Novel Approaches in Toxics Identification, Environmental Forensics, and Exposure Assessment

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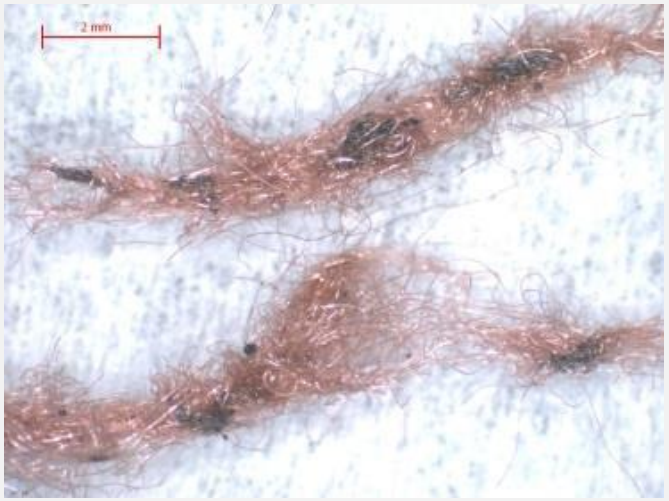

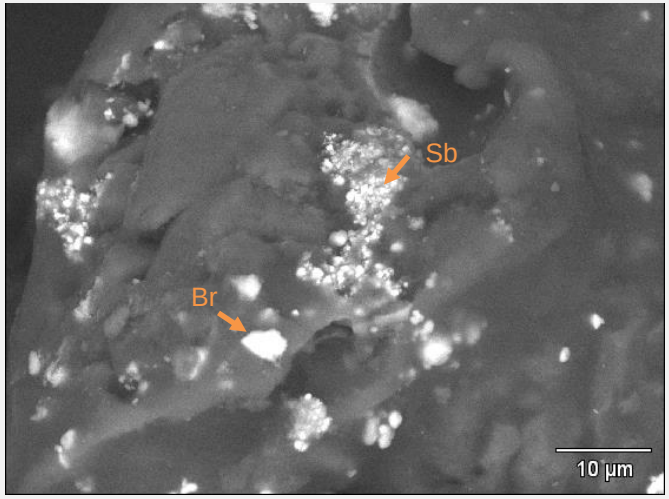

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- PJE Quintana (San Diego State University, School of Public Health)
- Joe De Vita and Leela Rao (CARB Mobile Source Control Division)
- Gary Casuccio (RJ Lee Group, Monroeville, PA)
- Robert Willis (US EPA, RTP, NC)

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Federal	EPA Region 9, FBI, HUD
CA Inter-agency	CARB Monitoring and Laboratory Division, CA Dept. of Justice
CA Intra-agency	EHIB, FDLB, DWRL, CLPP, MDL, EHLB (IAQ, BC)
County Public Health	Sacramento, San Francisco, Monterey
Regional Air Pollution Control Districts	Mendocino, Imperial

Outline

1. Introduction
2. Toxics Identification
   - Consumer products, foods, medicines, and religious materials
   - Natural Occurrences of Asbestos (NOA)
3. New Exposure Assessment Methods
   - Spore detection
   - Wildfires and CAFO PM
4. Environmental Forensics
   - Suspicious/threat powders
   - Pb sources in food and buildings
   - Flame retardants
   - Regional air quality incidents and contaminant releases

1. Introduction

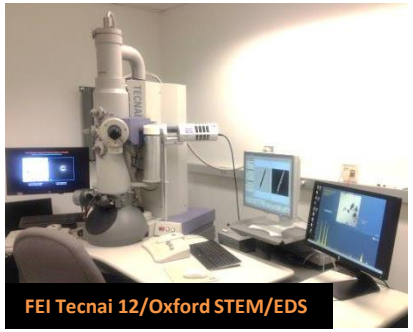
- Goal: identify unknown, suspected toxics and their likely sources

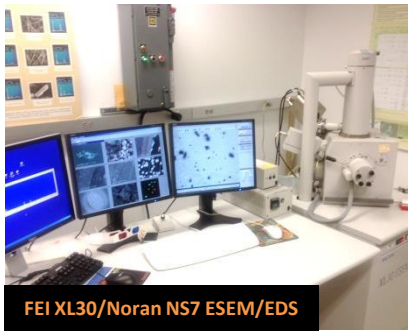
  1. Microscopy to measure individual particles' size, chemistry, morphology
  2. Passive samplers to capture chronic air exposures
  3. Portable sensors to capture acute, intermittent air exposures

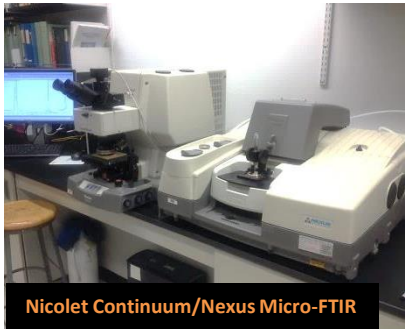
EHLB Microscopy

- Optical techniques:
  - Low-power Stereozoom Microscopy
  - Polarized Light Microscopy (PLM)
  - Differential Interference Contrast Microscopy (DIC)
  - Phase Contrast Microscopy (PCM)
- Electron Microscopy:
  - Scanning Electron Microscopy/ Energy Dispersive Spectroscopy (SEM/EDS)
  - Scanning Transmission Electron Microscopy/ EDS/Selected Area Electron Diffraction (STEM/EDS/ SAED)
- Molecular (vibrational) micro-spectroscopy:
  - Fourier-transform infrared (FTIR) Microscopy
  - Raman Micro-spectroscopy (RMS)

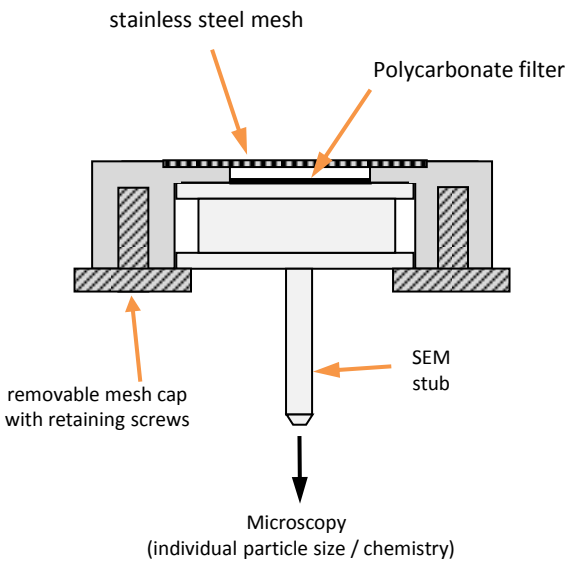
Nikon Eclipse E600


FEI Tecnai 12/Oxford STEM/EDS


FEI XL30/Noran NS7 ESEM/EDS


Nicolet Continuum/Nexus Micro-FTIR

UNC passive airborne particulate matter (PM) samplers



- Silent (personal or residential sampling)
- Do not require power (remote locations)
- Inexpensive
- Multiple deployment to map spatial variability

Portable, continuous-monitoring sensors

CO

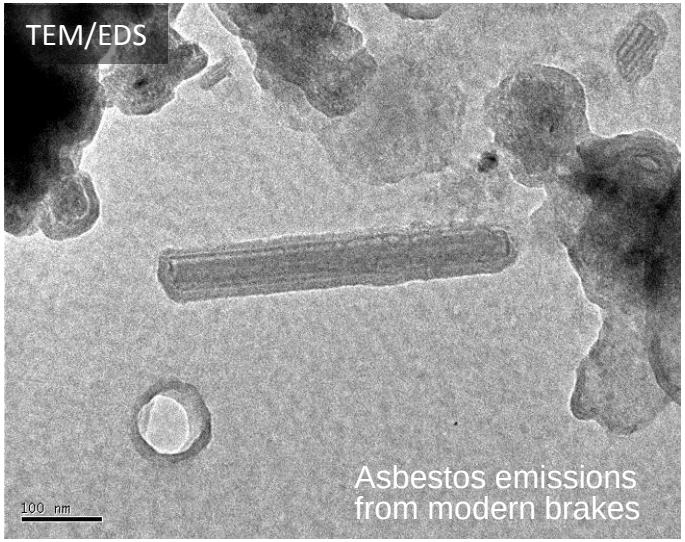
$PM_{2.5}$

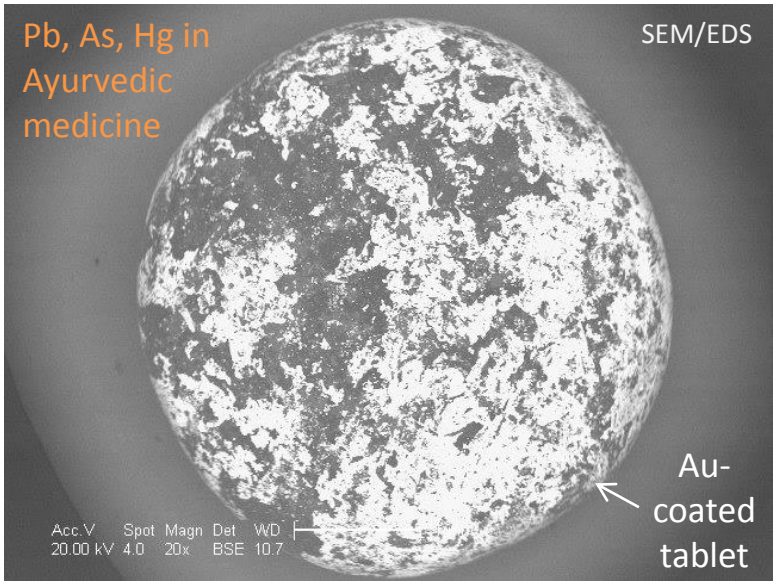
- Small pumps or passive, powered by batteries
- Dataloggers for post-investigation download
- Detect contaminant ‘spikes’ on the order of minutes or seconds

