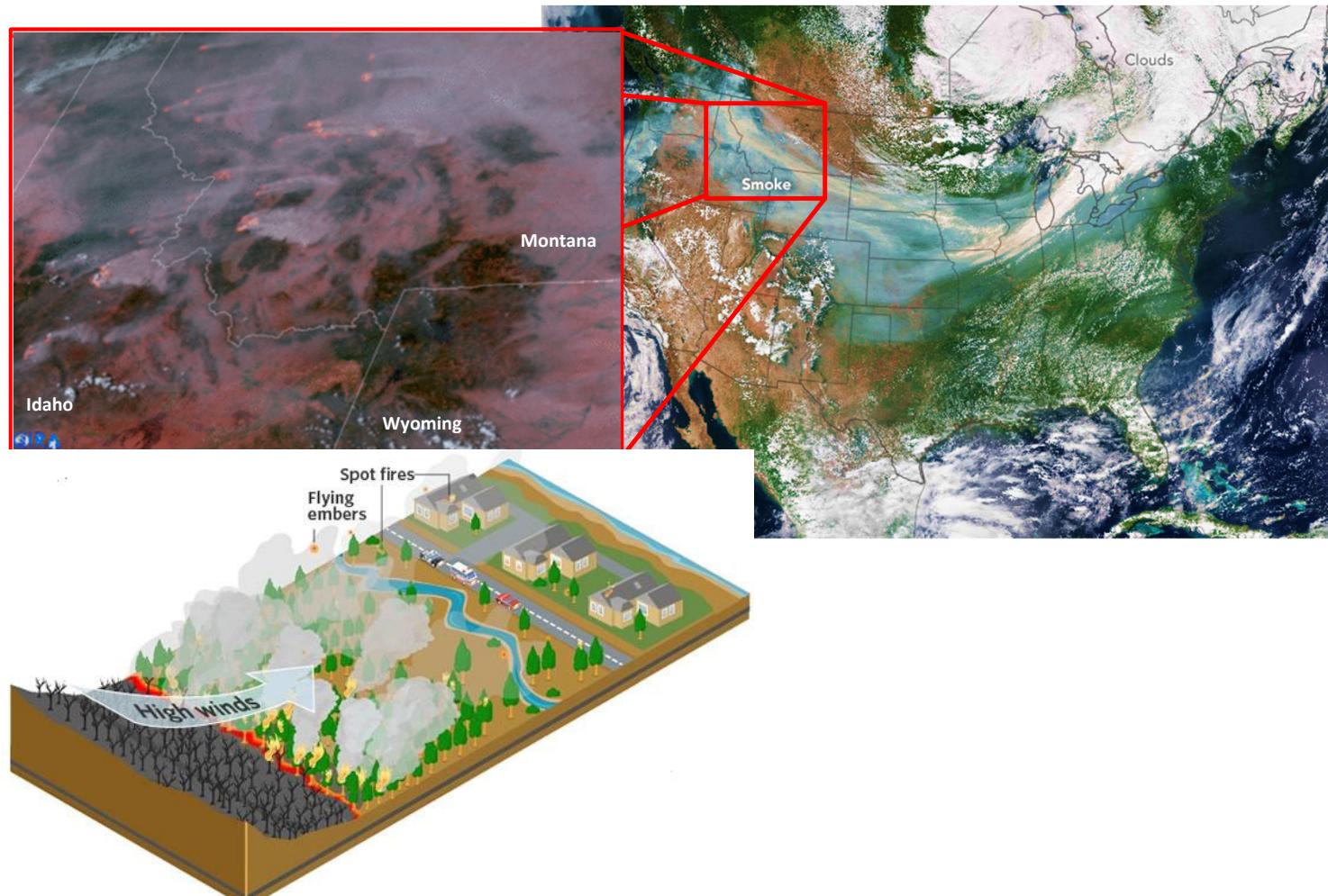
- Jake McDonald



Extra slides

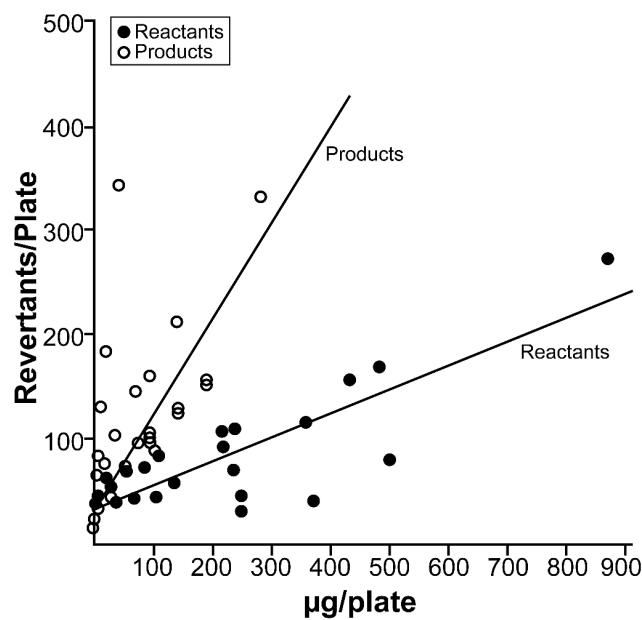
What About Atmospheric Aging of Wildfire Smoke?

September 4, 2017

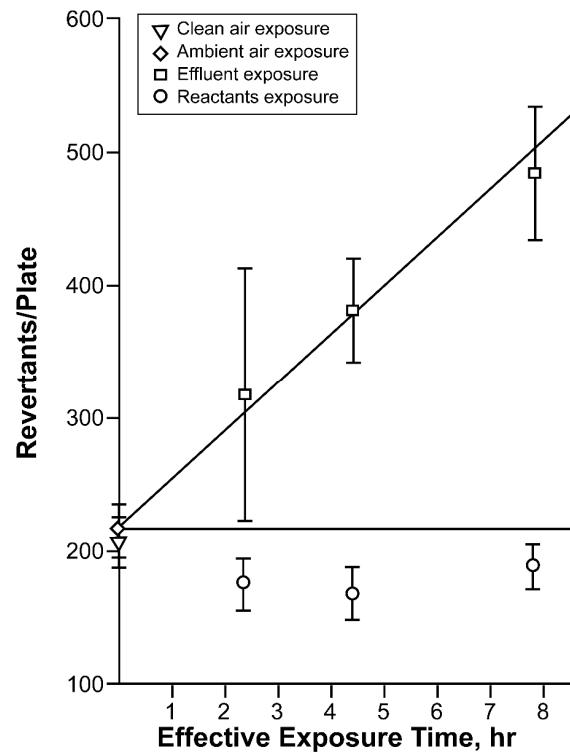


Mutagenicity of Fresh and Aged Wood Smoke

[TE Kleindienst et al., ES&T 20:493, 1986]

