

Wildfire smoke and ash: Particle size, chemistry, and measurement needs

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Smoke & Ash Exposure & Measurement Issues

- Wildfire smoke exposures associated with increased hospitalization rates and symptoms (respiratory, cardiovascular, and cerebrovascular) 4, 5, 21, 36, 43, 45
- Assessing indoor smoke risk with PM_{2.5} sensors alone possesses several challenges:
 - Wildfire emissions = mixture of particle- and gas-phase chemicals produced by incomplete combustion of various fuels (biomass + building materials and vehicles)
 - AQI for wildfire smoke based on health effects of non-wildfire mean PM_{2.5} exposure for 24 hr
 - Wildfire exposures have potentially different health effects, sensor responses, & metrics:
 Different potential toxics (organic carbon, VOCs, and metals)⁴
 Different PM optical properties depending on mix of smoke/urban/rural, size distributions ⁴⁶
 PM_{2.5} may not track subcomponents (PM₁) or PM₁₀ (PM_{coarse})
 PM sensors report elevated smoke excursions (hours or weeks) of unknown significance

Particle size distribution impacts indoors:

- 1) infiltration
- 2) filtration
- 3) deposition
- 4) inhalability







Wildfire PM Size & Chemistry

•Organic carbon (OC) - 100-500 nm spherical "tar balls" with minor K 37, 47, 48

- Dominant in smoldering biomass (wildfires, cookstoves, crop burning) 1, 10, 15, 30, 33, 37, 41
- Carboxylic acids, polycyclic aromatic hydrocarbons (PAH = potential carcinogens) 7, 34, 47
- OC PM from peat fires causes decreased cardiac function ²²

•Elemental carbon (EC [BC]) - chain agglomerates of 20-60 nm soot with sorbed OC

- Minor component of biomass fires ^{1, 37}
- Short term health effects stronger for diesel BC than general PM (heart rate variability) 3, 14, 35

•Ash - > 1 um inorganic remnants of plants and building materials 37, 49

- Plant ash: K, Cl, Ca, Si, S, Na; enriched Cr(VI), As, Mn, Pb, and Sb ^{8, 23, 25, 32, 44}
- Building materials: asbestos, fiberglass, Pb, Cr, As, Cu, Hg from paint, electronics, solder, pipes
- Inhalation of PM₁₀₋₂₅ causes inflammation and irritation ²; caustic (pH = 10-12)⁷

•Burning petroleum and plastic emissions - 150 nm - 10 um OC

- Oil: coarse PM₁₀ coke with V and Ni; impacts heart rate variability more than normal PM₁₀^{20, 27, 28, 29}
- Wood composites: >10x more PM₂₅ than burning wood, increases with fraction of adhesives ¹²
- Vinyl polymers (e.g. PVC pipe, siding, furniture) produce ash + PAHs

Wildfire tar balls

Non-wildfire diese

Wildfire ash



Paint with 1 um Pb 40



Asbestos in brakes 11

Wildfire Gas Chemistry



• Wildfire smoke gas hazard types, measured close to fire ^{12, 38, 39}

Type of gas-phase hazard	Gas species
Asphyxiants	CO, CO ₂ , H ₂ S
Irritants and allergens	NH ₃ , HCl, NO _x , phenol, SO ₂ , isocyanates
Carcinogens	benzene, styrene, formaldehyde

• Gas chemical concern groups based on Hazard Ratios = EF / TLV 5

Hazard ratio groups	Gas species
Group 1	CO, formaldehyde, acrolein, NO _x
Group 2 (One order of magnitude less)	benzene, CO ₂ , [PAH], NH ₃ , furfural
Group 3 (Two orders of magnitude less)	acetaldehyde, 1,3-butadiene, methane, methanol, styrene, acetonitrile, propionaldehyde, toluene, methyl bromide, methylethylketone, acetone, methyl chloride, xylenes, phenol, tetrahydrofuran, methyl iodide, mercury

- Hazardous gas emissions from associated burning products and building materials ¹²
 - Polystyrene plastics: benzene, phenols, and styrene
 - Vinyl compounds: acid gases (HCl and HCN) and benzene
 - Wood products: formaldehyde, formic acid, HCN, and phenols
 - Roofing materials: SO_2 and H_2S