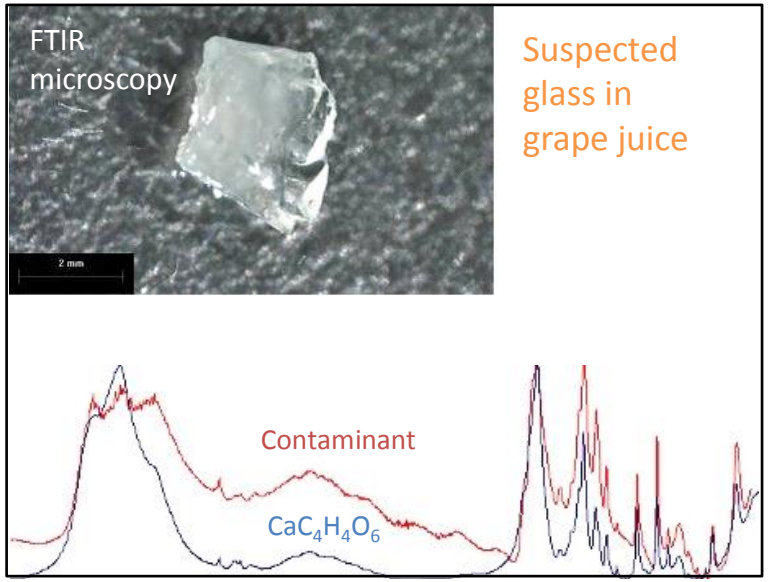
2. Toxics Identification

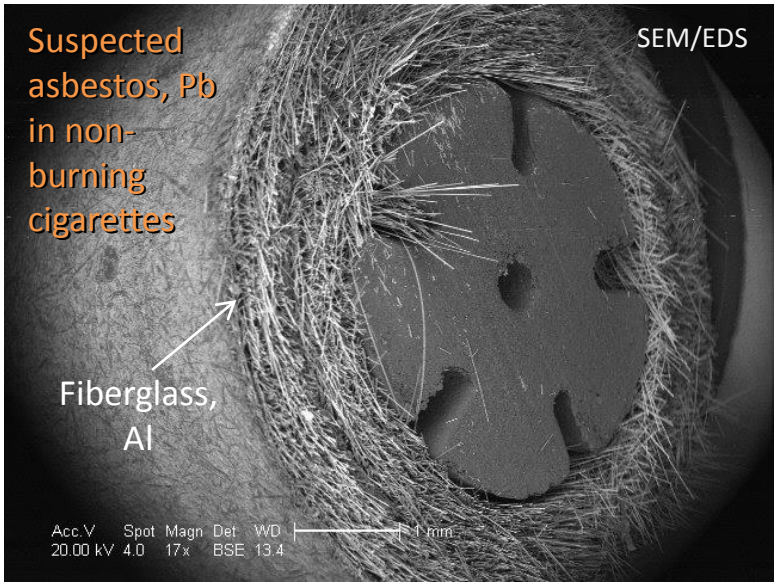
- Microscopy especially useful if:
  - Minimal sample volume (~1 mm^3)
  - Difficult matrices or non-destructive analysis required (e.g., non-soluble solids)
  - Toxicity specific to particle shape or crystal phase, rather than chemistry (e.g., asbestos)
  - Heterogeneous distribution of toxics within substance (e.g., thin coating on surface)

ID of toxics and unknowns in consumer products, foods, and medicines









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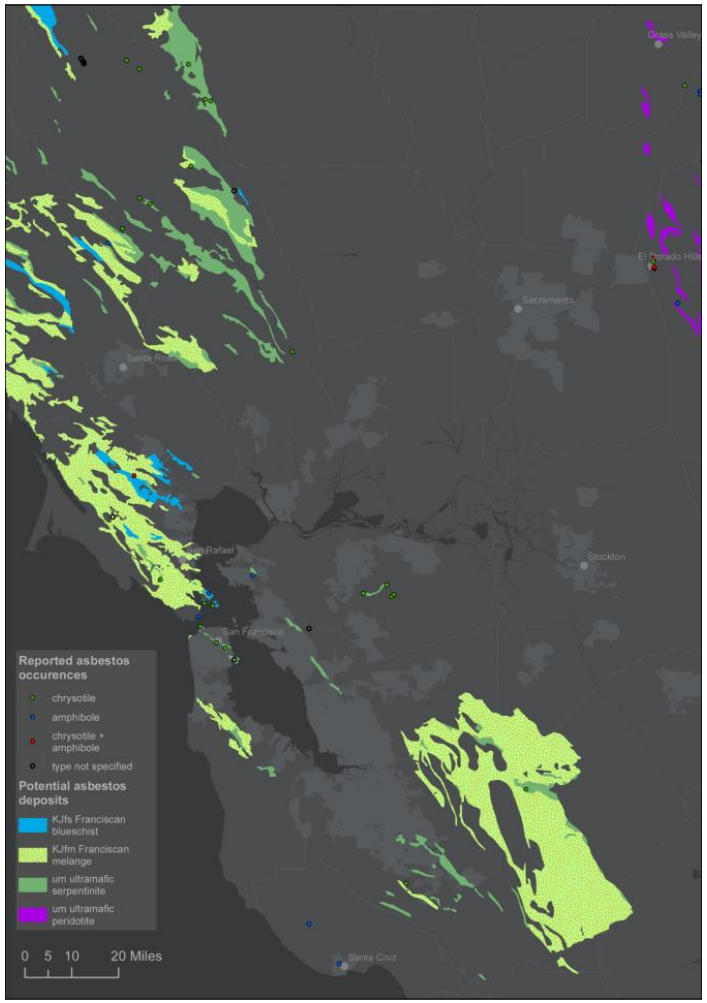
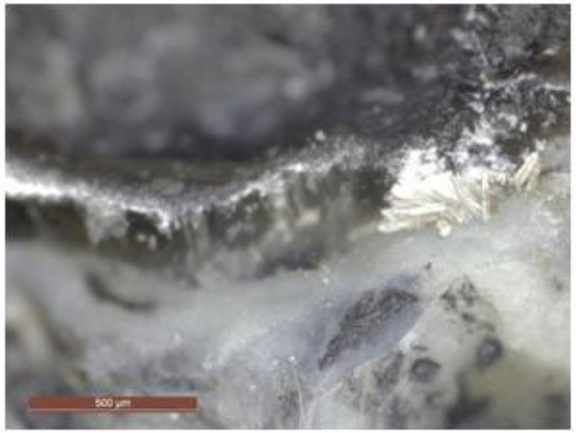
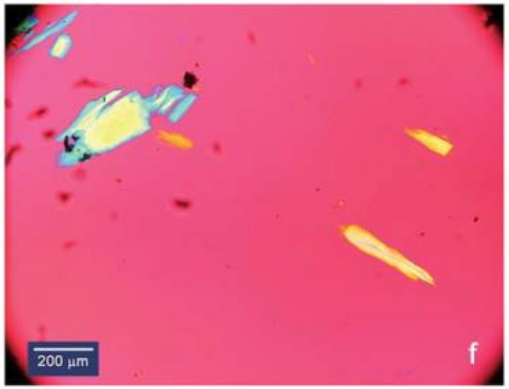
ID of Natural Occurrences of Asbestos (NOA) vs. intermixed, non-asbestiform phases

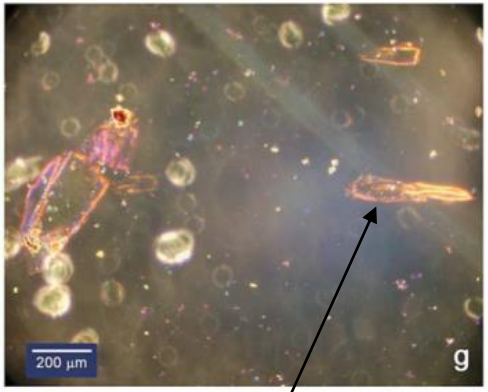


GIS Map of Potential NOA Deposits in Serpentinite and Franciscan Melange rocks

Optical Microscopy (stereozoom, PLM)