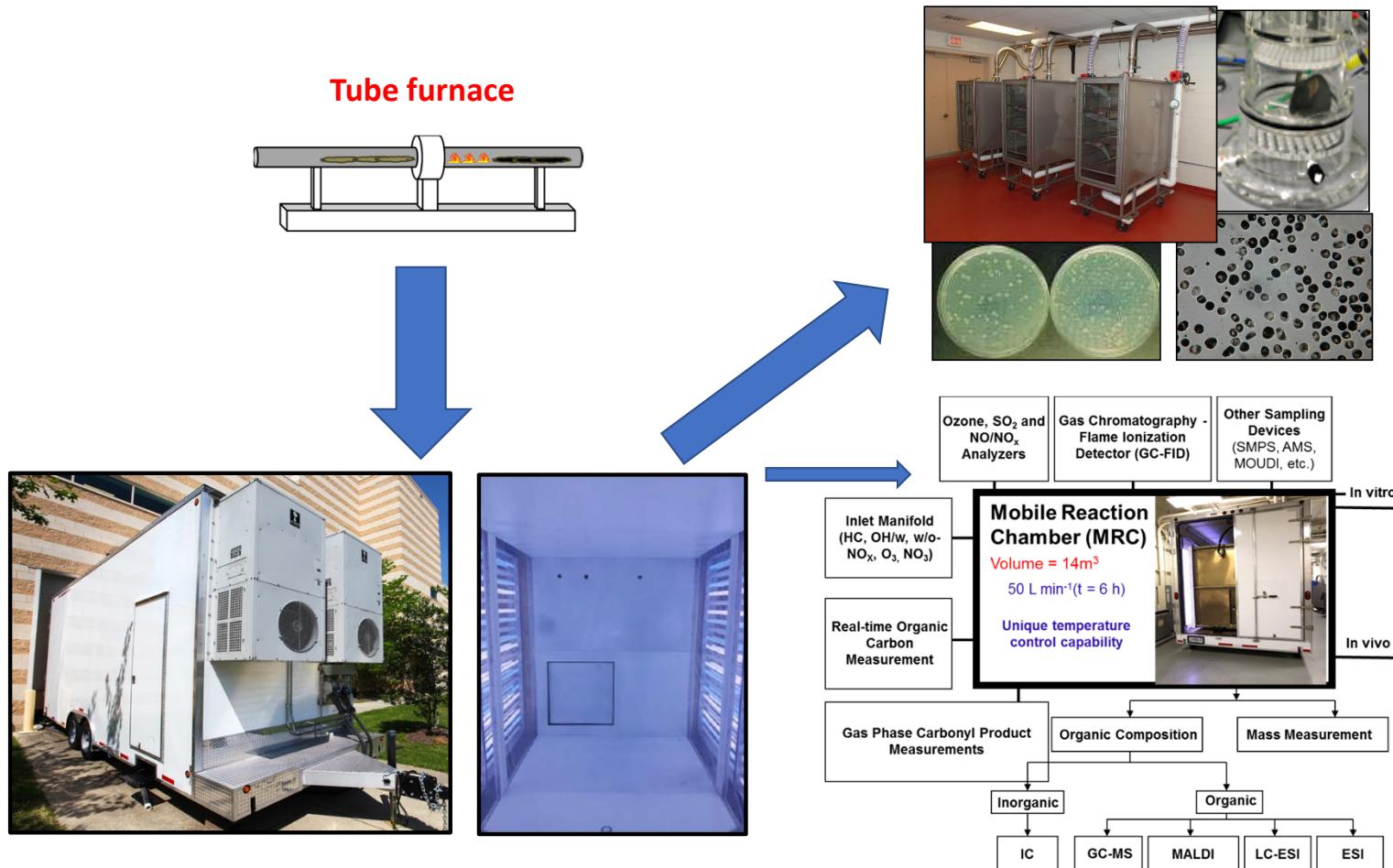


Dichloromethane extracts of PM were 3X more mutagenic in TA98 (+/ - S9) with UV lights on (reactants) than when lights were off (products).

