United States Environmental Protection Agency

Physical and Chemical Properties of Anthropogenic Aerosols: An Overview

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Outline and objectives

I. Review the EPA Air, Climate, and Energy program and major emission source sectors

II. Describe combustion particle formation and atmospheric dusts

III. Introduce examples of the latest EPA developments in the mobile emissions sector

IV. Describe EPA's advancements using several combustion emissions research projects

V. Provide perspective on the challenges facing characterization of combustion emissions and air pollution

Air, Climate, Energy (ACE)

http://www.epa.gov/airscience/

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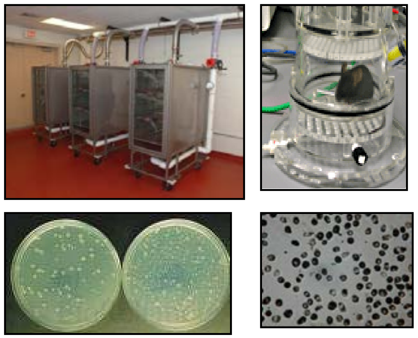
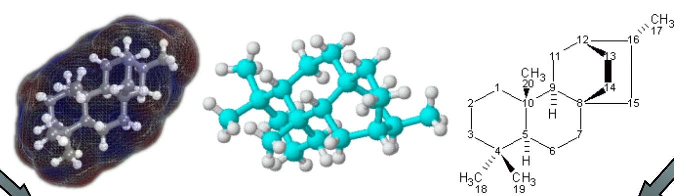
Clinical and Animal Toxicology



Molecular biology



Epidemiology

U.S. EPA partners:
• Federal/State agencies
• Health Effects Institute
• Academia (EPA STAR Program)
• PM Research Centers
• Industry laboratories

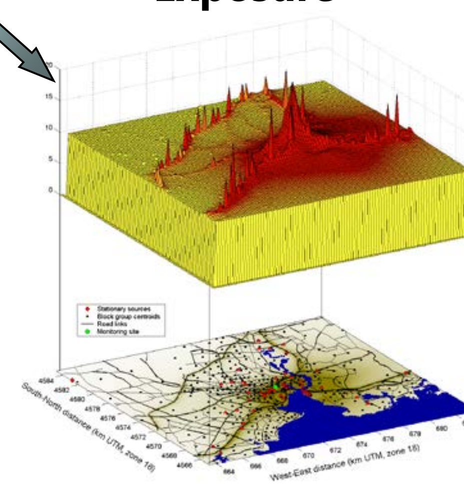
Source to effects

Emissions

EPA Ambient Monitoring

Modeling the atmosphere and climate

Exposure



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Major source emissions sectors

Fires
- Ag field burning
- Prescribed and wildfire

Fuel Combustion
- Electric Power
- Industrial
- Commercial
- Institutional
- Residential
- Biomass, gas, coal, oil

Industrial Processes
- Cement and Chemical
- Mining
- Oil and gas production
- Refineries

Mobile
- Aircraft
- Vehicles
- Locomotives

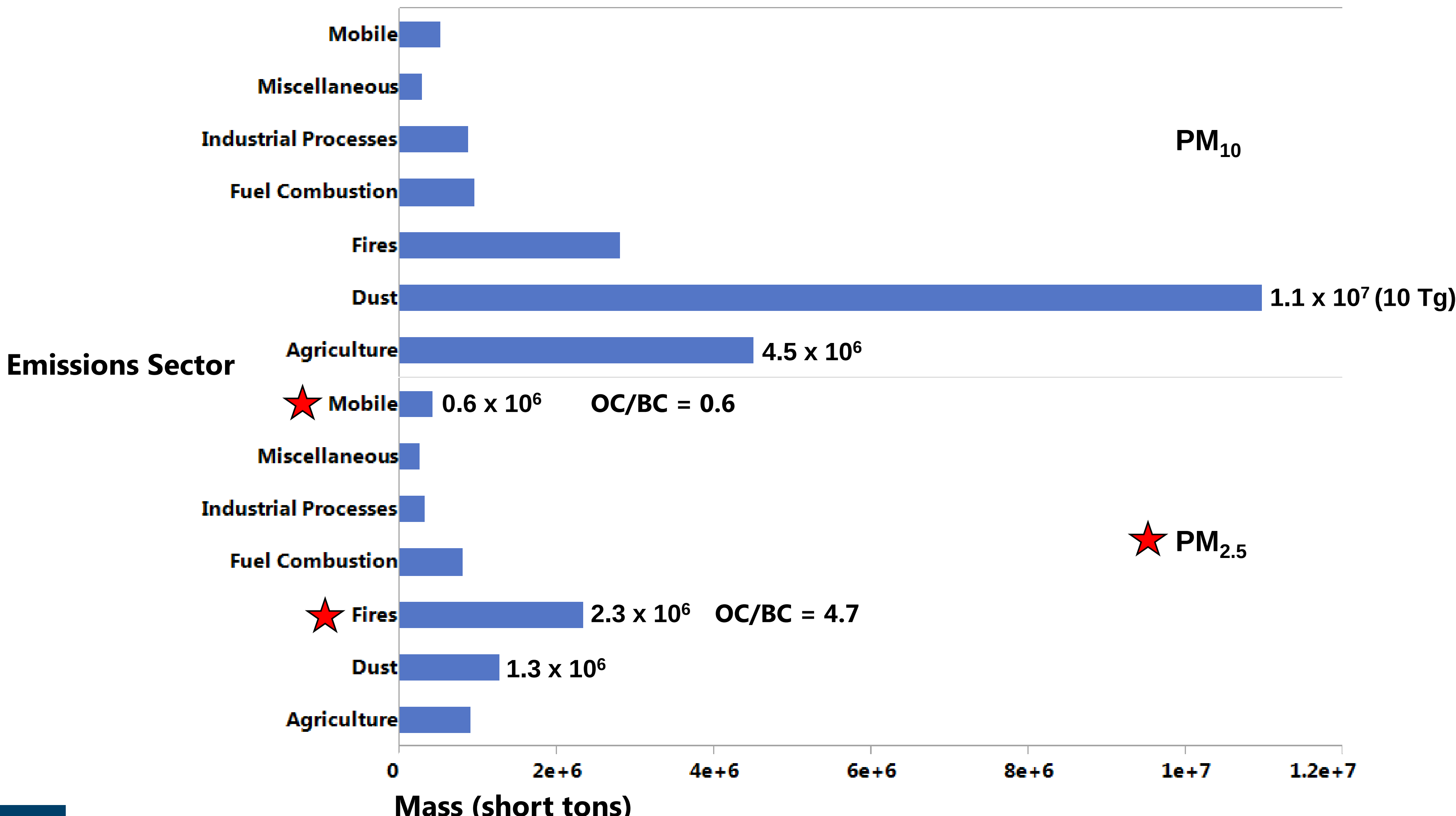
Dust
- road dust

Agriculture
- livestock
- crops

Solvent
- Dry cleaning
- surface coatings

Miscellaneous
- cooking
- Gas stations
- Waste disposal

National PM emissions by sector - 2011



Yu et al. (2012) Science, *337*, 566-569.

- **Asian outflow (~60 Tg/yr; 3% of which is below 2km)**

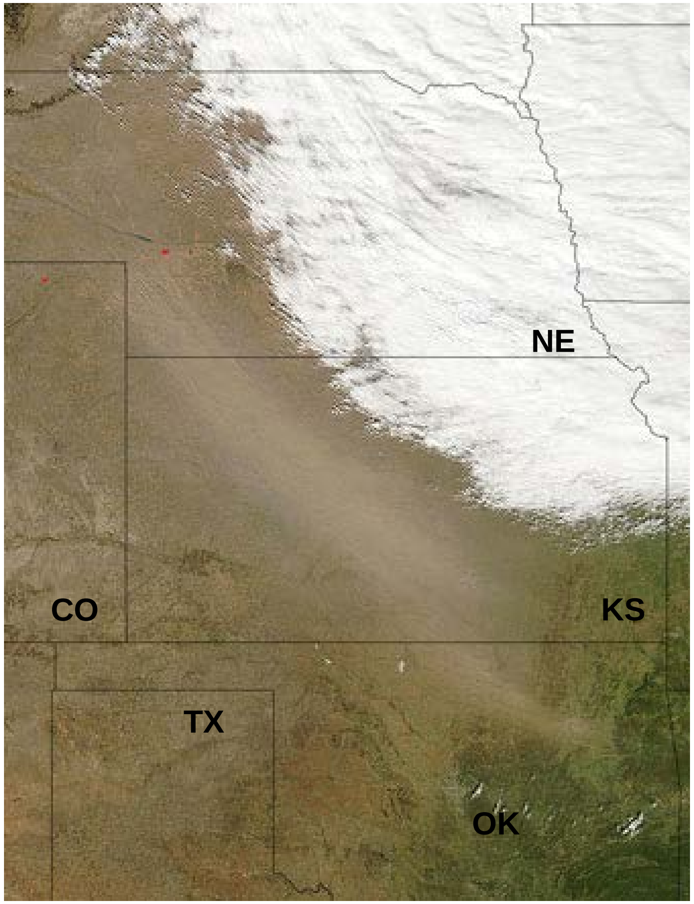
Air Quality Impacts of Dusts

- **Geological and climate**
  - large-scale regional events (seasonal)
  - long-range transport (1000 km +)
  - vertical distributions up to several km
  - cloud interactions
  - scattering (Fe absorbs)

- **Chemical properties**
  - predominantly metals with some organic matter
  - dusts adsorb organic pollutants (encapsulation)
  - influences atmospheric processing

- **Health and visibility**
  - Dust Bowl Storms

MODIS (Aqua) October 2012
Agricultural Dust Storm



~800 km wide dust plume

Incomplete combustion and carbon particle formation

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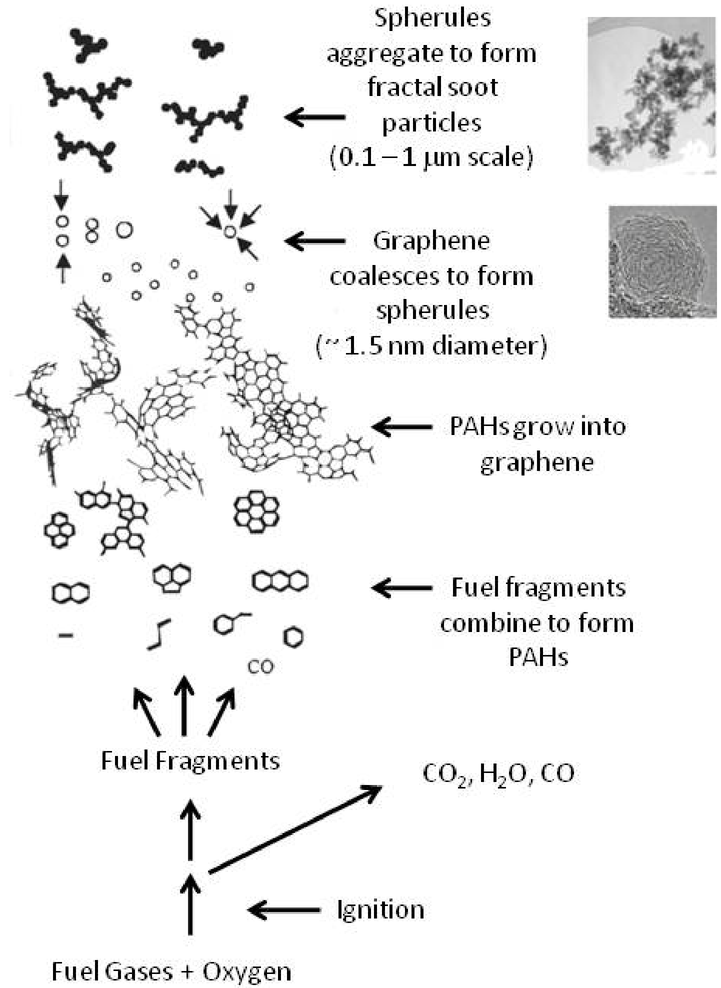
Optical properties