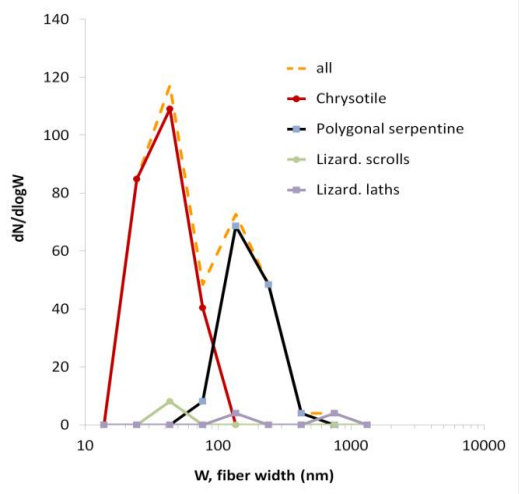


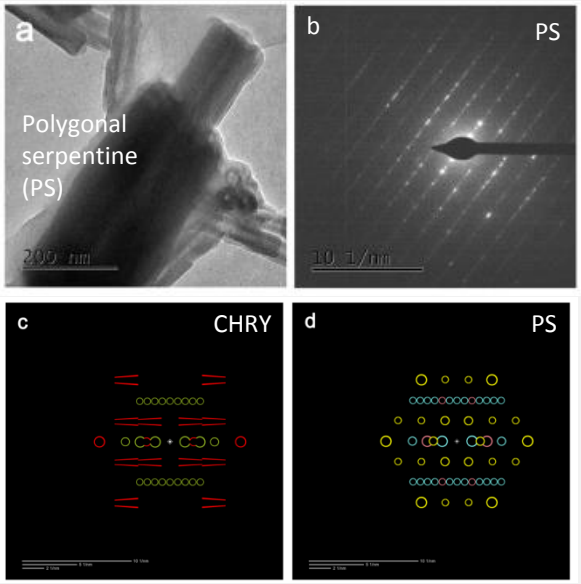




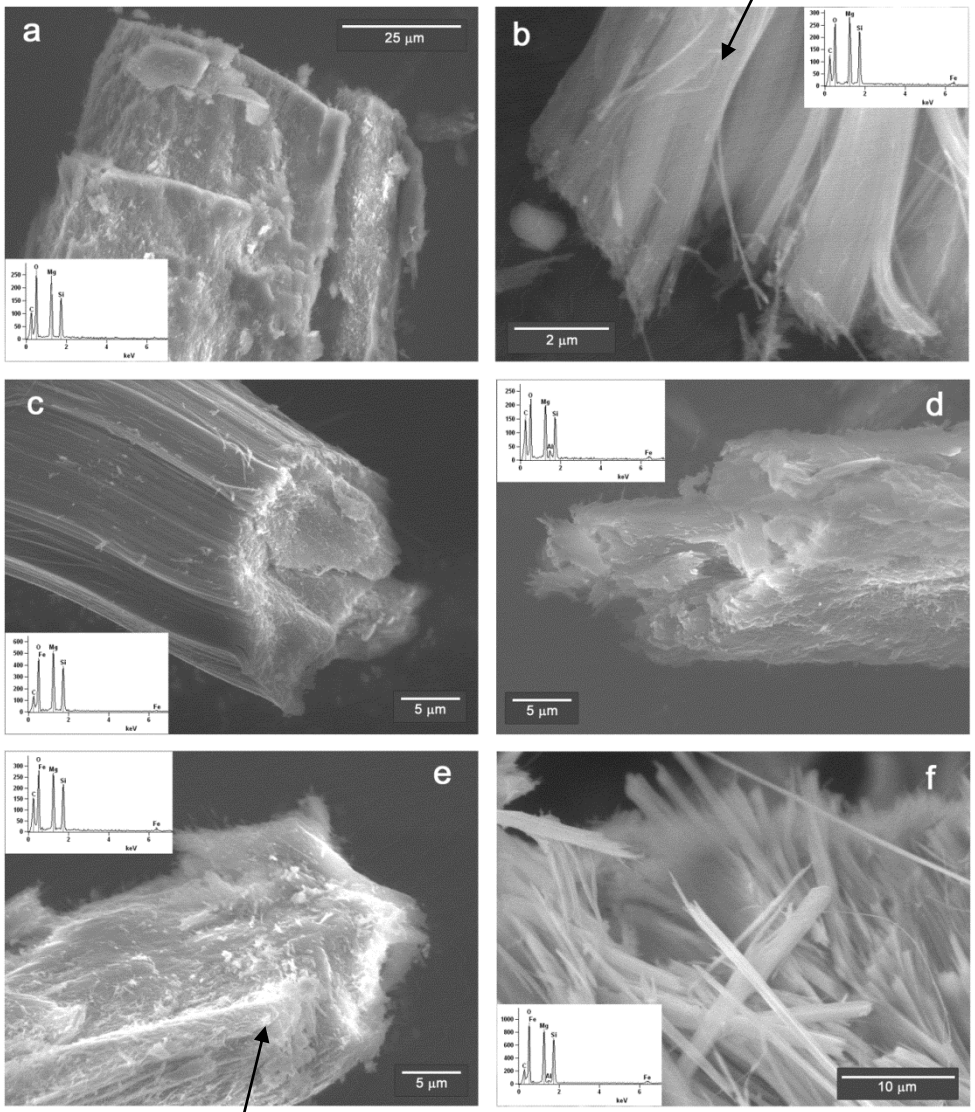
ID ambiguous with PLM

ID of Natural Occurrences of Asbestos (NOA) vs. intermixed, non-asbestiform phases





TEM/SAED/EDS



Non-asbestiform serpentine fiber

ESEM/EDS

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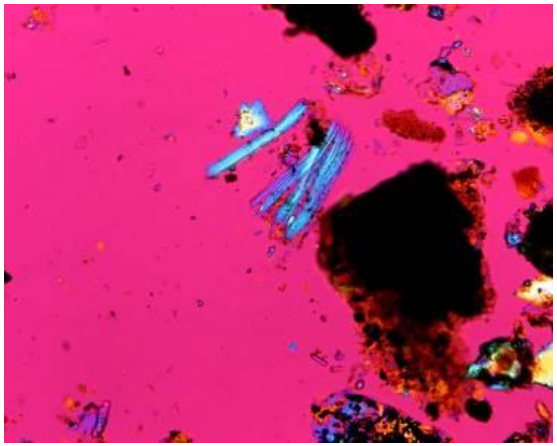
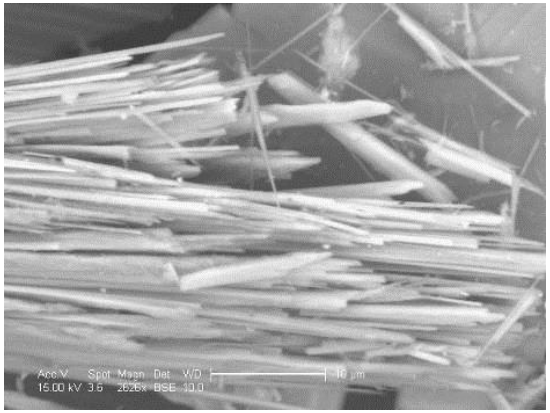
Mineral fiber library (ongoing)

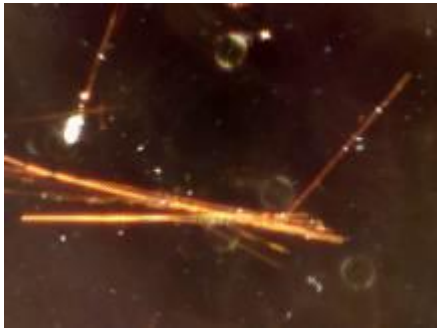
[PLM, SEM/EDS, TEM/EDS/SAED]

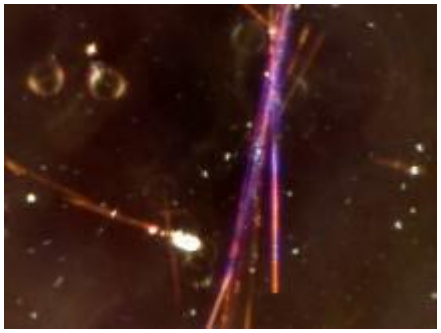


PLM of NOA in gravel (chrysotile)

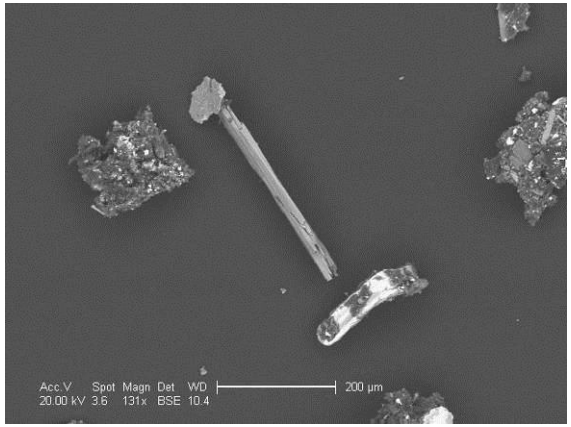


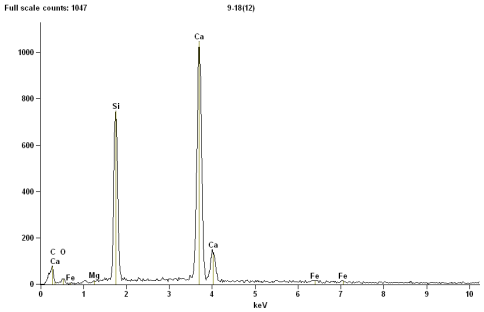
SEM of amphibole cleavage fragments (anthophyllite)





PLM of Libby mine fibers (winchite/richterite)



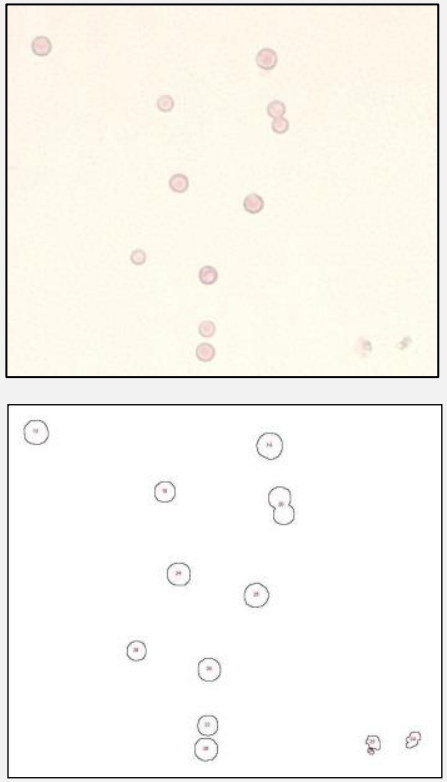


SEM/EDS of non-asbestos fibers in brakes (wollastonite)

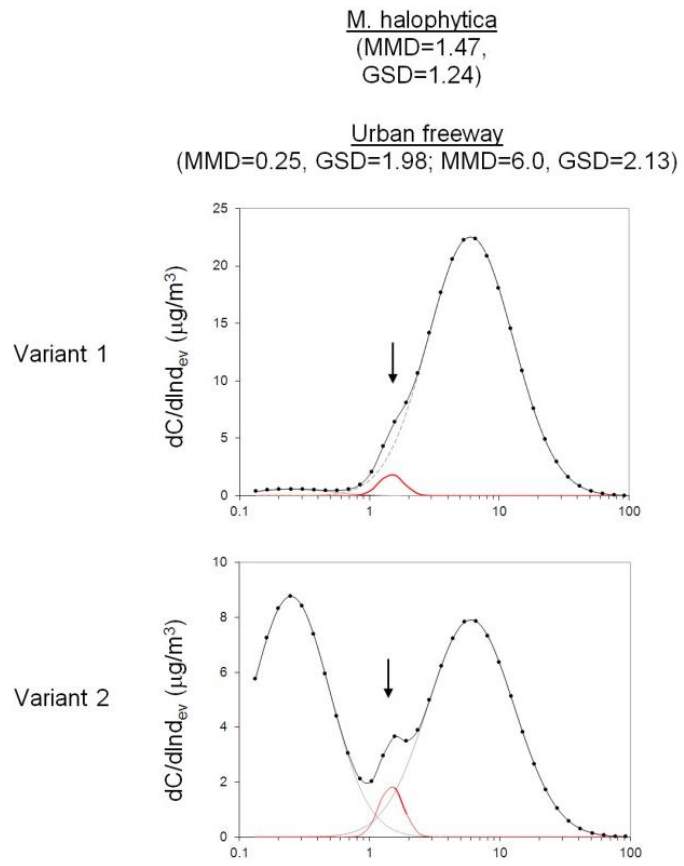
3. New Exposure Assessment Methods

- Improved exposure assessment methods needed for public health investigations
  - More rapid assessments needed for urgent responses
  - Easily deployed samplers for community measurements that can be mailed back to lab

Rapid, automated fungal and bacterial spore detection

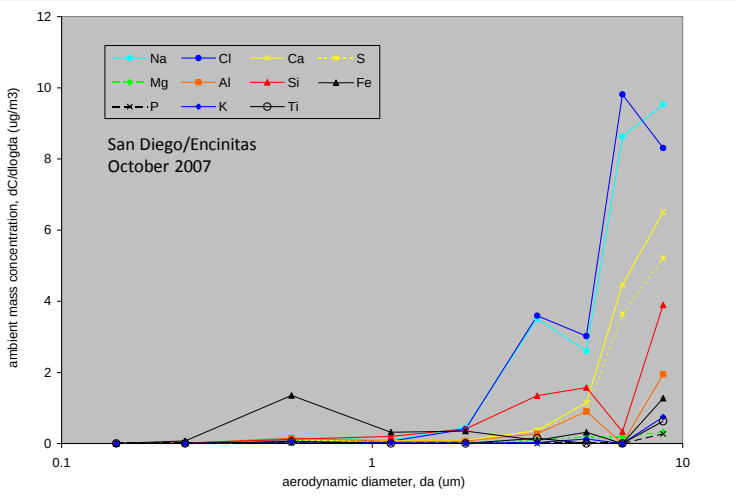


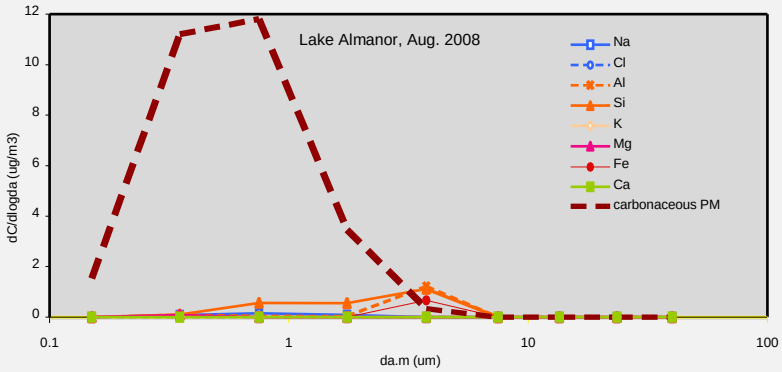
Inexpensive slit-impactor cassettes and microscopy image analyses