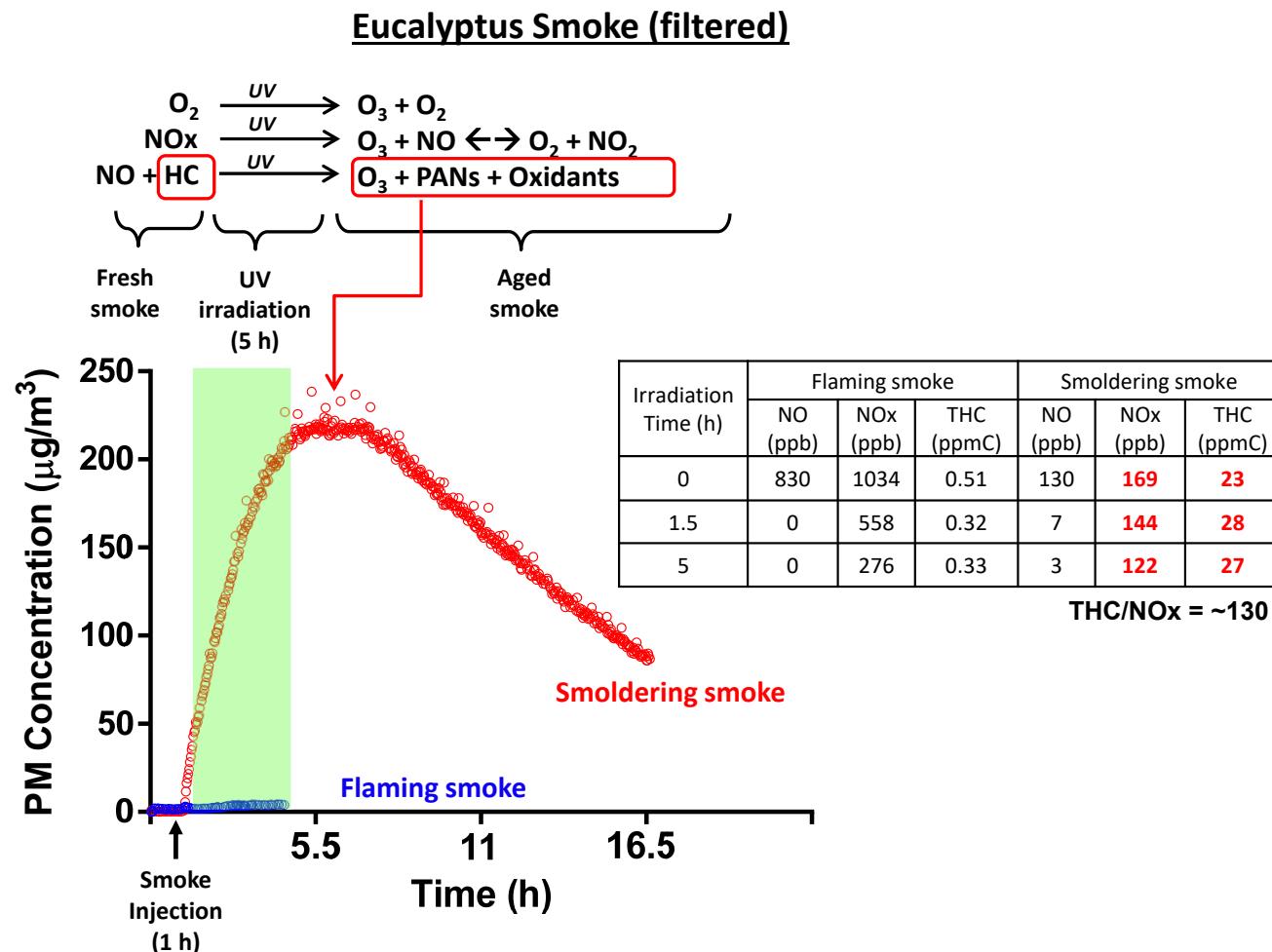


Gas-phase emissions from combustion of burning oak produced 36 revertants/h in TA100 (same + or - S9) with UV lights on. No mutagenicity was observed with lights off.

Photochemical Aging of Smoke with Real-Time or Subsequent Health Impact Testing.