“Black” carbon (particles)

Other light absorbing carbon – may be brown, yellow, or transparent to visible light. (Molecules that will condense into liquid form in atmospheric particles)

Chemical properties



Physical state

Nonvolatile, refractory, solids

semivolatiles, solids, liquids

Volatile precursors

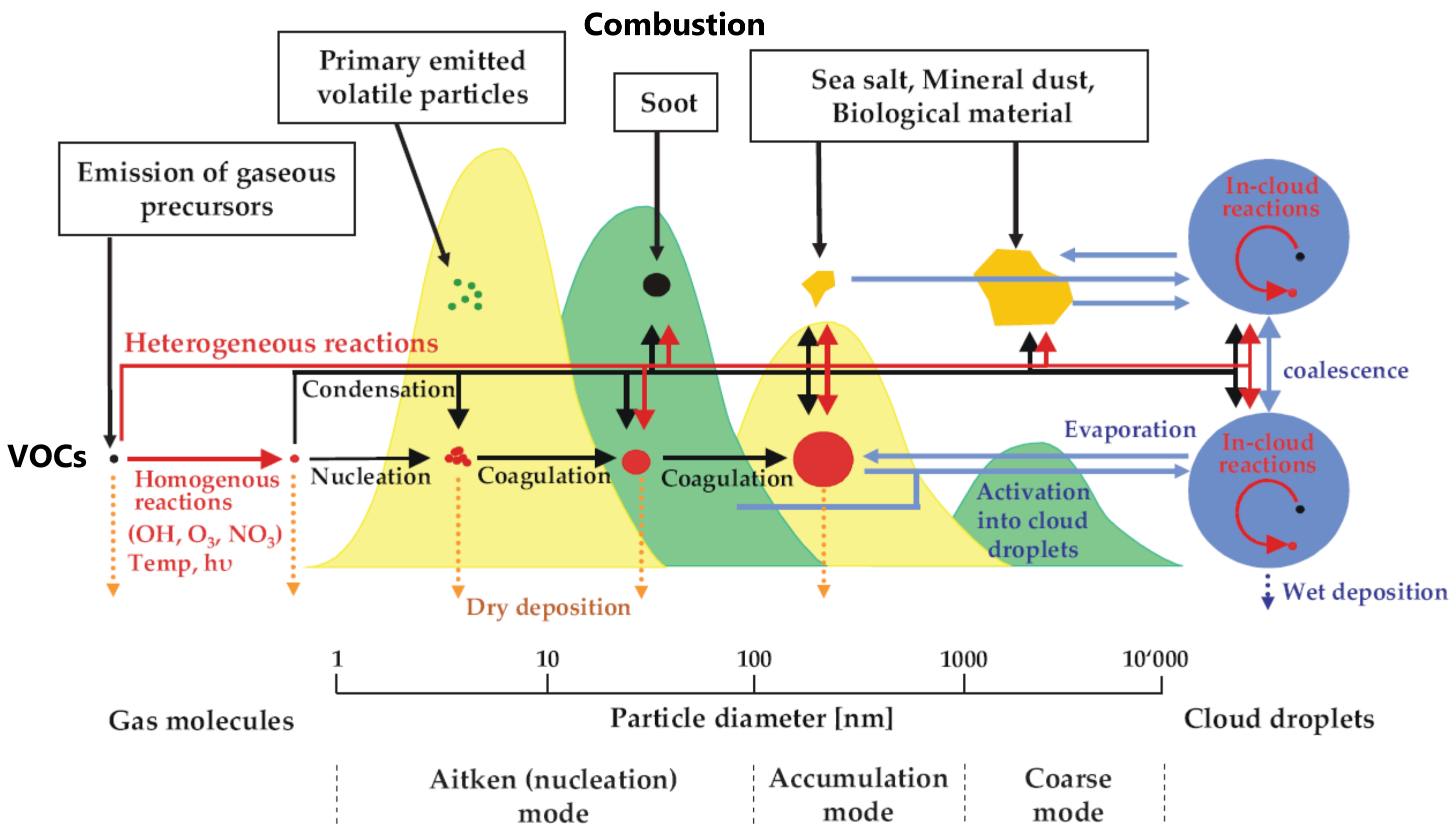
classical - solid, liquid, gas,
non classical - glass, gels

With help Bockhorn, H., *Soot Formation in Combustion, Mechanisms and Models*, 1994.

Atmospheric processing of combustion aerosols

Aerosol Sources

Raes et al., Atmos Env, 34 (25), 4215-4240, 2000



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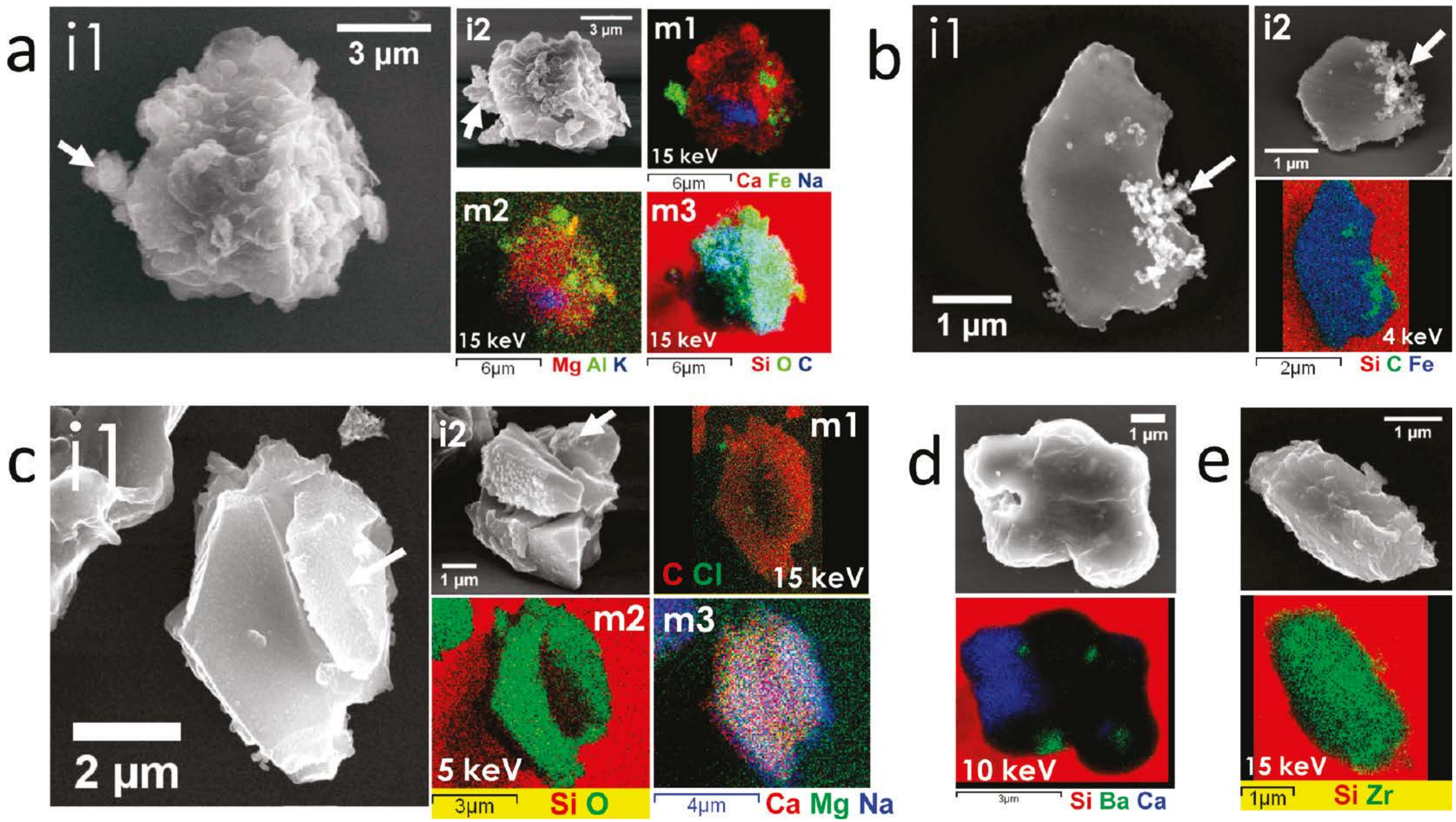
SEM-EDX (HR) mapping of elements



Atmospheric aerosol particles in LA, Cal

- heterogeneously mixed, inclusions, surface adducts
- Will lead to FIB-SEM

Credit: Conny and Norris, *ES&T* (2011) ACS Publications High quality. High impact.

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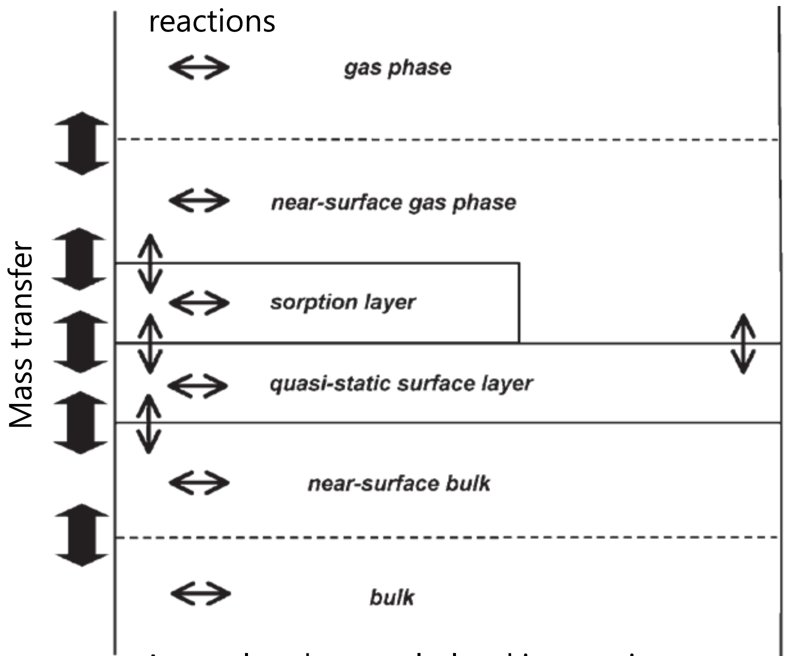
Aerosol interaction possibilities