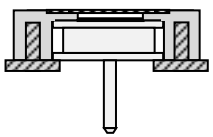
Particle size distribution anomalies (monodisperse peaks) from continuous particle monitors

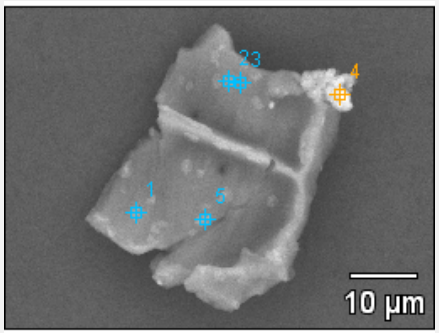
Passive PM monitoring in response to community concerns

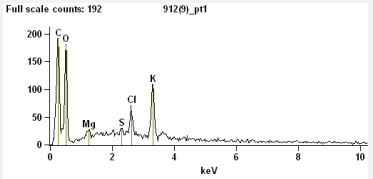


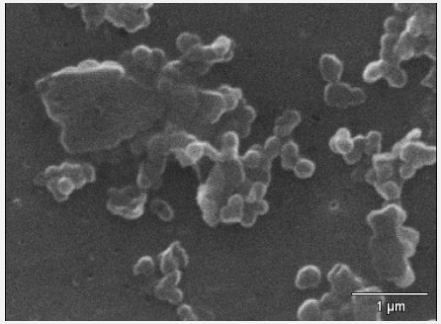


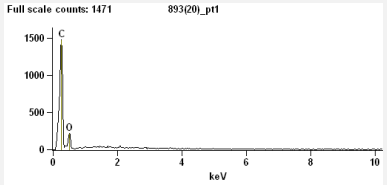
Wildfire sampling in nearby communities with passive sampler PM (chemistry size distributions)









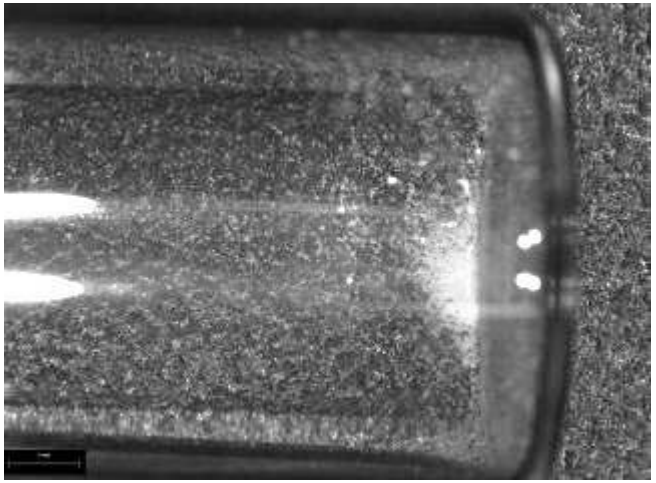


Passive sampling of airborne PM_{10} in community near CAFO

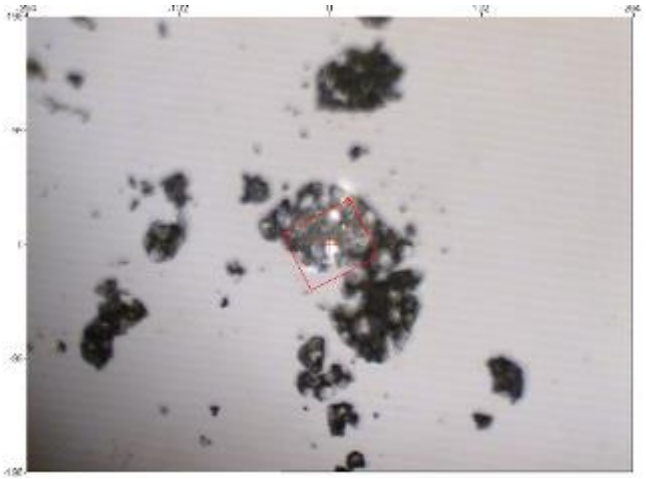
4. Environmental Forensics

- Determine likely source of exposure
  - ID culprit, suggest control measures, and prevent further exposure
- Source ID methods
  - Individual particle analyses: unique intermixed species or formation mechanisms
  - Match to bulk reference materials or library data
  - Sample in multiple locations to capture upwind/downwind
  - Compare to public data (GIS maps, time series)

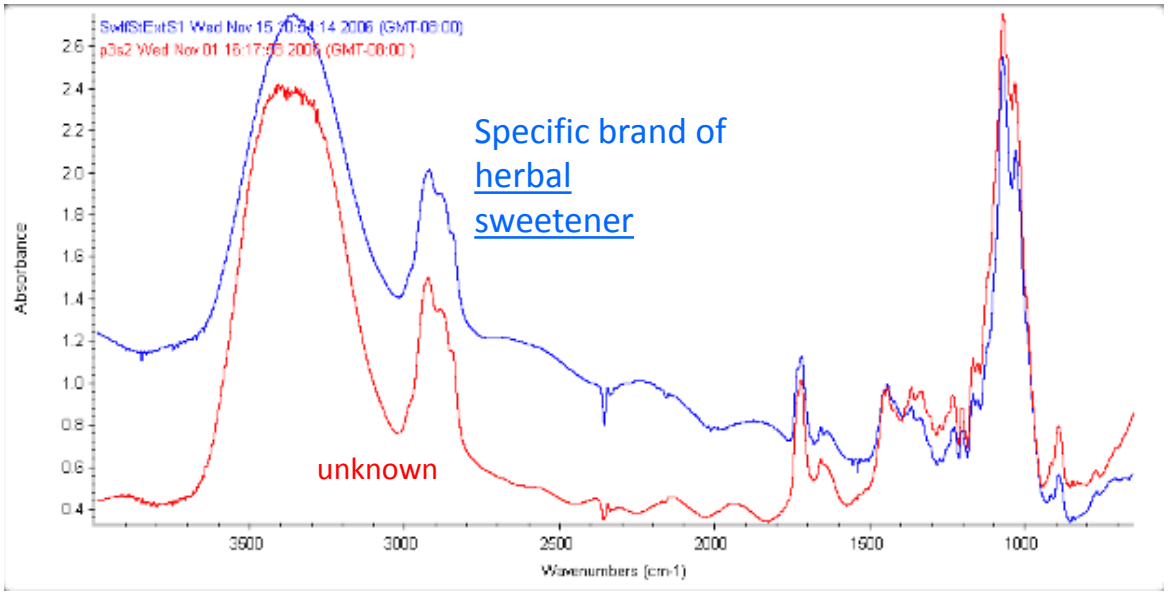
Source ID of White Powders in Suspicious Threat Letters (hoaxes)



Stereozoom image of sample residue in vial

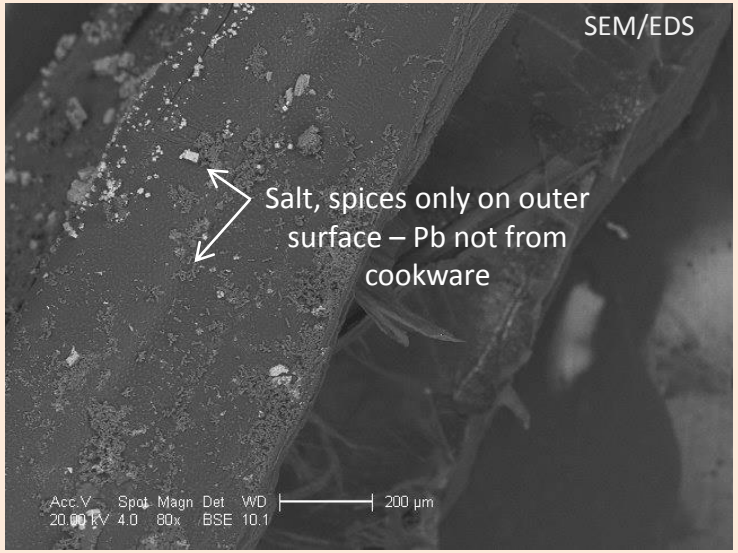


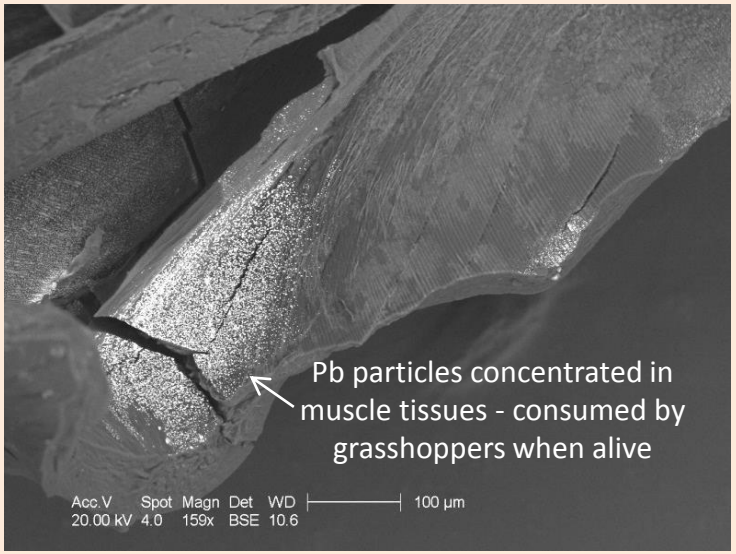
FTIR microscope apertured on target particle