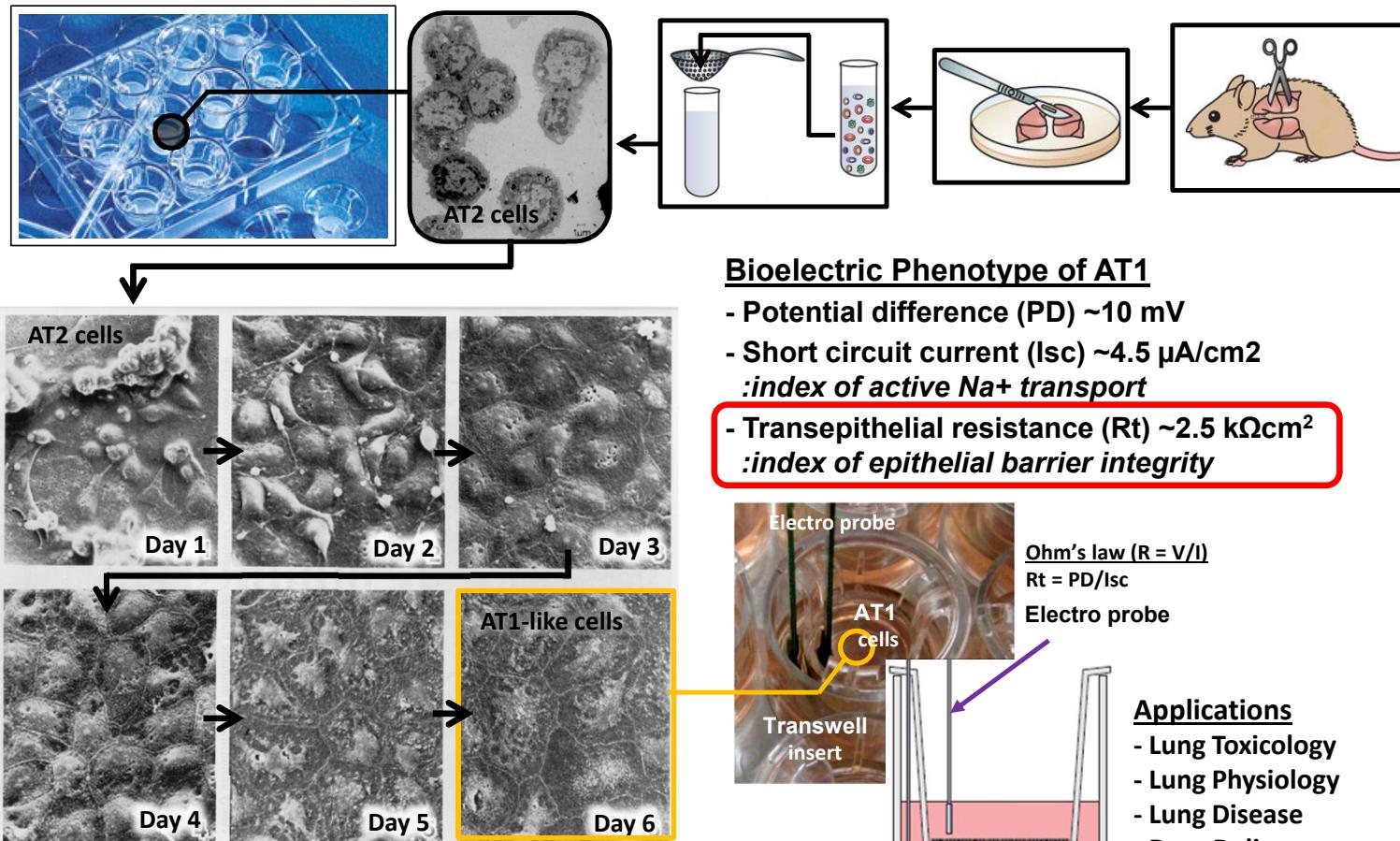


Photochemically Aged Wood Smoke, 2018



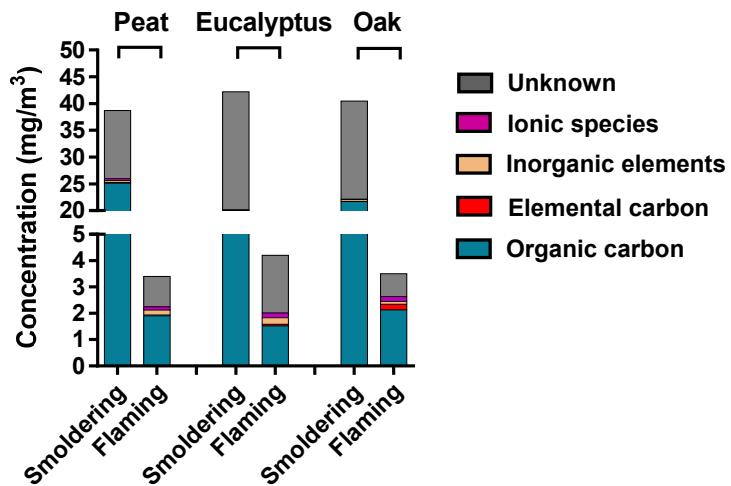
Characteristic (unit)*		Peat		Oak		Eucalyptus	
		Smoldering	Flaming	Smoldering	Flaming	Smoldering	Flaming
Measured Values	MCE (%)	86±0	97±0	84±0	98±0	84±0	99±0
	CO (ppm)	115±1	81±1	56±1	59±2	79±1	79±2
	CO ₂ (ppm)	721±5	2,794±40	297±5	2,942±65	415±6	5,358±63
	NO (ppb)	227±54	5,109±892	39±0	1,812±233	30±2	1,863±209
	NO ₂ (ppb)	0±0	1,292±187	0±0	502±154	0±0	909±127
	NO _x (ppb)	227±54	6,380±1,079	39±0	2,303±384	30±2	2,758±332