General double-layer surface model



small molecules

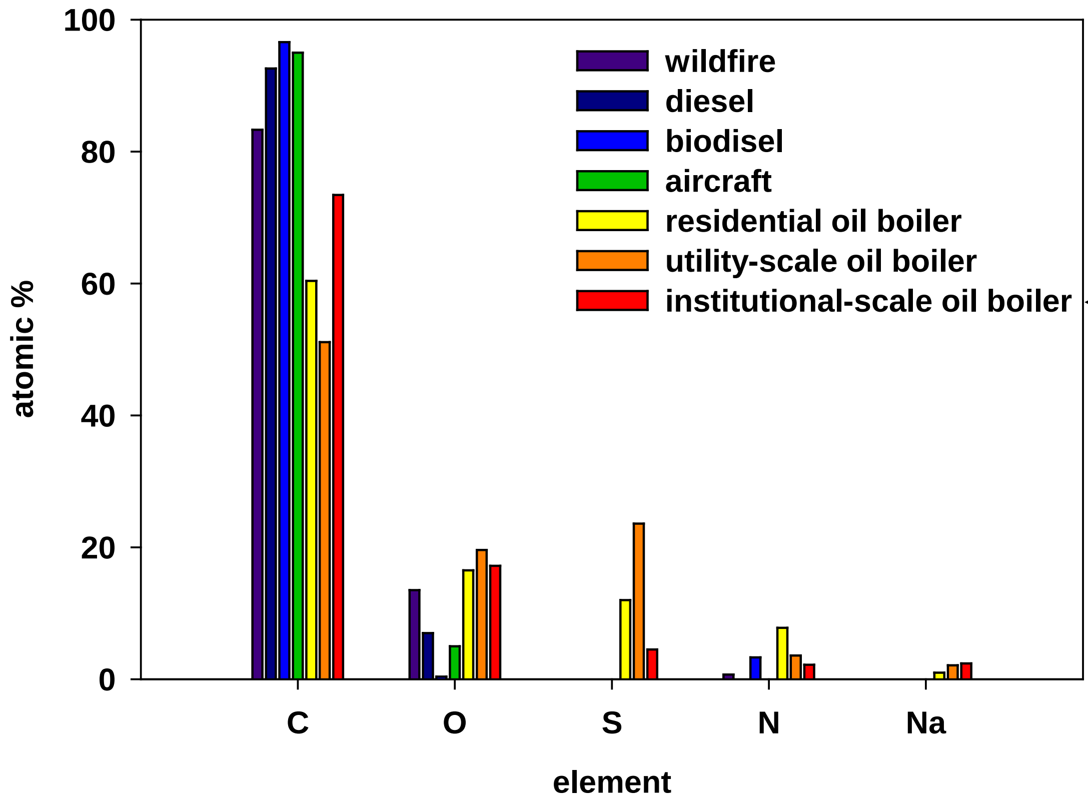
10,000+ organic chemicals, refractory C

Aerosol and aerosol-cloud interactions

- Mixture
- Multi-phase, interfacial mass transport
- Diffusion
- Equilibrium and thermodynamics
- Chemi- and physi-sorption
- Chemical reactions and kinetics
    - within or across phases
- Species concentration

Pöschl et al. (**2005**) *Angew. Chem. Int. Ed.* , *44*, p. 7520

Surface composition of source aerosols (XPS)



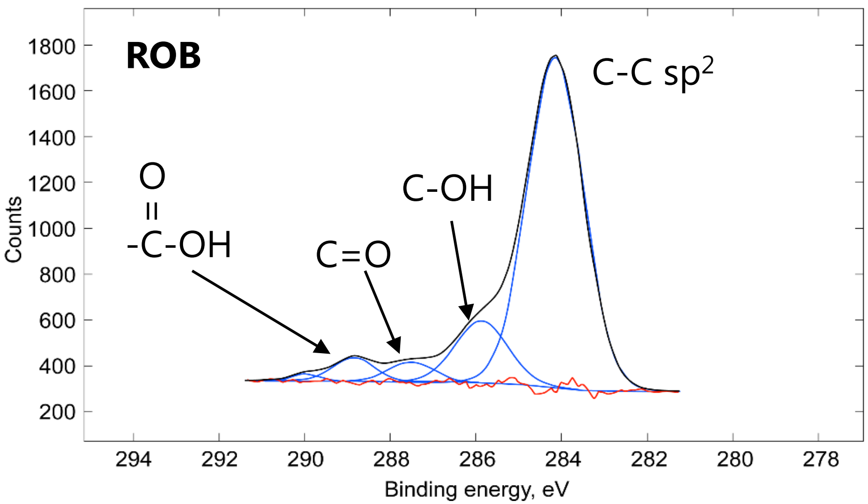
agreed with bulk S composition

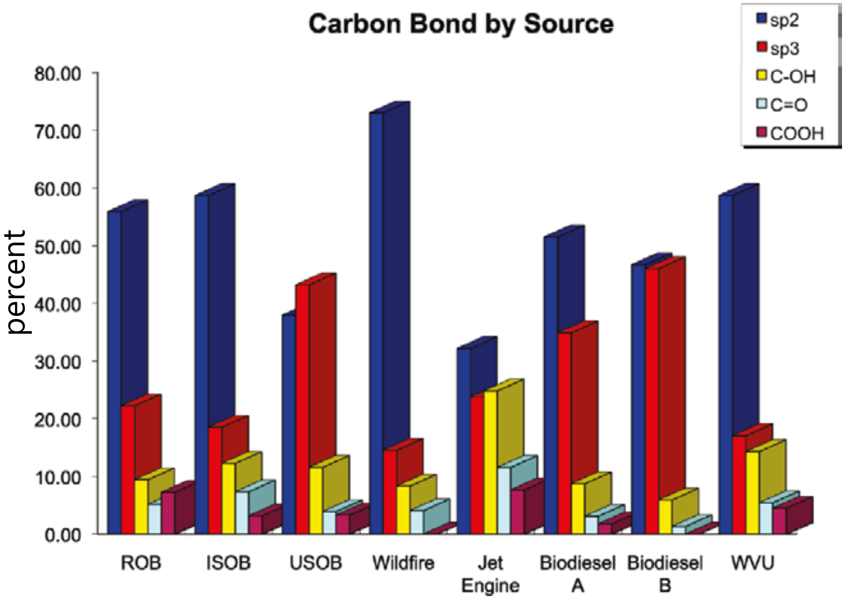
- mostly surface carbon
- oil boilers show reduced C
  - contain S and O (sulfate)
- biodiesel lacked surface O
- wildfire - surface OM:OC ratio = 1.2

VanderWal et al. (**2011**) *Anal. Chem.*, *83*, p. 1924

Surface functional group composition (XPS)

high-resolution scan over C1S region





- slight shift in C1s binding energy indicate different oxygen functional groups
- percentages of carbon atoms apportioned to oxygen functional groups
- different carbon bonding states at the particle surface

VanderWal et al. (**2011**) *Anal. Chem.*, *83*, p. 1924

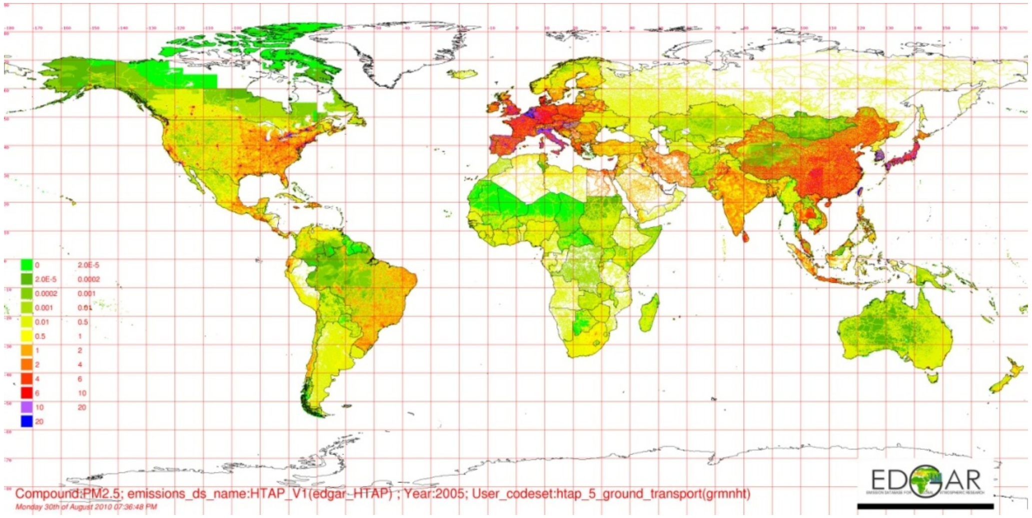
Transportation/Mobile sector emissions research

dynamometer research

on-road research

near-road research

aircraft emissions



2005 Global ground transportation $PM_{2.5}$ emissions

European Commission Joint Research Center—Emissions Database for Global Atmospheric Research

Biofuels

- The 2007 Energy Independence & Security Act (EISA) mandated renewable fuel use in the transportation sector
  - EPA sets Renewable Fuel Standards (RFS) annually (flexibility)
  - 36 billion gallons of renewable fuels by 2022

Volumes Used to Determine the Proposed 2014 Percentage Standards

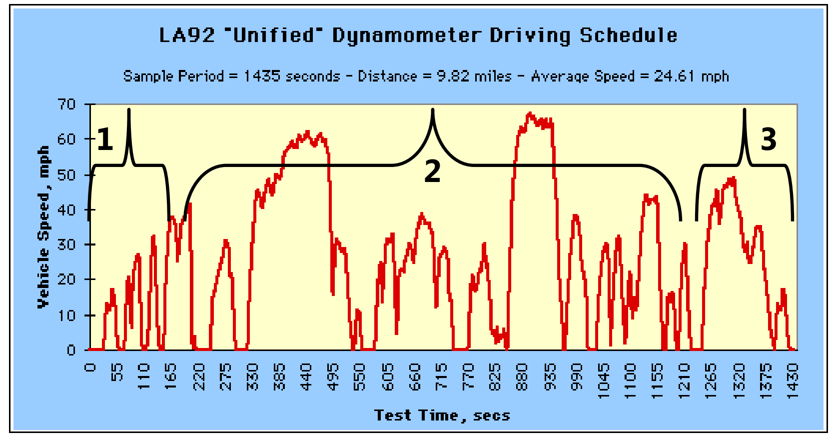
Category	Volume[a]	Range
Cellulosic biofuel	17×10^6 gal	$8\text{-}30\times10^6$ gallons
Biomass-based diesel (FAMEs)	1.3×10^9 gal	1.3×10^9 gal[b]
Advanced biofuel (non-corn EtOH)	2.2×10^9 gal	$2.0\text{-}2.5\times10^9$ gal
∑Renewable fuel	15.2×10^9 gal	$15.0\text{-}15.5\times10^9$ gal

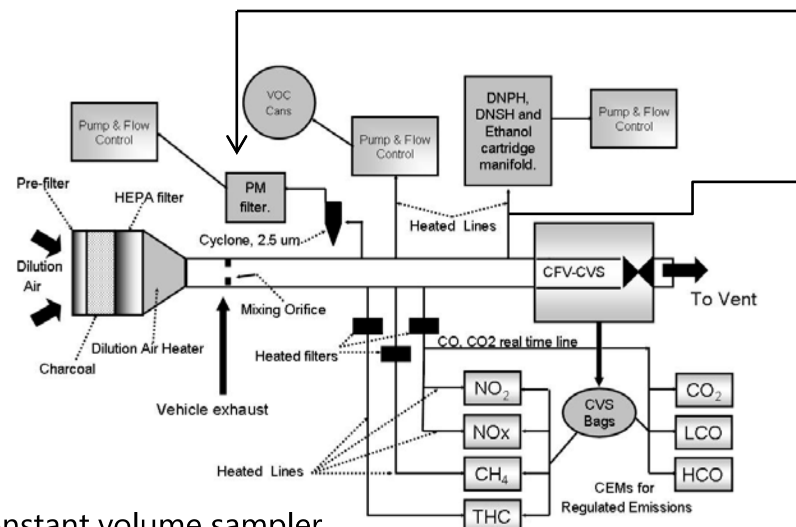
[a]All volumes are ethanol-equivalent, except for biomass-based diesel which is actual
[b]EPA is requesting comment on alternative approaches and higher volumes