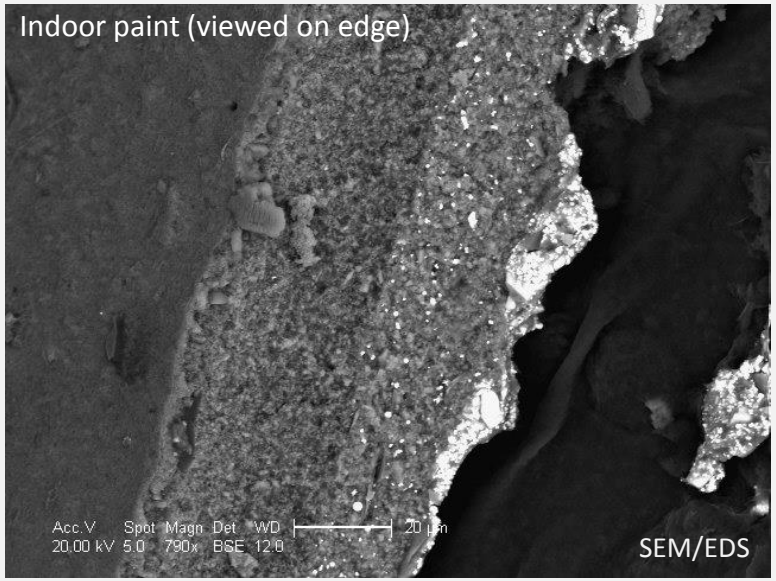
FTIR microscope spectral match

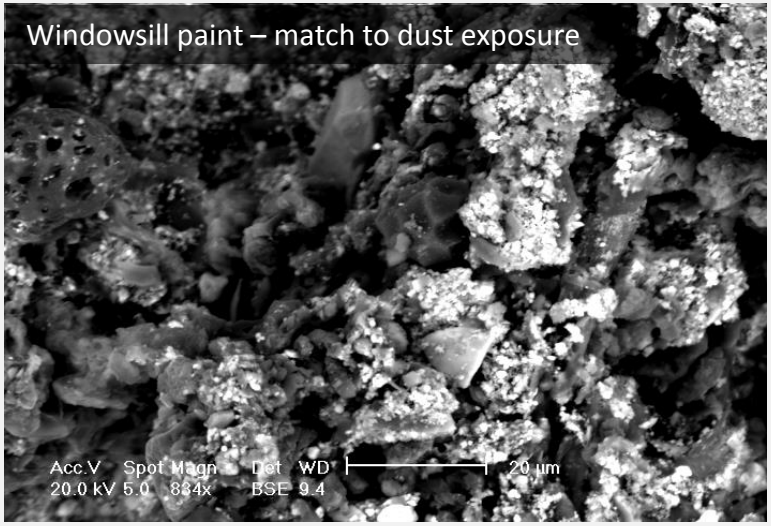
Source ID of Toxics in foods and buildings





Pb in *chapulines* (grasshopper snacks)



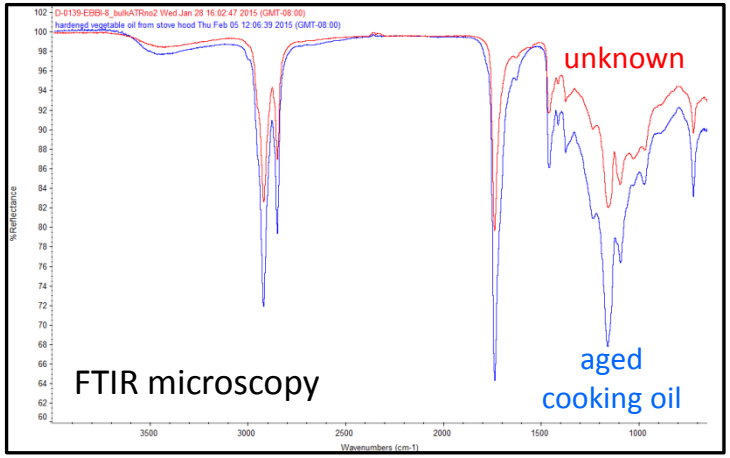


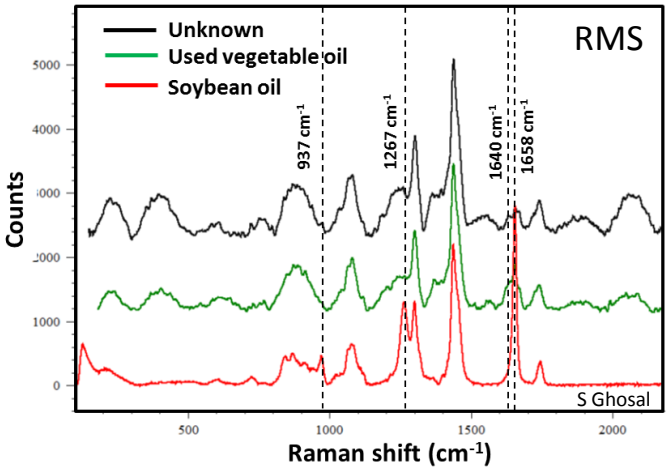
Pb particles in public housing dust

Source ID of SF Bay bird feather contamination

- ID = triglyceride / C18 fatty acid ester with diminished unsaturation
- best match to reference sample: used, aged vegetable oil

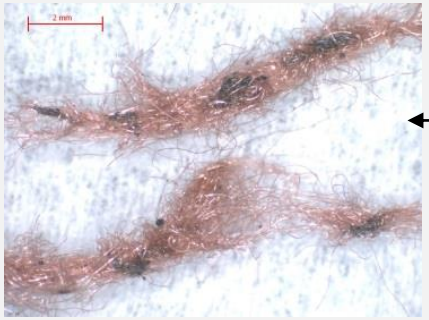
Optical microscopy – thickened 'goo' on feathers



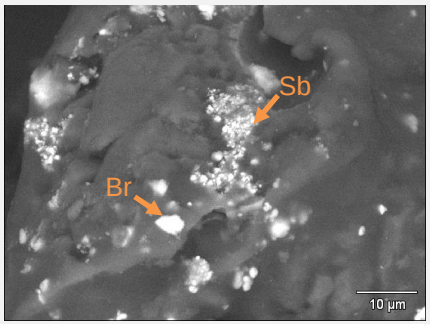


Flame Retardant Morphology and Concentrations in Consumer Products (ESEM/EDS)

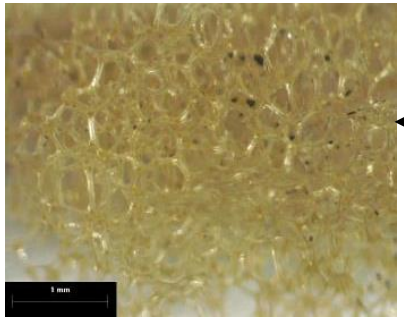
Black FR particles adhered loosely to red van seat upholstery fibers (12.5x)



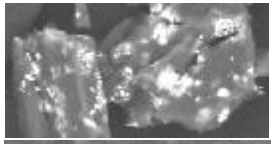
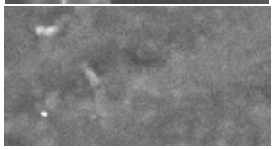
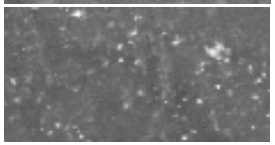
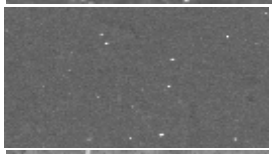
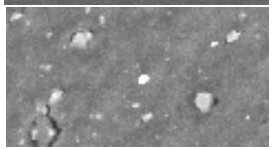
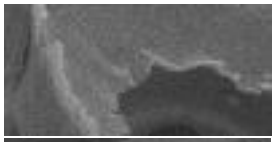
Black FR particles in SEM/EDS (3,200x)



Black FR particles visible in foam, which contained a second, continuously distributed Br species (20x)



Consumer products

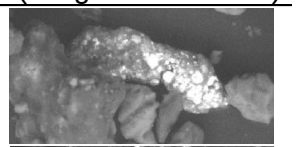
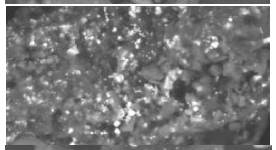
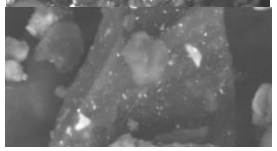
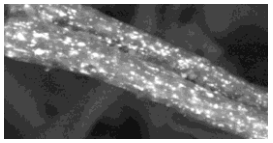
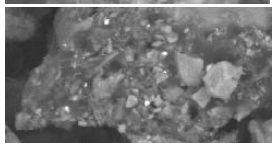
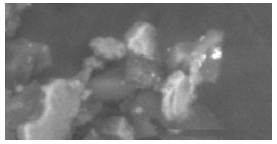
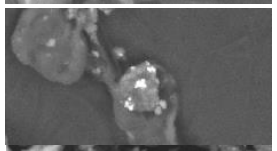
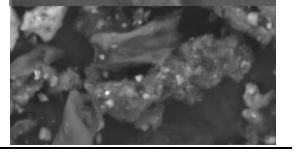
Material type	$w_{FR, avg}$ [%] P [%]	Cl [%]	Br [%]	% Metal synergist	Typical morphology (image=80 um wide)
Van seat upholstery coating	<1	8.6	10 (discrete)	3.3 Sb	
VCR	--	<1	7 (con-tinuous)	<1 Bi-Cl	
Television	--	--	15 (discrete)	2.9 Sb	
Computer monitor/ CRT	2.3 (0.9)	<1	--	<1 Sb	
Car visor covering	--	36.0	--	<1 Sb	
Van seat PUF	<1	--	7 (con-tinuous)	--	
Car visor PUF	<1	3.3	--	--	

Flame Retardant Morphology and Concentrations in Environmental Dusts (ESEM/EDS)

- 6 indoor dust samples
- Range of dust-averaged [Br] by SEM/EDS = (ND – 73ppm)
- Correlation of SEM/EDS with GC/MS:

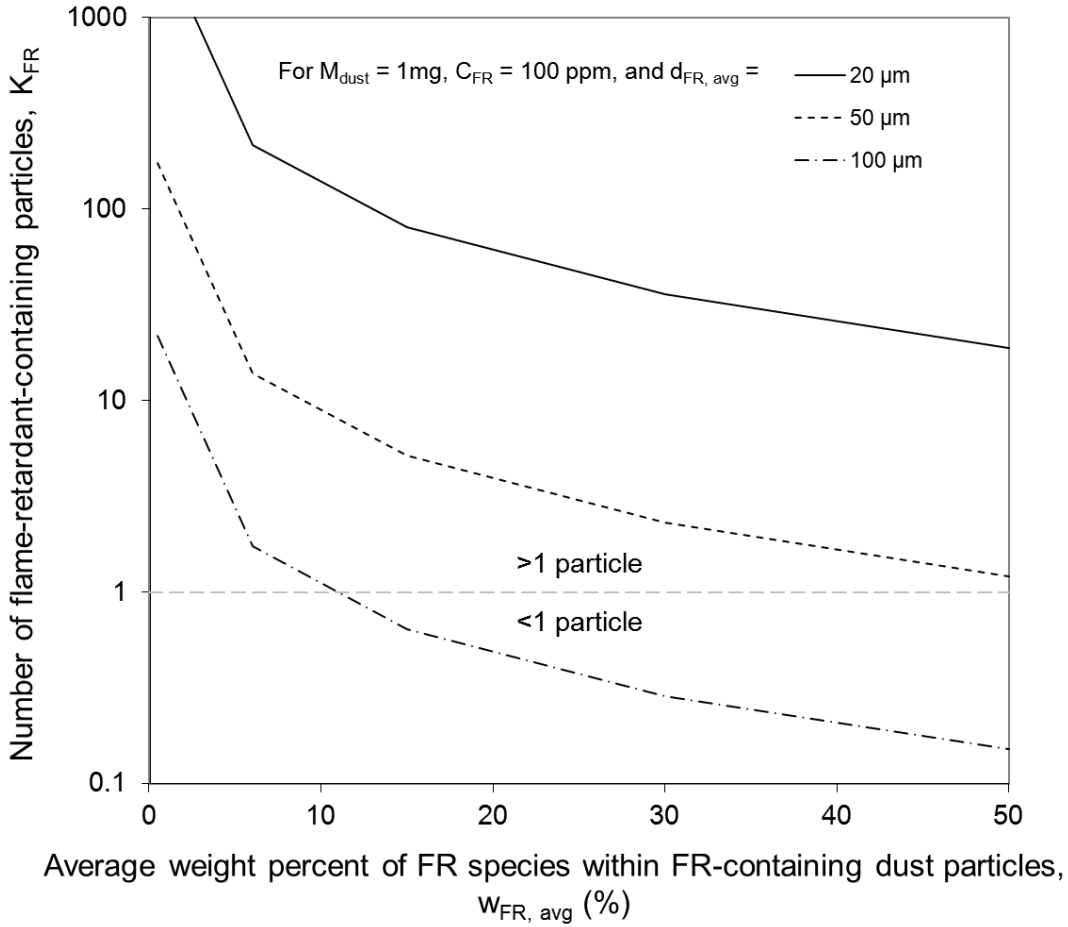
GC species	r_p (all)	r_p (without sample #3)
BDE-209	**0.66**	**0.98**
BDE-47 + BDE-99	-0.07	-0.33
BDE-47 + BDE-99 + BDE-209	0.44	0.40

Environmental Dusts

Particle type	$w_{FR, avg}$ [%] P [%]	Cl [%]	Br [%]	% Metal synergist	Typical morphology (image=80 um wide)
A	<1	1.5	31 (discrete)	10.9 Sb	
B	<1	1.7	6 (discrete)	15.8 Sb	
C	--	--	5 (discrete)	1.8 Sb	
D	--	15.0	--	9.9 Sb	
E	--	--	12 (discrete)	3.1 Sb	
F	--	--	3 (discrete)	<1 Sb	
G	--	3.0	11 (discrete)	6.1 Sb	
H	--	<1	--	5.6 Sb	
I	--	--	--	1.8 Sb	

Equation to predict heterogeneity of dusts containing high-FR-content particles

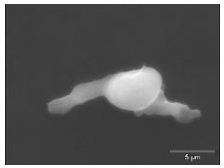
$$K_{FR} = \frac{C_{FR} \times M_{dust}}{(w_{FR,avg}/100) \times (\pi \rho_{k,avg} d_{FR,avg}^{3}/6)}$$

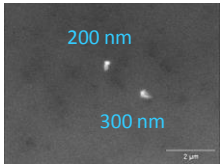


Agricultural Burning

Imperial Co.

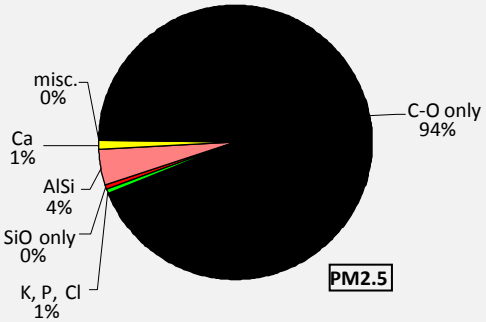
- Burn source profile obtained from burned grass reference and 24-hr PM samplers on downwind telephone pole, engulfed by ground-level plume
- Downwind sample: 17x higher PM2.5 than upwind; dominated by "**C-O only" (soot)** and "K, P, Cl" (biogenic ash)

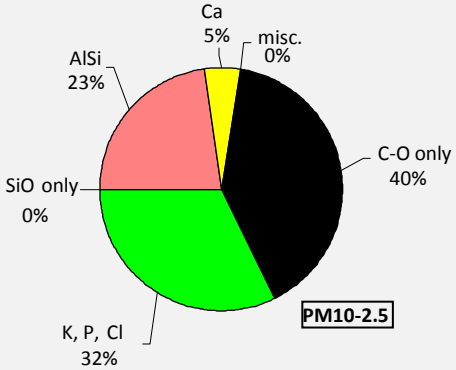




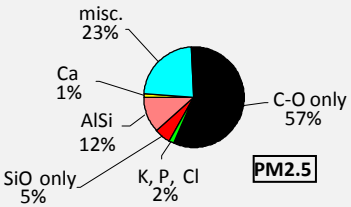
[SEM/EDS]

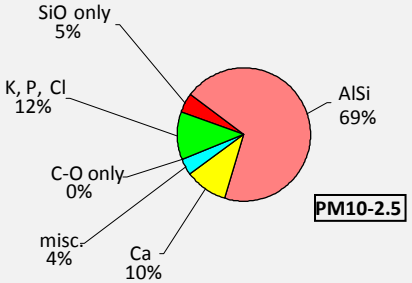
Directly downwind, 0.2 miles away



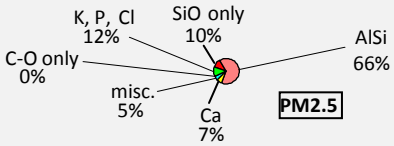


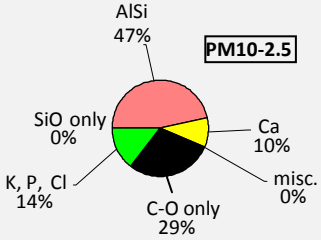
45º from downwind, 0.3 miles away





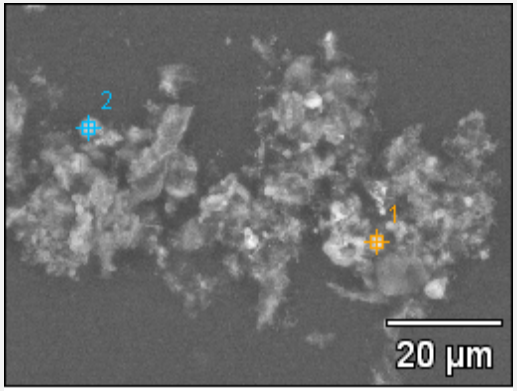
Upwind, 3.5 miles away

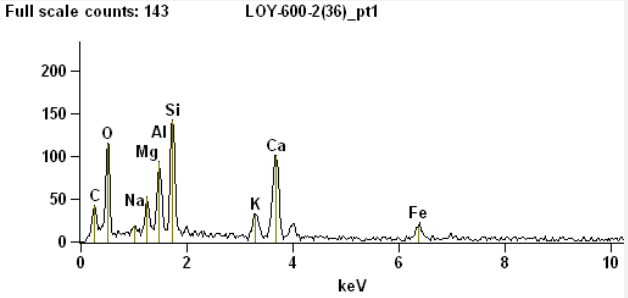




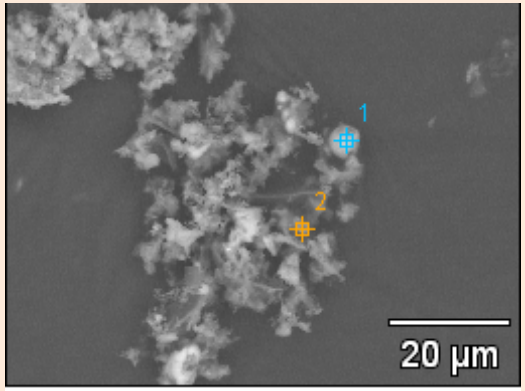
Black dust in small Sierra community with biomass facility

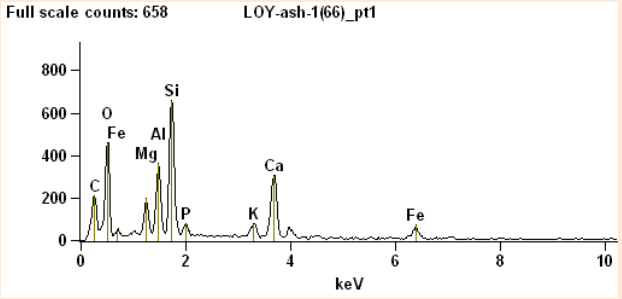
(Photo: CARB)





Airborne dust

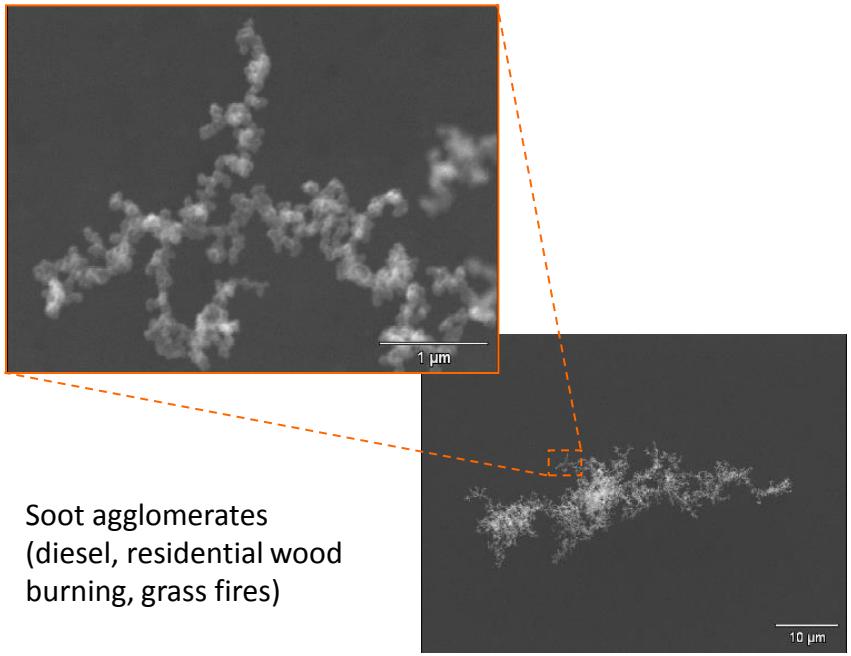




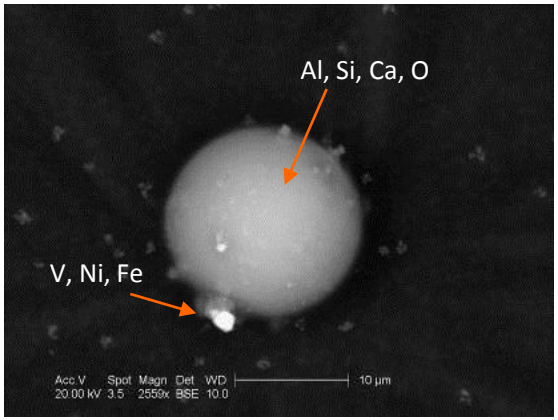
Bottom ash from local biomass cogeneration facility