	VOCs (ppb)	2,677	1,694	4,072	1,682	1,911	760
	PM (mg/m ³)	38.7±0.4	3.4±0.1	40.5±0.8	3.5±0.1	41.4±0.6	3.7±0.1

Alveolar Epithelial Type I Cells (*Primary Cell Model*)

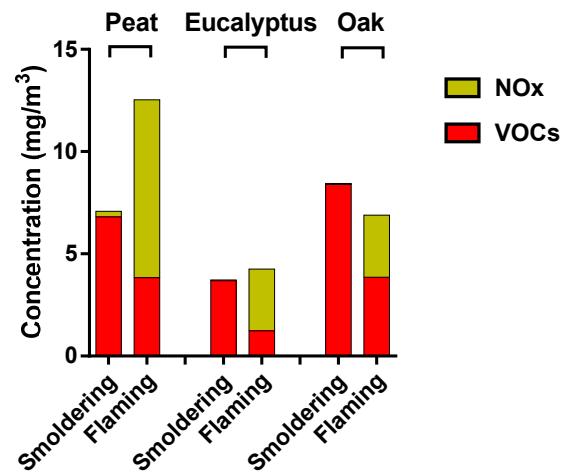


Chemical Components of Biomass Smoke

PM Phase



Gas Phase



- Total carbon accounted for ~50 – 60% of PM from the smoke under any combustion conditions.
- Inorganic elements and ions were higher in the flaming smoke PM.
- Acetaldehyde, formaldehyde, and acrolein were found to be a major component of VOCs.