- As part of these requirements, EPA must:
  - Assess the impacts of changes in ethanol and other fuel properties on emissions and ambient concentrations of air toxics and criteria pollutants
  - Ensure "anti-backsliding" of air quality impacts and propose regulations to mitigate any adverse air quality impacts

Emissions Testing of LDVs running on ethanol fuel blends

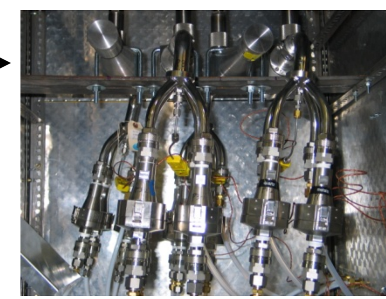
- 48″ roll chassis dynamometer (Burke-Porter, model 4100) simulated vehicle road load simulation
- Used a “drive-in” climate chamber for vehicle temperature control (-7°C and 24°C)
- Fuels e0, e10, and e85, 3 Tier 2 light-duty vehicles (2008)





collected phases 1,2, and 3

SP2



constant volume sampler
1:10 dilution

- 47 mm quartz fiber filter-PUFs
  - OC-EC (NIOSH Method 5040)
  - SVOC, particle-phase speciation (TE-GC-MS)

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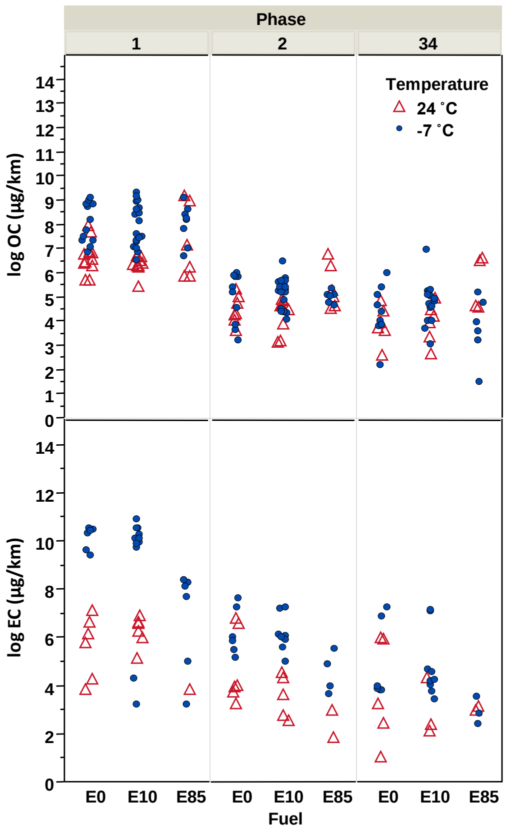
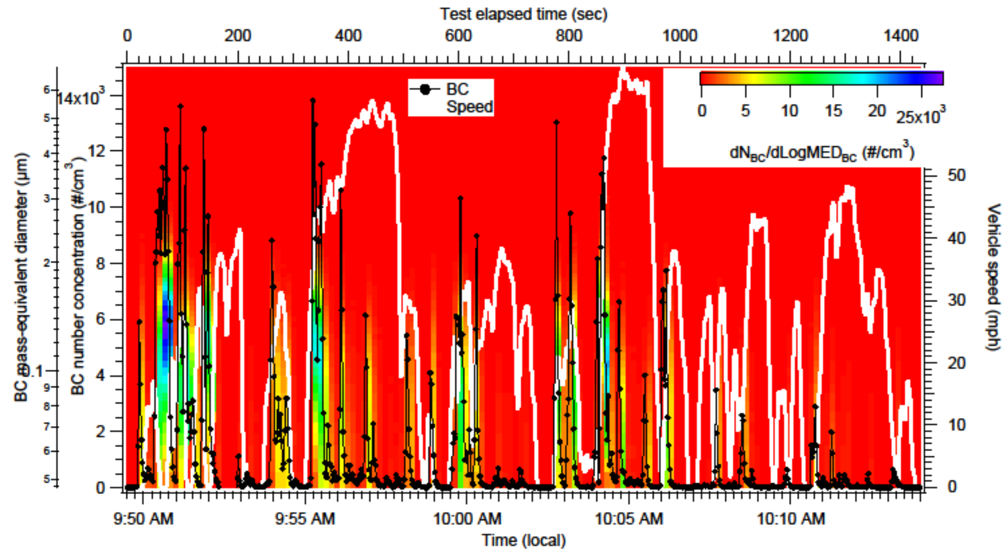
OC-EC and BC in LDV PM

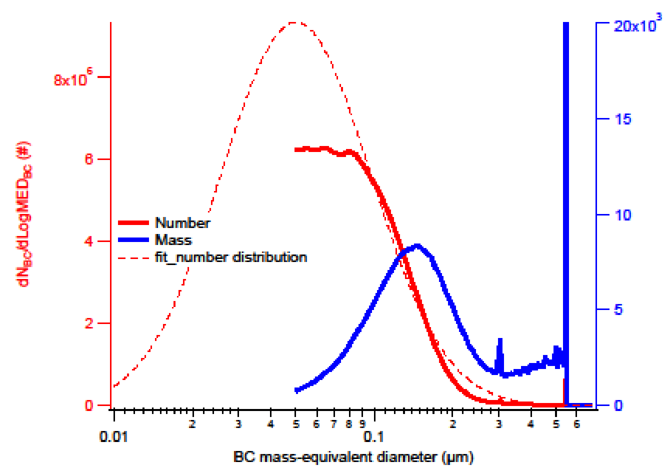
OC_{123} = 30-618 μg/km
EC_{123} = 1-2784 μg/km



- total C/PM = 1 ±0.7
- EC/PM decreases with e-content
- phase 1 > phase 2 > phase 3,4
- temp. influences OC and EC emissions
- C/PM relatively unaffected

e10 and 23 °C, d_a = 50-500 nm

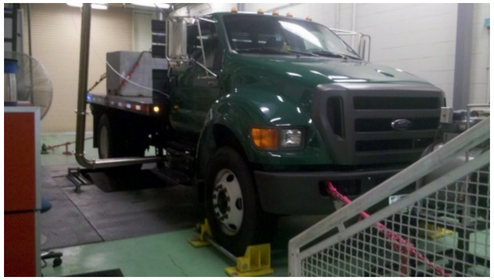




VOC emissions of medium-duty diesel trucks

- 2011 Dodge Ram 2500
- GVWR = 9,600 lb
- NAC/DOC/DPF

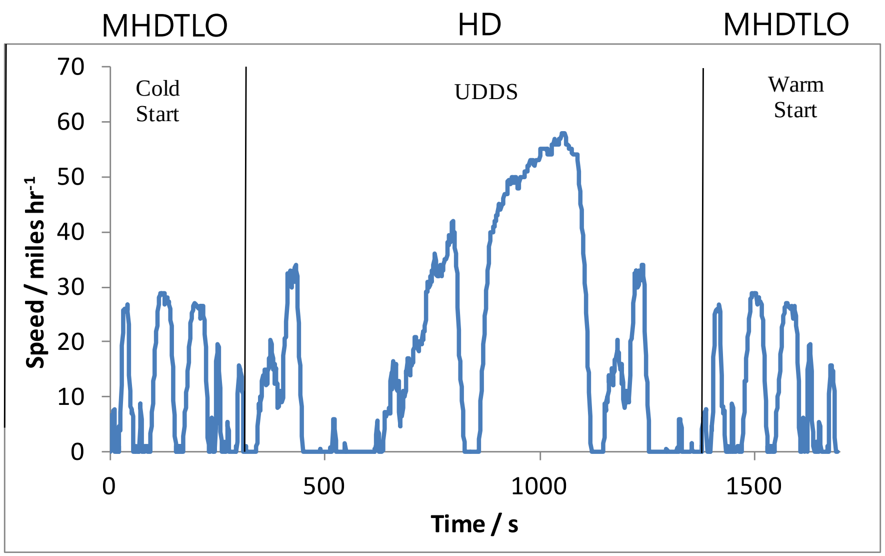
- 2011 Ford F550
- GVWR = 19,500 lb
- SCR/DOC/DPF



- 2011 Ford F750
- GVWR = 25,999 lb
- SCR/DOC/DPF

- **Variables**
  - Fuels: ULSD and B20 (soy)
  - Weight: laden/unladen (F550)
  - Temperature: -7 ºC and 21.7 ºC (F750)

EPA-TO11 and EPA TO-15

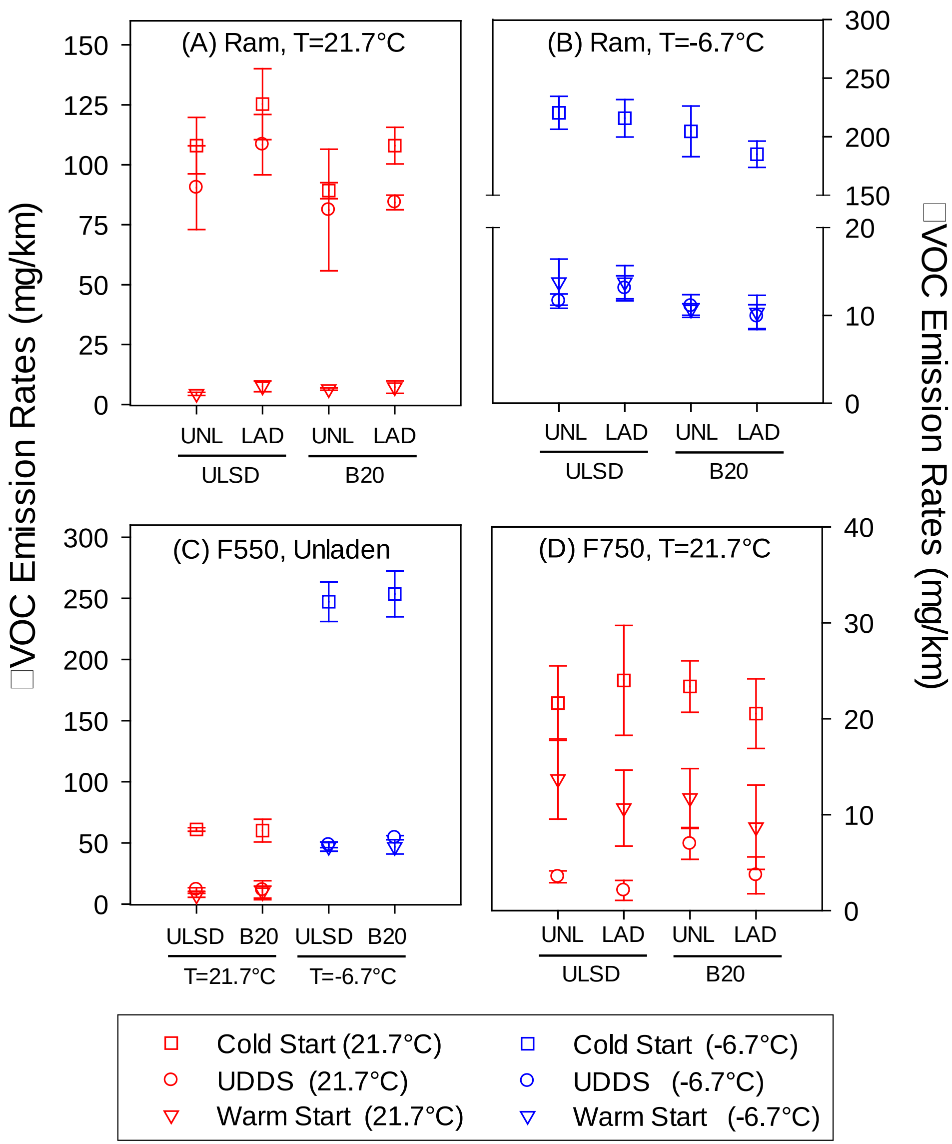


Clark et al. SAE Technical Paper, 2003-01-3284

George et al. *ES&T*, in review.