Combustion aerosol library (ongoing)

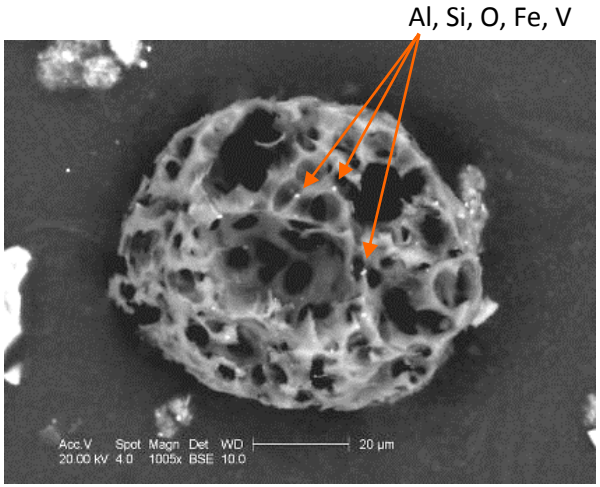
[SEM/EDS]



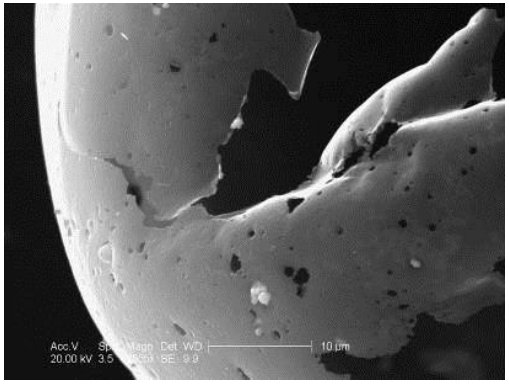
Soot agglomerates (diesel, residential wood burning, grass fires)



Fly ash (complete combustion)



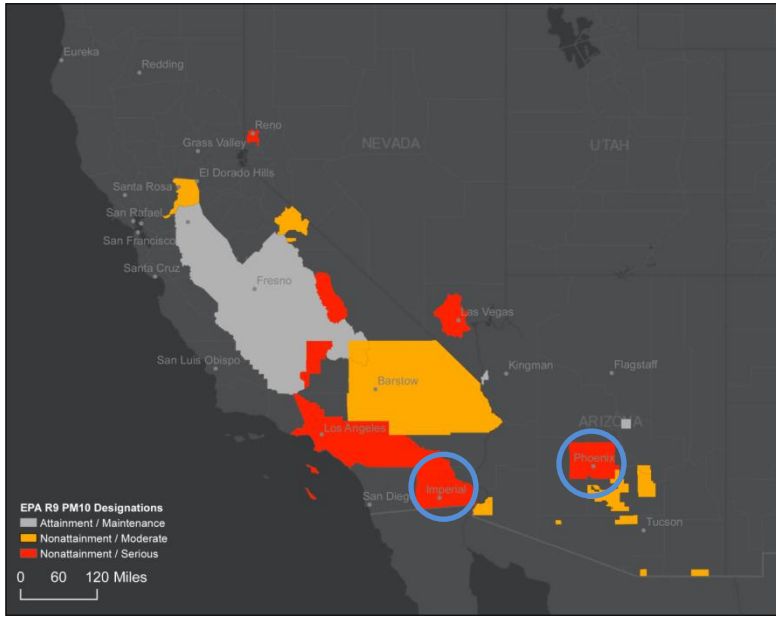
Char (fuel oil)



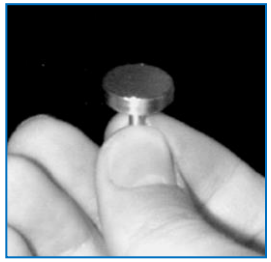
Carbon spheres (incomplete combustion)

ID of Particle Sources in high-PM Urban Desert Regions using SEM/EDS, Passive Sampling, and GIS

Dust storm, Phoenix (meteorologynews.com)



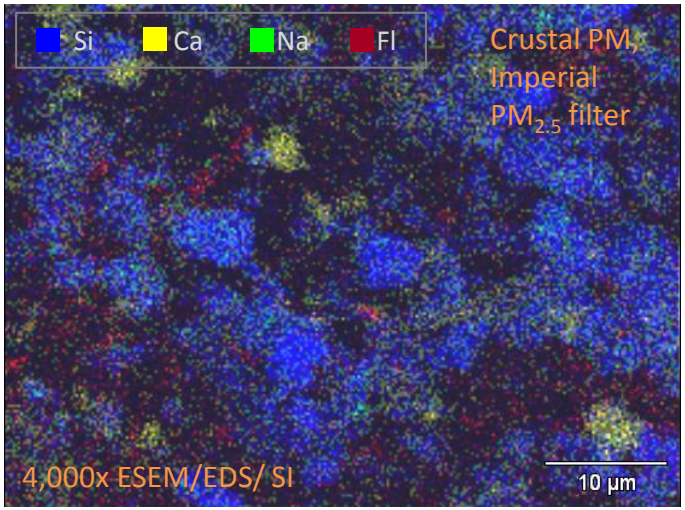
Imperial Valley, CA and Phoenix, AZ designated as PM10 Non-Attainment areas

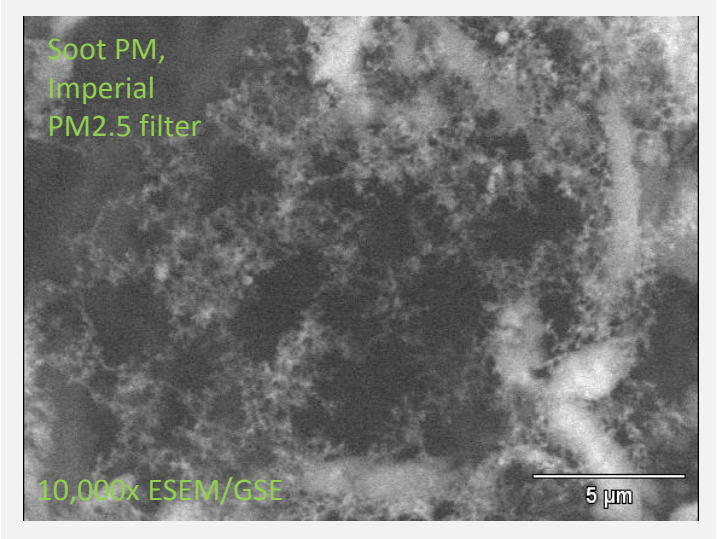


EPA FRM PM and passive UNC PM samplers

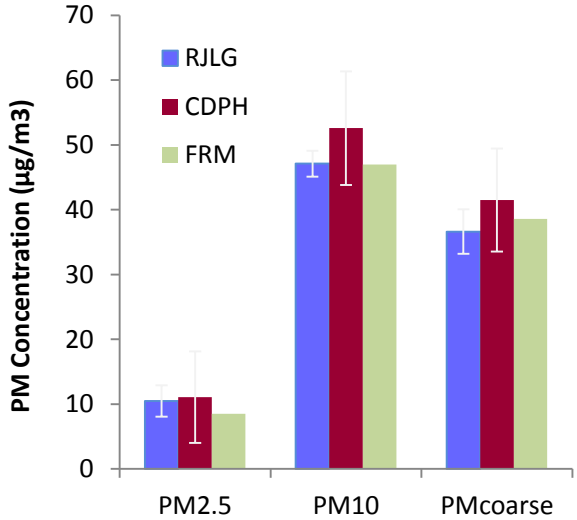
SEM/EDS of Imperial and Phoenix PM shows mostly **windblown dust** (sometimes, soot from combustion also)

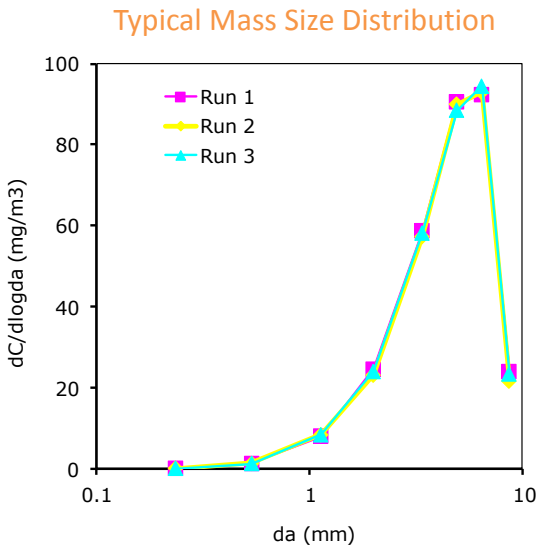
- $PM_{2.5}$ and -PM_{10} filters: large, crustal particles (2.5-15 µm, 10-30 µm)