Wildfire PM and Gas Measurement Options



Wildfire emissions measurement type	Reported Analyte	Measured quantity			
Continuous monitors/sensors (fastest response and time resolution)					
Laser photometers; optical particle counters*	PM _{2.5} , (PM ₁ , PM ₁₀)	Light scattering (d _{min} = \sim 0.3 um for low cost)			
Beta attenuation	PM _{2.5} , PM ₁₀	Beta radiation absorption			
Aethalometers	BC or UVPM	Light absorption			
Aerodynamic/electrodynamic particle sizers	PM size distributions	Single particle TOF/electric mobility			
Photoionization/photoelectron detectors	Total VOCs/PAHs	Ionization current			
Long path UV spectrometers	VOCs, NO _x	UV absorption			
Electrochemical/MOx sensors or colorimetric tubes*	VOCs/total HCs, CO, NO _x	Chemical reaction with substrate			
Portable GC-MS or PTR-MS	VOCs	Retention time & m/Q			
NDIR or OP-FTIR	VOCs, NOx, CO, CO ₂	IR absorption			
Samplers (need to take back to lab to analyze)					
Filters or impactors	$PM_{2.5}$, $PM_{10-2.5}$, PM_{10} ; PAHs, metals	Gravimetric PM; Retention time & m/Q			
Electron microscopy (Impactors, ESP, thermal, passive samplers*)	PM size distributions, shape, chemistry	Single particle electron/X-ray energy			
Active or passive* sorbent tubes, badges, or gas canisters	VOCs, NOx, PAHs, formaldehyde	Retention time & m/Q			
Other					
Satellite/remote sensing (outdoor only)	PM _{2.5} , PM _{10-2.5} , PM ₁₀	Aerosol optical depth			

*Lowest-cost devices



Measurement example: PM size distributions, Sources = smoke + ash + urban PM background



Passive PM samplers + BAM 1020, SF Bay Area Nov 2017-18 (NASA HAQAST study with BU, SJSU, RJLG, and QC-CUNY)

Non-wildfire PM types



Castillo et al, Atmos. Environ, 2020

1-month samples dominated by PM1 from 2-week smoke episode



Wildfire PM (Fine and coarse C with Cu, Zn, and Ni)



Wildfire PM (200-500 nm tar balls)







Measurement example: Wildfire smoke-specific tracers



Multi-wavelength aethalometer (UVPM/BC)

 best indicator of biomass smoke presence in PM



Measurement example: Smoke event I/O size distribution ratio + indoor metals



- Multi-room, intermittent air cleaner
- Filter = low cost, opportunistic sample (SEM, ICP)
- Lower reductions possible with dedicated air cleaners¹⁸









Enriched indoor PM metals during wildfire

 consistent with outdoor data from same episode (CARB, 2021)

	Accumulation rate*			
	(ng/	cm²/day)	Katio	
	Wildfire	Background	(wildfire/background)	
Copper	0.40	0.23	1.73	
Zinc	3.35	1.12	2.98	
ead	0.21	0.06	3.70	

*Accumulation rate is the measured mass of metal per area of filter, minus that of the blank filter, per day furnace filter was in use. The wildfire filter was in use 44 days and the background filter was in use 156 days.



Ongoing CPDH projects combining sensors-samplers

- •2021-23 PM + air cleaner intervention in farm community homes (swamp coolers) (with PHI/UCSF/IIT/Central CA EJ Network)
- •2021-23 PM + BC + PAH + noise exposures inside AB617 homes in CA Central Valley (with UCB/UCM)
- •2021-22 PM + Cr (VI) in PM₁₀ ash in communities near fires (with Stanford)
- •PM + VOC + PAH + metals + oxidative stress in vulnerable communities (proposal submitted with PHI/NYU/CCEJN)





Smoke & Ash Measurement Needs

- Low-cost PM sensors are good tools for assessing key questions:
 - What are indoor exposures during fire episodes, and how can <u>clean air spaces</u> be achieved in vulnerable communities?
 - What is the spatial variability <u>across complex topography</u> during a smoke episode? <u>Within</u> buildings operating air cleaners?
- The use of <u>multiple, complementary measurement methods</u> are needed to answer other questions:
 - Can the above be demonstrated for specific compounds or PM sizes?
 - <u>Smoke tracers</u> (UVPM; PM₁)
 - Ash tracers (PM_{10-2.5})
 - <u>Toxics</u> (PAHs, metals, VOCs)
 - What measurable health effects are associated with <24 hr exposures? Multiple days/weeks?
 - What is the wildfire contribution to <u>PM exposure burdens</u> for urban and rural communities?
 - Can <u>window opening guidance</u> be improved using indoor/outdoor PM/temperature sensors?