VOC emissions of medium-duty diesel trucks

George et al. *ES&T*, in review.



- Load weight effect was not significant
- Cycle and T significantly increased VOC emissions
- Ram had highest emissions
- B20 had minor effect on total VOC emissions
    - Reduced BTEX
    - Absolute changes ±18 mg/km

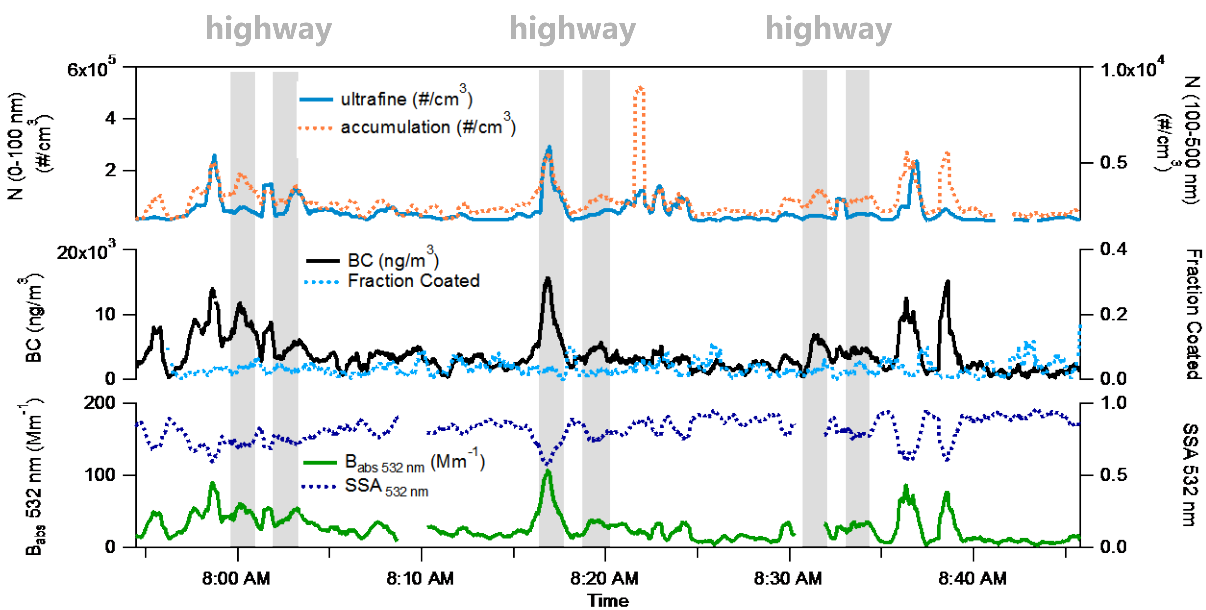
- DPF regen (variable)
    - Carbonyls increase during UDDS
    - Carbonyls decrease during warm start

On-road research – Experimental methods

- RTP, NC on-road study
- GPS and window mounted video camera
- 8 mile loop over 1.5 hr, repeated laps ($n \geq 5$)
- morning and evening commuting times were used over 3 days
- Engine exhaust particle sizer (EEPS) – mass and conc. 6 nm-560 nm
- BC – aethalometer, SP2, and PASS-3 (405 nm, 532 nm, 781 nm)
- periods of interstate congestion

Holder et al., (2014), *Atmos. Environ.*,88, pp. 183-191; Hagler et al. (2010), *JAWMA*, 60, pp 328-336

On-road research – Results



Time series of particle number concentration, absorption, single scattering albedo, BC concentration, and the fraction of 200 nm BC particles that are coated. The shaded areas correspond to times when the electric vehicle was on I-40.

- 30 sec running average of a 50 min commuting period
- spikes were highest on highway and intersections
- UFP and accumulation modes loosely correlate
- accumulation mode best correlates to BC_{aeth}, SSA, absorption
- coating measured for particles of 195 nm -205 nm
- particle coatings were lower during congestion

Holder et al., (2014), *Atmos. Environ.*,88, pp. 183-191

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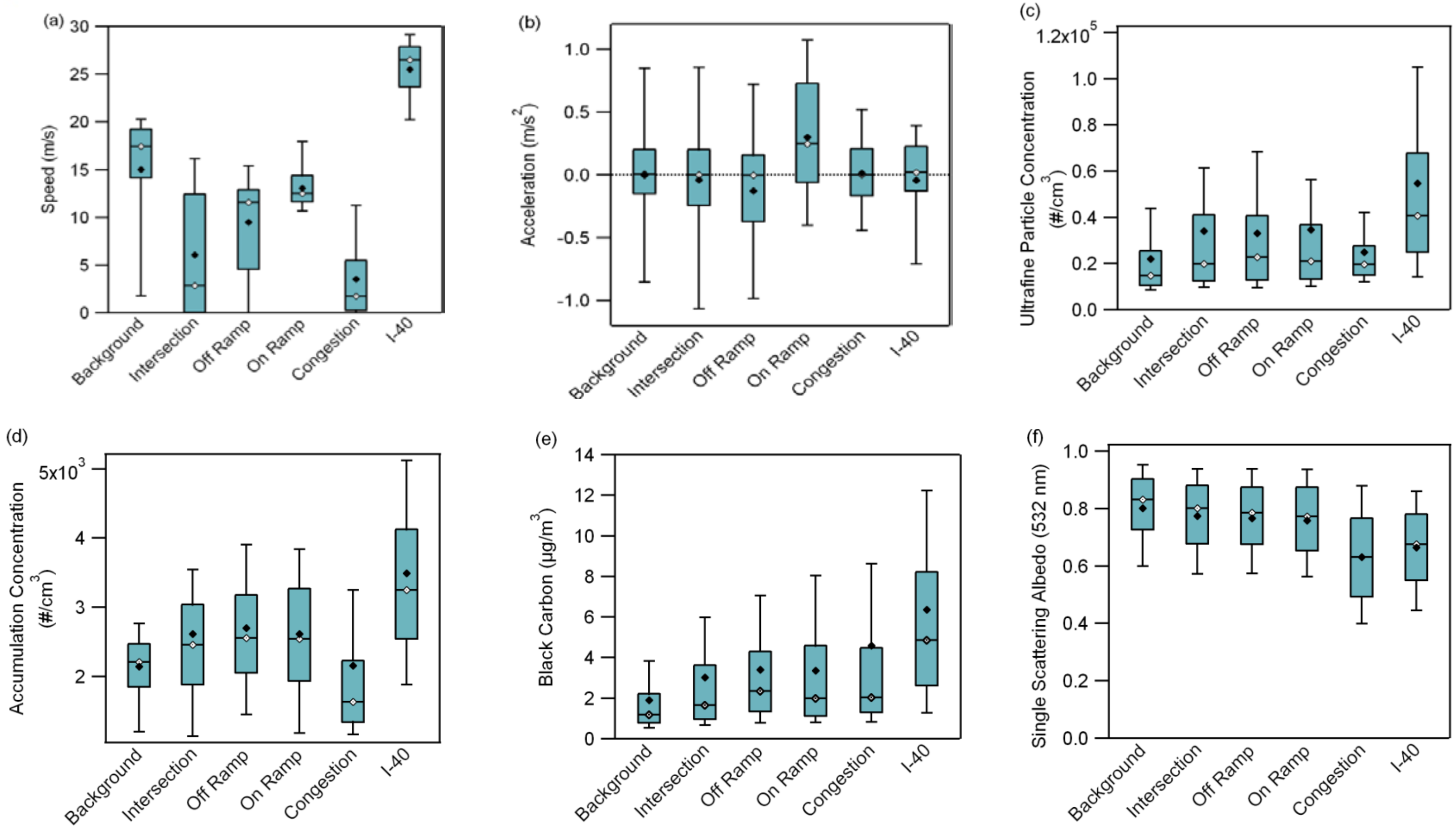
On-road research – Results



Box plots of (a) speed (b) acceleration (c) UFP concentration (d) accumulation concentration (e) BC (AE-42) (f) single scattering albedo at 532 nm for different driving conditions. The whiskers correspond to the 10th and 90th percentiles and the black diamond corresponds to the mean value.

- SSA was significantly lower on interstate and during congestion
- high vehicle speeds increased BC more than lower accelerations
- increased dilution possible at on-ramps

Holder et al., (2014), *Atmos. Environ.*,88, pp. 183-191

Chemical characterization of aircraft emissions

- airports are typically located in well populated urban centers
  - lack of compliance with standards and health concerns
  - major expansion expected
- contrail formation and climate issues
- limited information about aircraft particle emissions composition
- Aircraft Particle Emissions eXperiment (APEX) consortium formed
  - NASA, EPA, FAA
- assess the effects of fuel properties and operating conditions on PM emissions

Kinsey et al., (**2011**), *ES&T*, 45, pp. 3415-3421

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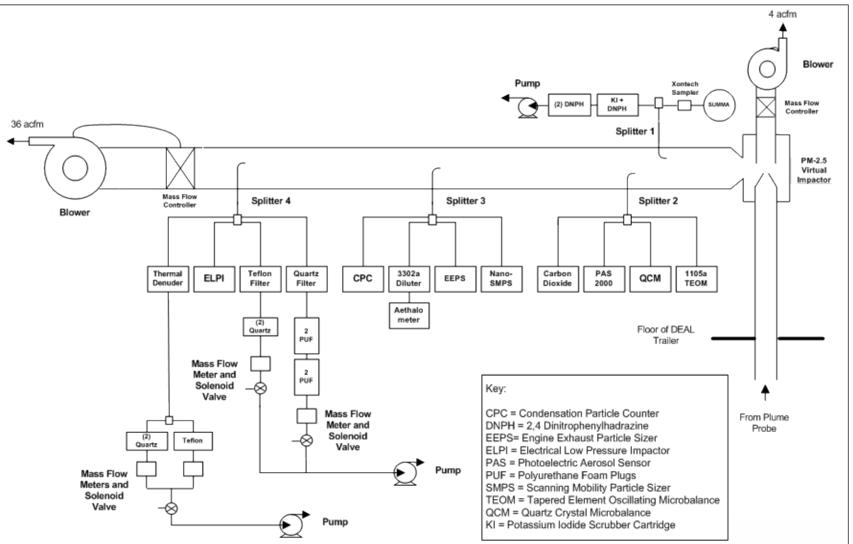
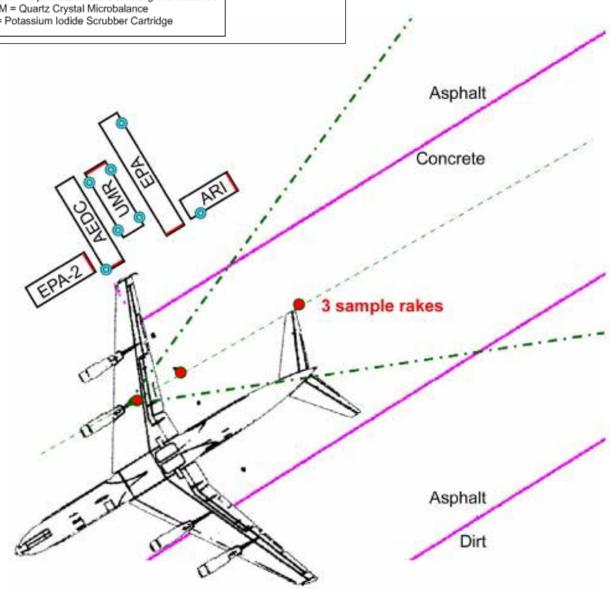
Aircraft emissions sampling