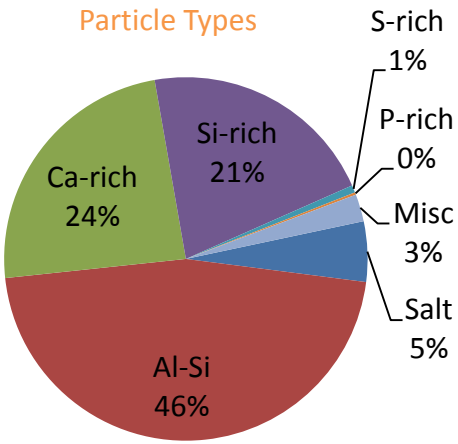




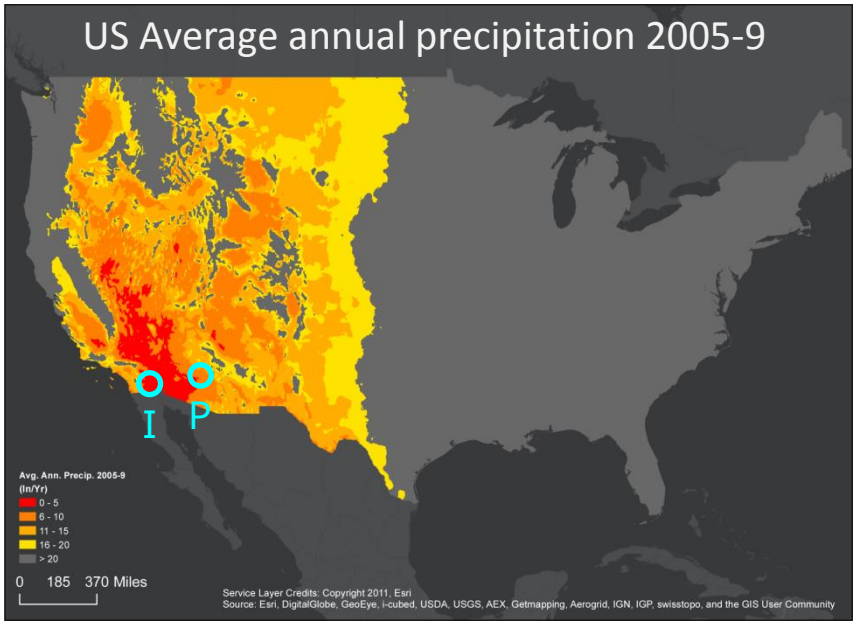
- Passive PM samplers: dominated by coarse, inorganic PM

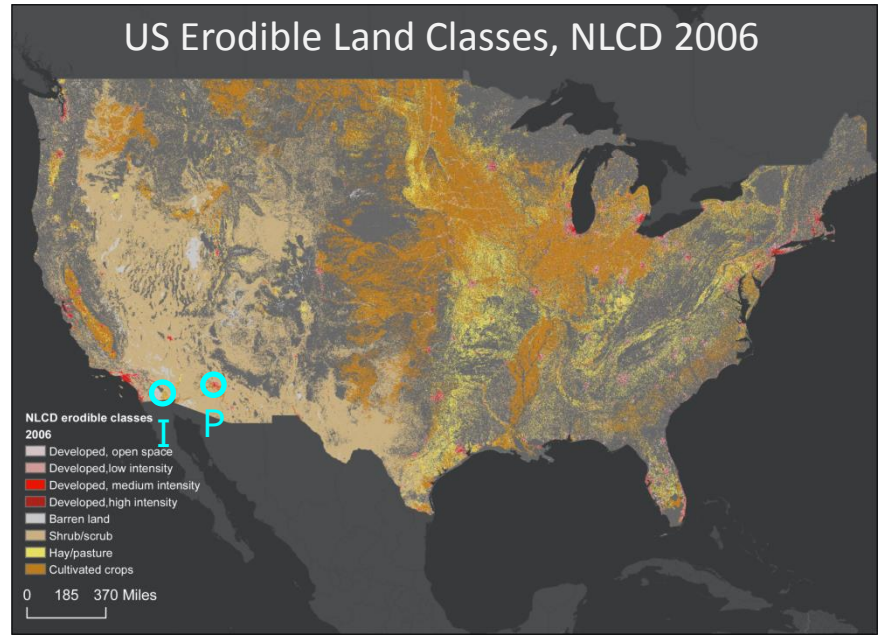


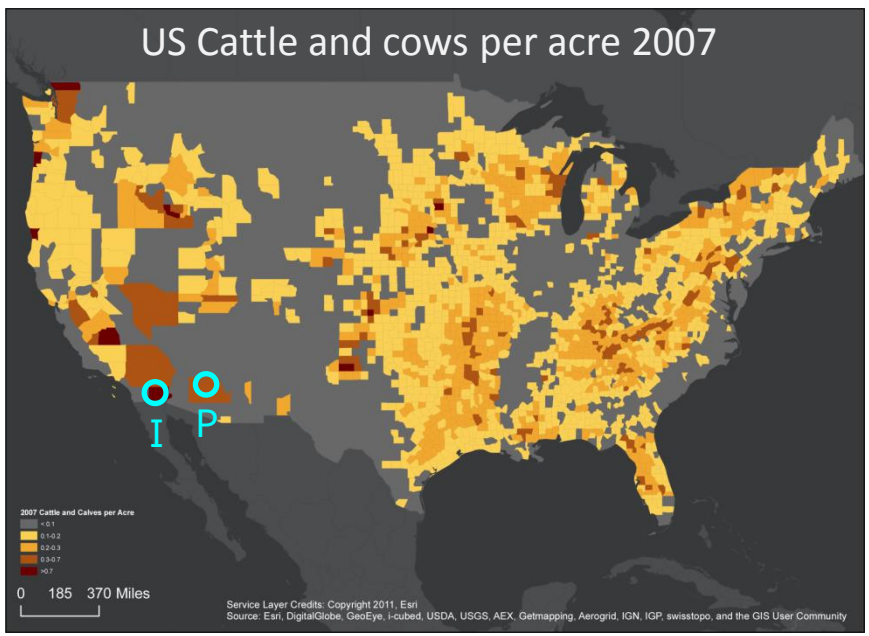


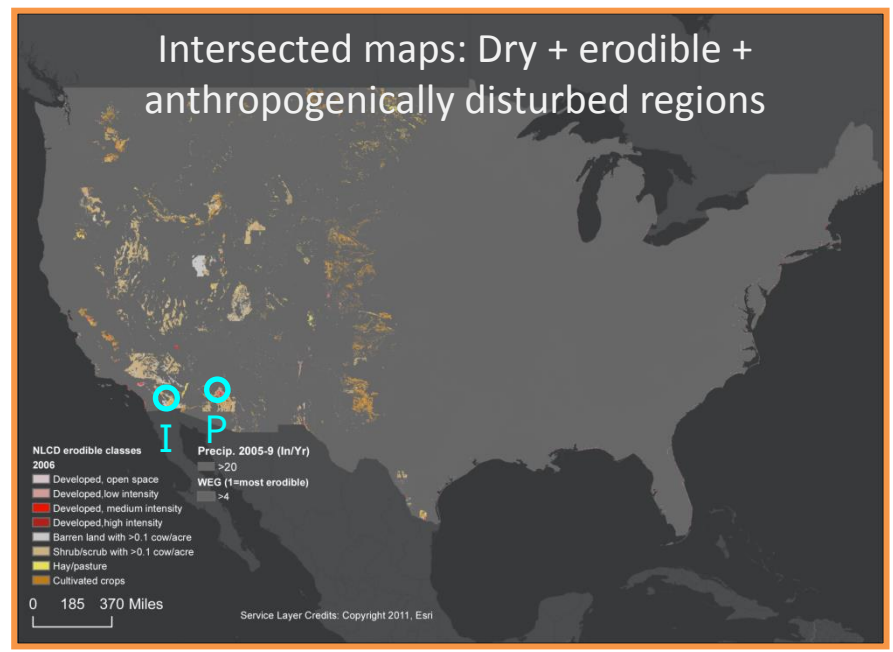


GIS maps of Imperial (I) and Phoenix (P) dust PM source parameters





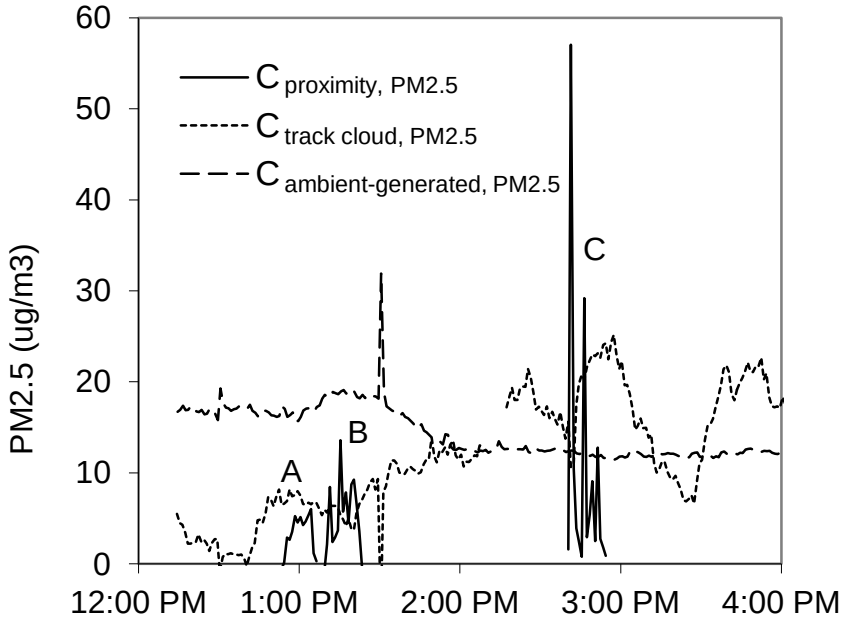


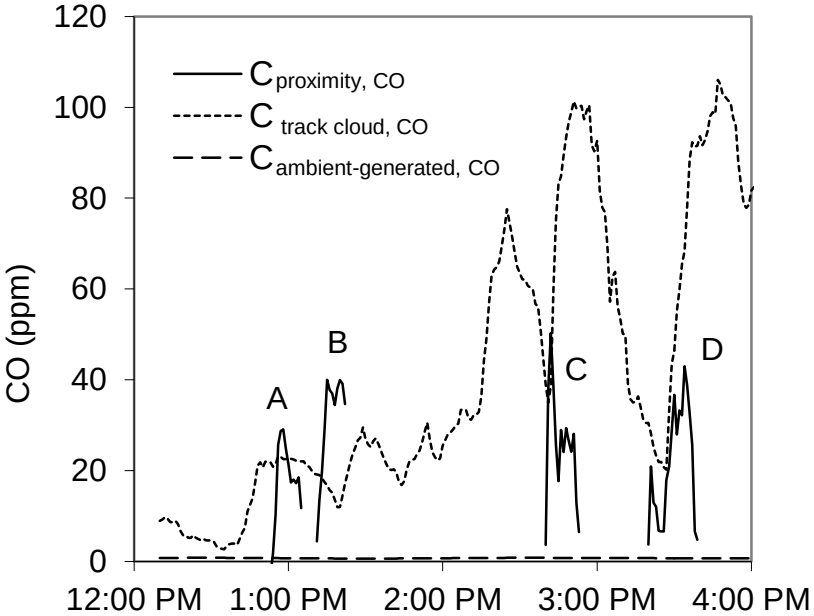


J. Wagner, CDPH/EHLB

ID of $PM_{2.5}$ and CO Sources inside Indoor Go-Kart Facility

Portable Sensors





J. Wagner, CDPH/EHLB

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