- test variables include:
  - fuel (base, high aromatic, high S [APEX 1])
- airframe and engine (N = 9)
- nominal percent rated thrust
- test campaign location (NASA-Dryden; Oakland International Airport; NASA-Glenn)

- 30 m sample rake with nozzle (anchored plume probe)
- EF calculations - carbon balanced
- time-integrated quartz filters used for SVOC analysis
- time-integrated Teflon filters used for ions/XRF
- thermal denuder used for PM volatility determination



Kinsey et al., (**2011**), *ES&T*, 45, pp. 3415-3421

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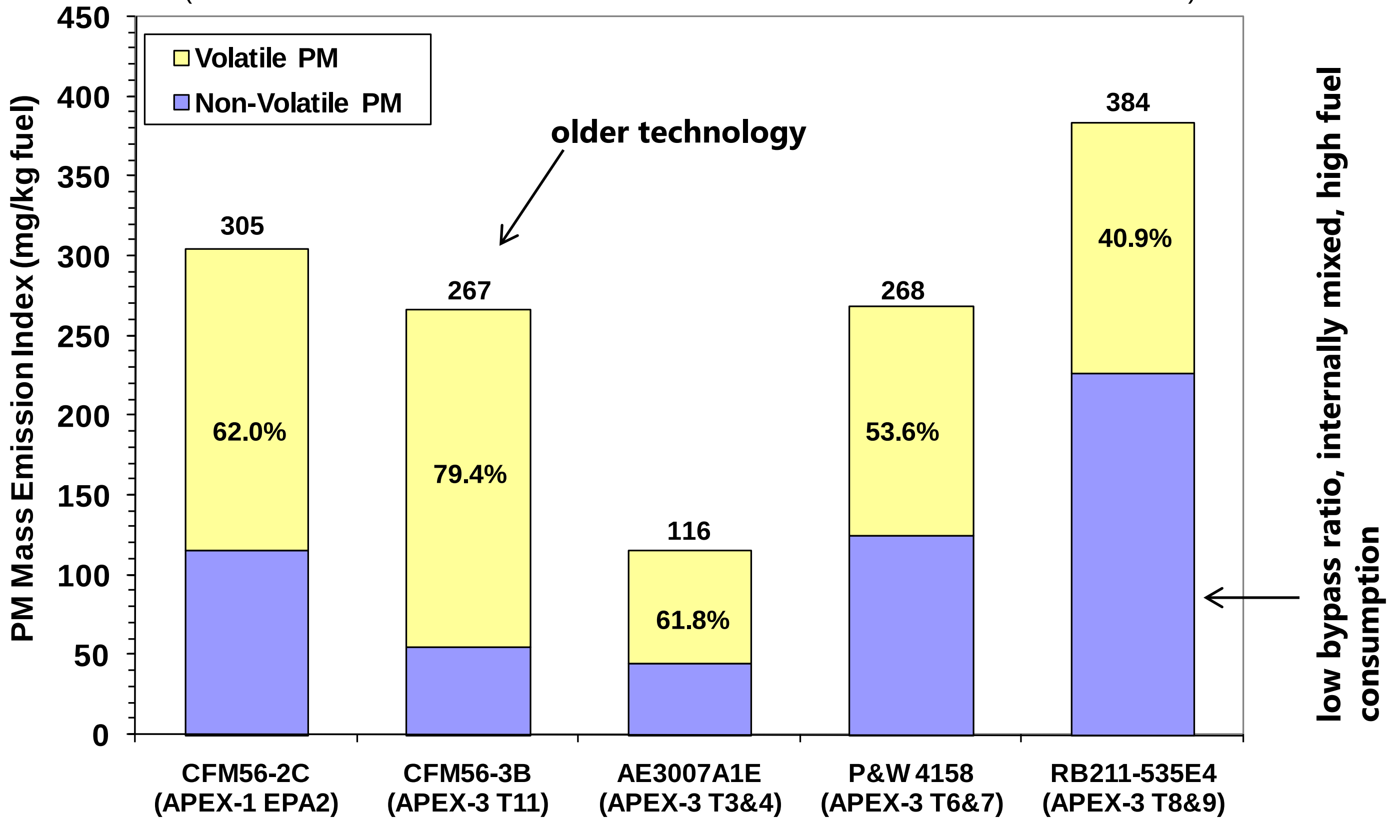
Effect of engine on the volatility fraction

(Non-volatile fraction determined behind thermal denuder set at 250 ˚C)



	CFM56-2C (APEX-1 EPA2)	CFM56-3B (APEX-3 T11)	AE3007A1E (APEX-3 T3&4)	P&W 4158 (APEX-3 T6&7)	RB211-535E4 (APEX-3 T8&9)
OC =	168 mg/kg	117 mg/kg	118 mg/kg	-	89.9 mg/kg
EC =	38.7 mg/kg	97.9 mg/kg	63.4 mg/kg	-	275 mg/kg

- PM mass emissions within a factor of 3
- up to 80% of PM mass is volatile
- a significant amount of the OC fraction is volatile
    - 30:1 dilution (higher effective dilution)

Kinsey et al., (**2011**), *ES&T*, 45, pp. 3415-3421

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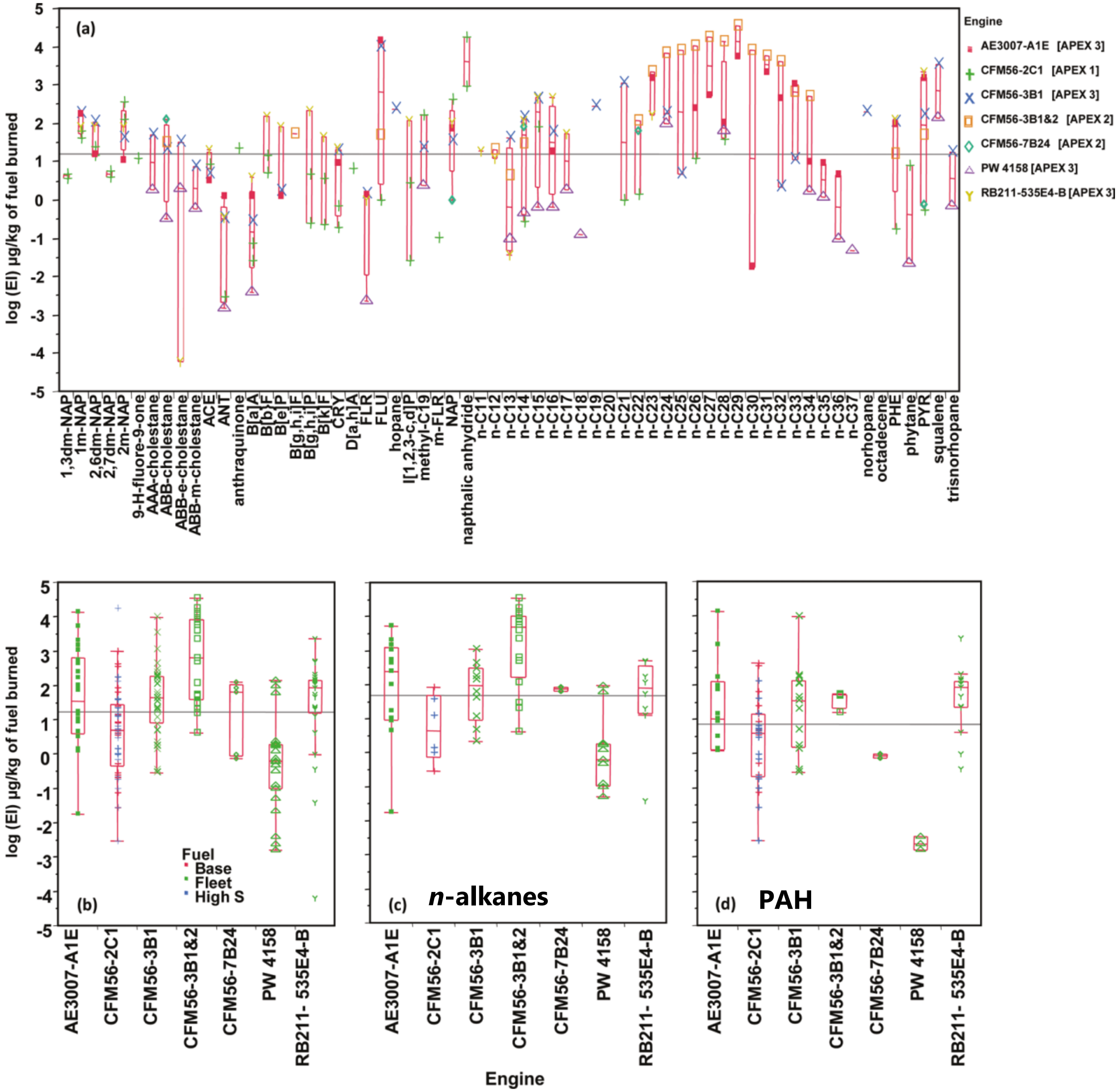
Aircraft SVOC emissions



- background and artifact corrected
- variability due to differences
  - engine pressure and age, thrust

- high S fuel did not influence SVOCs
- engine model/age does effect emissions
  - PW4258 (modern)
  - CFM56 (older)

Kinsey et al., (**2011**), *ES&T*, 45, pp. 3415-3421

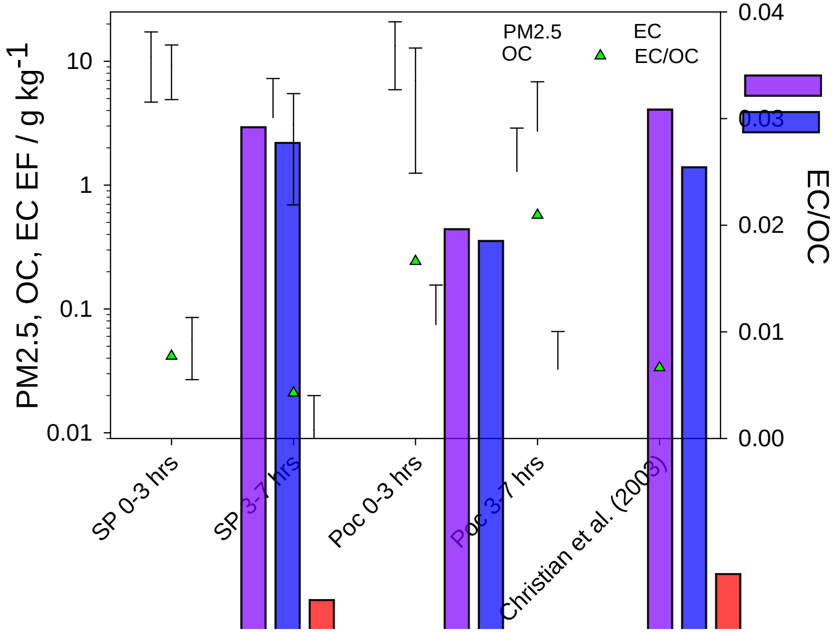
Biomass burning – peat mega-fires

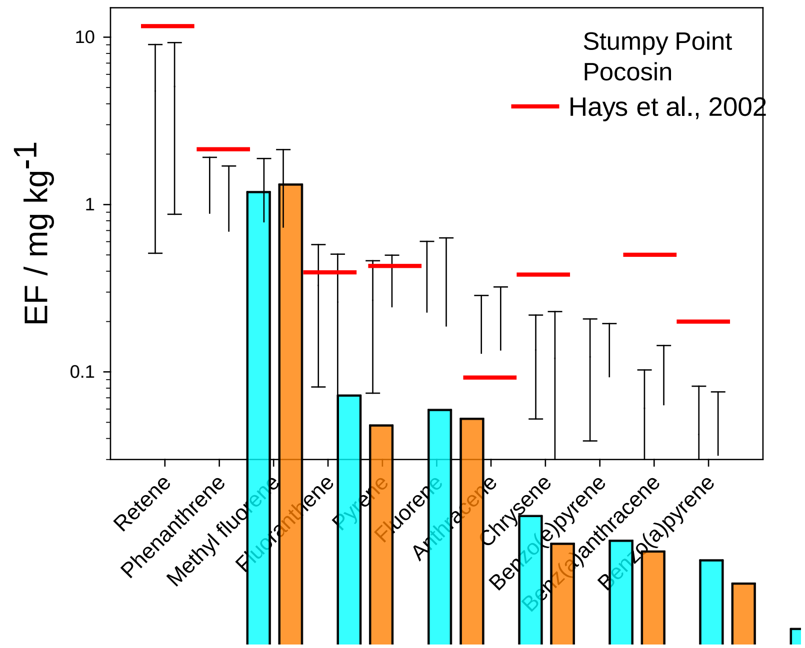
2008 NC peat fire – National Geographic News (MODIS)

- Residual or smoldering combustion
  - 1mm/min, >1 m deep, and consume 75 kg fuel/m^2
  - Months to years
  - Largest fires on earth
  - World wide (Russia, Borneo, Botswana)
- Largest reservoirs of terrestrial organic carbon (ancient)
  - Climate feedback
- Drought and drainage changes (anthropogenic)
- Reactive porous media varying mineral content and moisture
  - limits understanding of combustion and emissions chemistry

Rein G. (**2014**) *Wildfire Magazine,* May/June

Characterization of organic matter in PM emissions from peat burning





- Peat collected from NC coast
- Simulated open burning
- Measured VOCs, PM, carbon content
- Solvent extraction GC-MS

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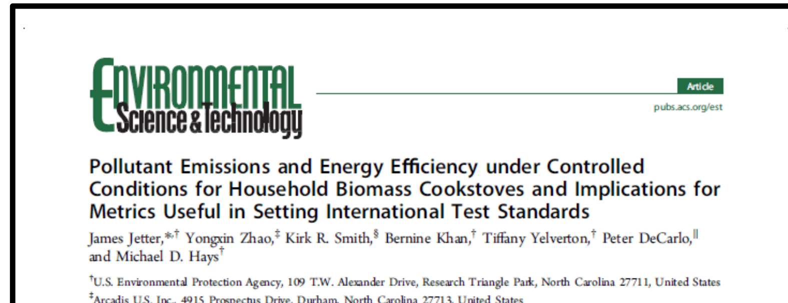
Cookstoves

- WHO estimates >4 million premature deaths annually due to household air pollution from cooking with solid fuels http://www.who.int/mediacentre/factsheets/fs292/en/
- Recent studies show cookstoves are a large source of global black carbon emissions http://onlinelibrary.wiley.com/doi/10.1002/jgrd.50171/abstract
- Clean cookstoves have potential multiple benefits but present challenges
- Global Alliance for Clean Cookstoves is leading a multi-national multi-disciplinary effort


Environmental Science & Technology Article pubs.acs.org/est

Pollutant Emissions and Energy Efficiency under Controlled Conditions for Household Biomass Cookstoves and Implications for Metrics Useful in Setting International Test Standards

James Jetter,*[†] Yongxin Zhao,[‡] Kirk R. Smith,[§] Bernine Khan,[†] Tiffany Yelverton,[†] Peter DeCarlo,[∥] and Michael D. Hays[†]

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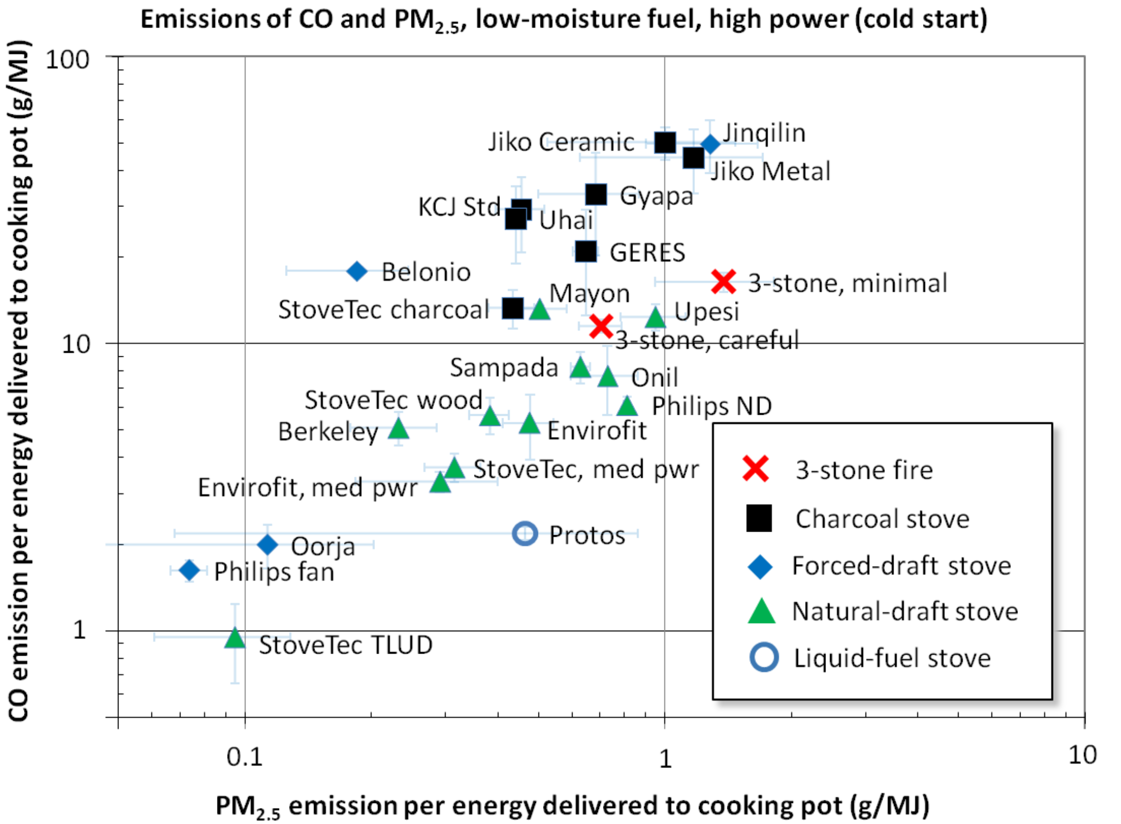
Stoves and laboratory testing

A. Ceramic Jiko, charcoal
B. Metal Jiko, charcoal
C. Belonio, rice hull
D. Onil, wood
E. Protos, plant oil
F. Mayon Turbo, rice hull
G. Oorja, pellet
H. KCJ, charcoal
I. GERES, charcoal
J. StoveTec, charcoal
K. Jinqilin CKQ-80I, cobs
L. 3-Stone Fire, wood
M. Upesi, wood
N. Uhai, **charcoal**
O. Gyapa, charcoal
P. Envirofit G-3300, wood
Q. Sampada, wood
R. Berkeley Darfur, wood
S. StoveTec TLUD, pellet
T. Philips HD4012, wood
U. Philips HD4008, wood
V. StoveTec, wood

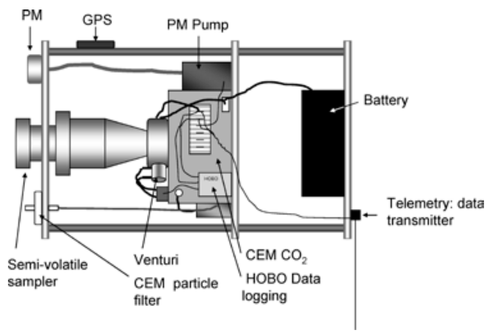
- Water Boiling Test
  - stove design, benchmarking, comparisons
  - **International test standards**
- Fuel consumption, energy efficiency, power
- PM (particulate matter), integrated samples: gravimetric
- PM, real-time: SMPS, APS
- CO (carbon monoxide), CO_2(carbon dioxide): infrared analyzers
- CH_4 (methane), THC (total hydrocarbons): FID analyzers
- NO_X (nitrogen oxides): chemiluminescence analyzer
- Black carbon: aethalometer, transmissometer
- Organic carbon, elemental carbon: thermal-optical analysis
- Aerosol light absorption and scattering, *in situ*: PASS-3 and nephelometer

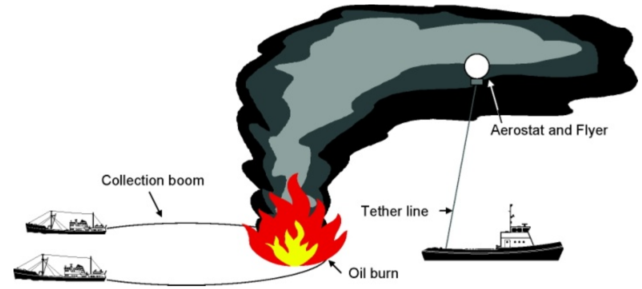
CO and $PM_{2.5}$ emissions from cookstoves

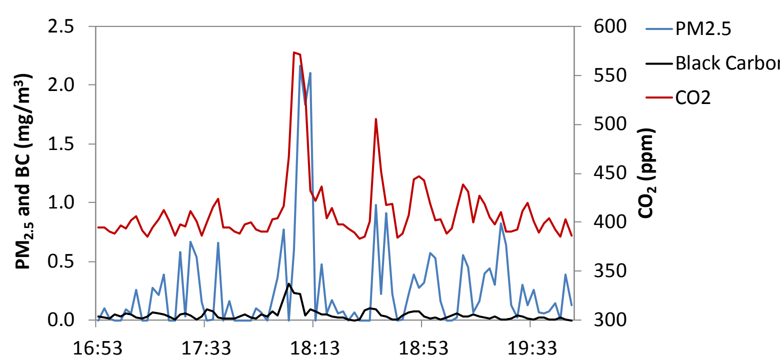


- 3-stone fire
  - simplest base case
- Charcoal stoves performed poorly in general
- Fan stove performance varied widely
- A natural-draft TLUD stove had remarkable performance with processed, wood-pellet fuel with low-moisture content

Aerostat (near-source)sampling







Published in: Johanna Aurell; Brian K. Gullett; *Environ. Sci. Technol.* **2010,** 44, 9431-9437.
DOI: 10.1021/es103554y

- 200-300 ft aloft
- vertical plume distribution (near source)
- 2-min average.
- ambient air CO_2 concentration: 390 ppm

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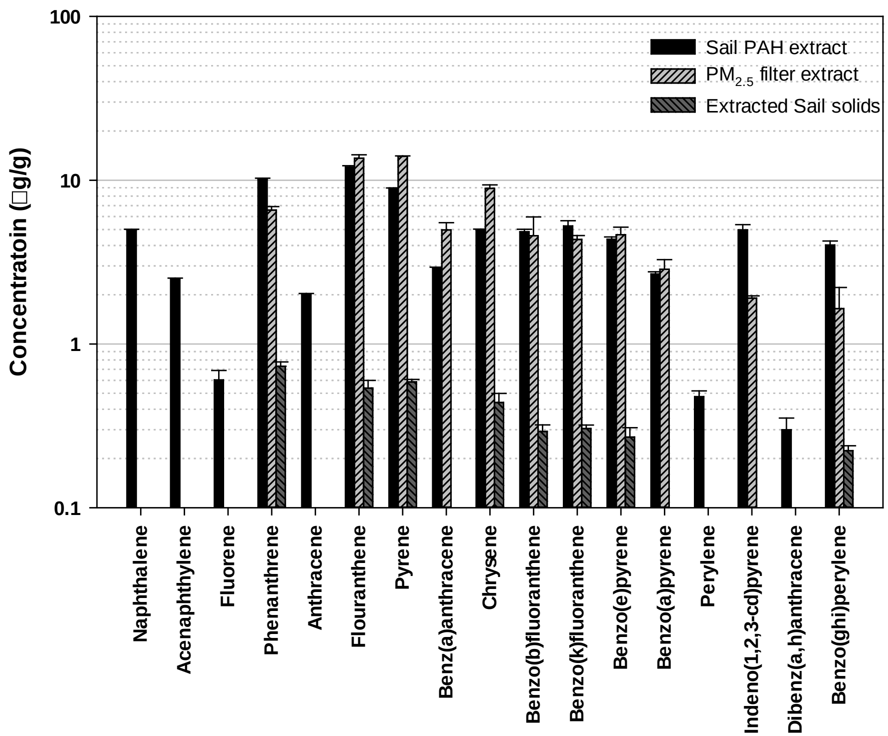
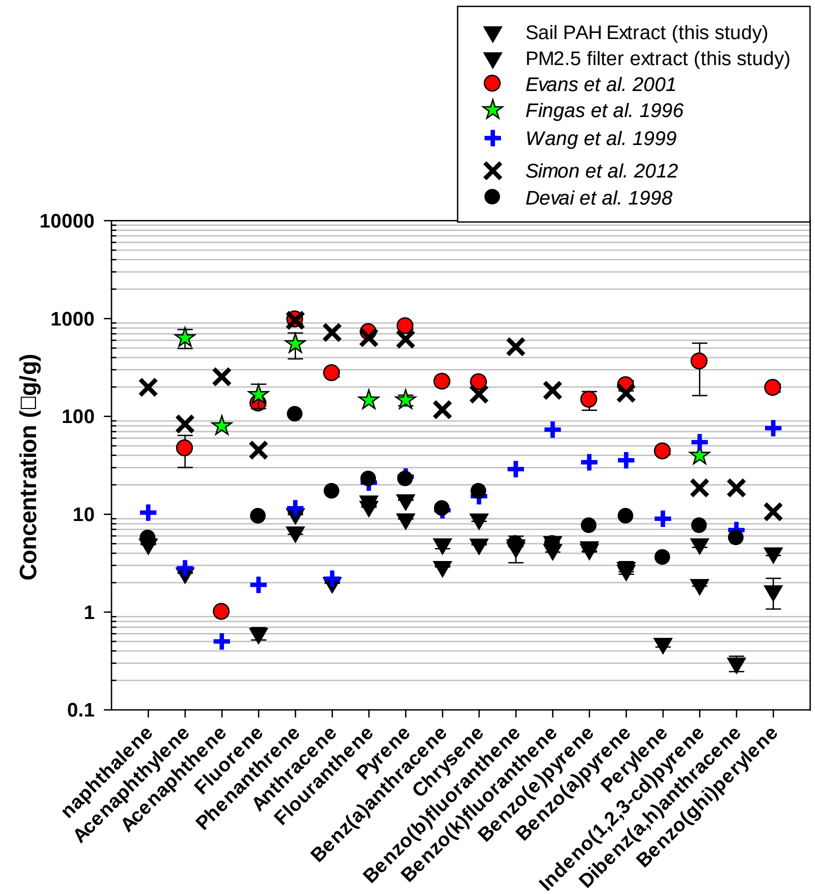
PAH concentrations from oil burning fires



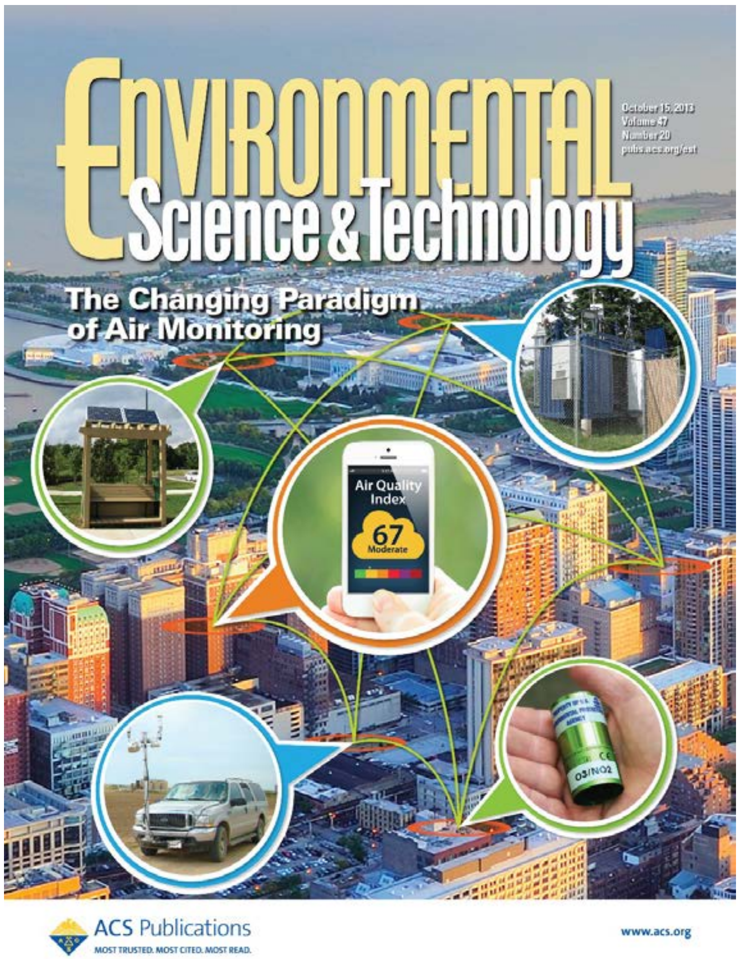


- passive sampling collected lighter PAH more effectively
- re-extracted solids had significantly less PAH

- ~80% of PM is EC (1.3 x 10^6 kg was emitted)
- 140 kg of priority PAH were emitted over 9 weeks
- lower PAH emissions compared with other fires

United States
Environmental Protection
Agency

Development of next generation air pollution source measurement technologies (NGAM).



- Fugitive and area source emissions are difficult to measure and model.
- Need to characterize diverse area sources such as oil and gas, refineries, and landfills

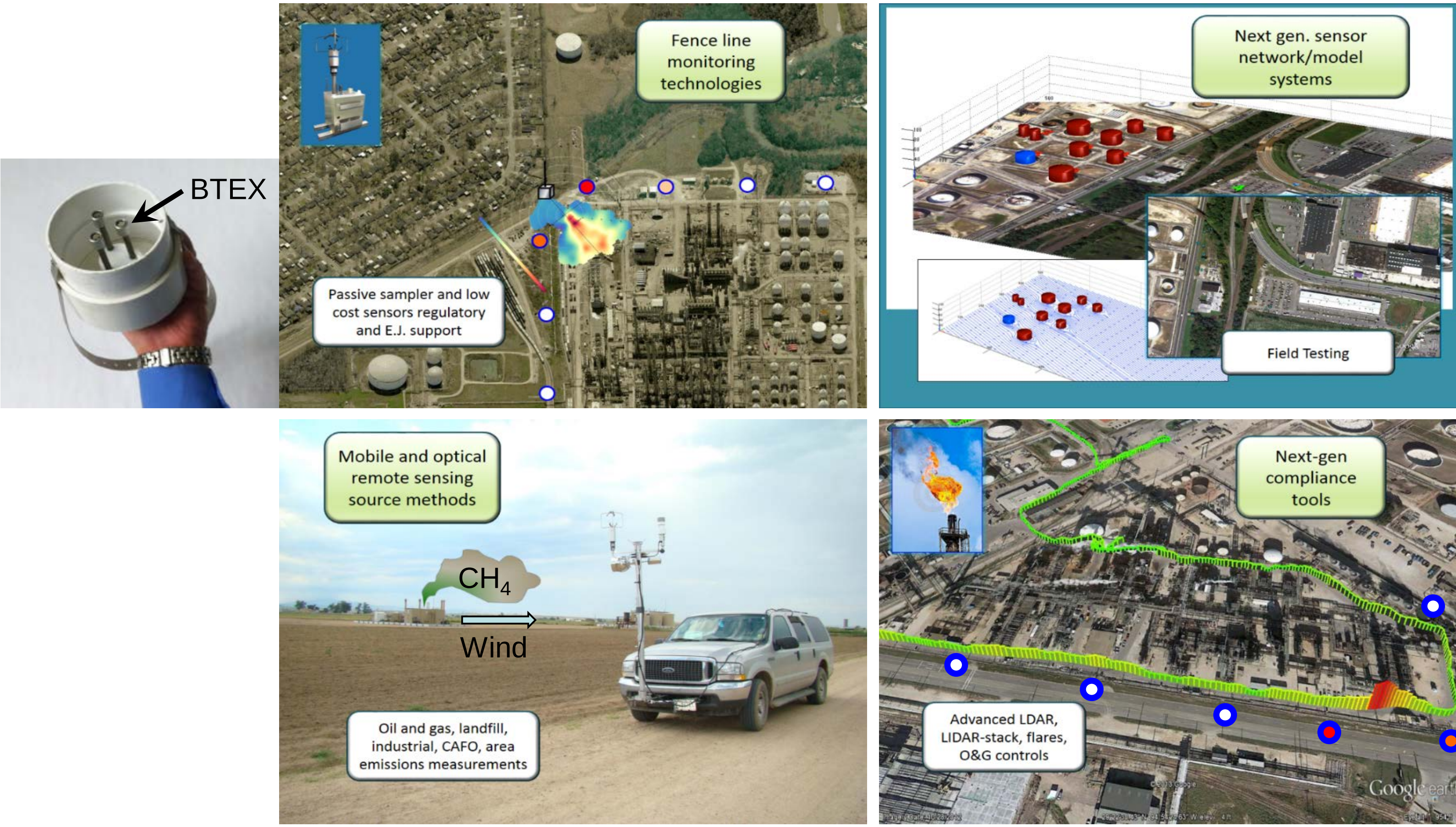
- NGAM combines
  - mobile measurements (GMAP)
  - low cost sensors,
  - optical remote sensing
  - passive fence line monitoring and infrared imagery

- Citizen science and environmental justice
- Regulatory tool

With assistance from Dr. Eben Thoma

Next Generation Air Monitoring Technologies

EPA United States Environmental Protection Agency



GMAP survey benzene

Optical leak detection

Thoma et al., (2011), *J. Air & Waste Manage. Assoc.*,61, pp. 834-842

Wrap-up

I. Emission factor science continues to evolve
II. Sampling methodology can advance relative to the nature of the emissions plume.
III. Bulk chemical properties of emissions may be just as important as molecular chemistry to understanding PM mass transformations in the atmosphere.
IV. EPA is advancing emissions science through its dynamometer operations, novel monitoring and measurements systems, and near-source emissions measurement programs.
V. Measurement of aerosol particle optical properties is emerging in importance due to climate relevance
VI. Next generation air measurement technologies are being integrated into regulatory and compliance efforts

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- William Preston (ARCADIS Inc.)