Real-world Emission Characterization

Judith C. Chow (judith.chow@dri.edu)
John G. Watson

Desert Research Institute
Nevada System of Higher Education
Reno, NV, USA

Presented at:
The Workshop on Vehicular Air Pollution and its Impact on Human Health
Indian Habitat Centre, New Delhi, India

September 2, 2011

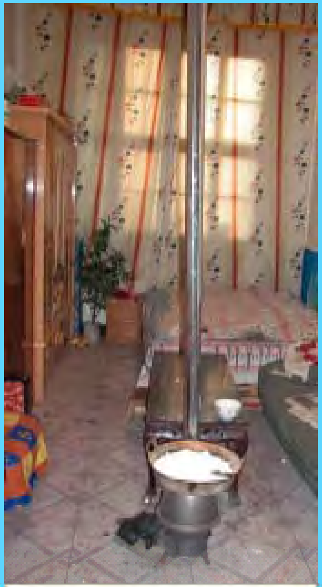
Objectives

- Contrast real-world emissions measurements for emission rates and emission profiles to those made for other purposes
- Present emerging technologies for improving source test methods
- Illustrate variations in organic carbon (OC) and elemental carbon (EC) abundances in vehicle exhaust and biomass burning source profiles

Real-world emissions need to be measured for emission inventories, source apportionment, and health assessment


Stack emissions


Ship emissions


Home heating


Domestic cooking


Roadside vehicle exhaust monitoring


Diesel vehicle exhaust sampling


Cooking emission sampling atop laboratory cookstoves

Key Issues in Emission Testing

- Emissions measured for one purpose are typically inaccurate for other purposes

- Need to measure emission rates, particle size, chemical composition, and temporal variations

Roadside vehicle exhaust monitoring

Diesel vehicle exhaust sampling

Cooking emission sampling atop laboratory cookstoves

Real-world emissions represent hardware, processes, operating conditions, and fuels.

(This contrasts with most emission tests that are made for certification and compliance)

- **Certification:** Verify that a process design is capable of achieving emissions below a regulated limit. (e.g., FTP engine tests)
- **Compliance:** Determine that in-use processes are within permitted values (e.g., vehicle smog tests, periodic stack tests, and opacity tests)
- **Emissions trading:** Relate actual emissions to allowances (e.g., continuous SO_2 monitors)
- **Emission inventories:** Real-world emissions for pollution planning
- **Source apportionment:** Speciated emissions for source and receptor modeling

Emission Characteristics

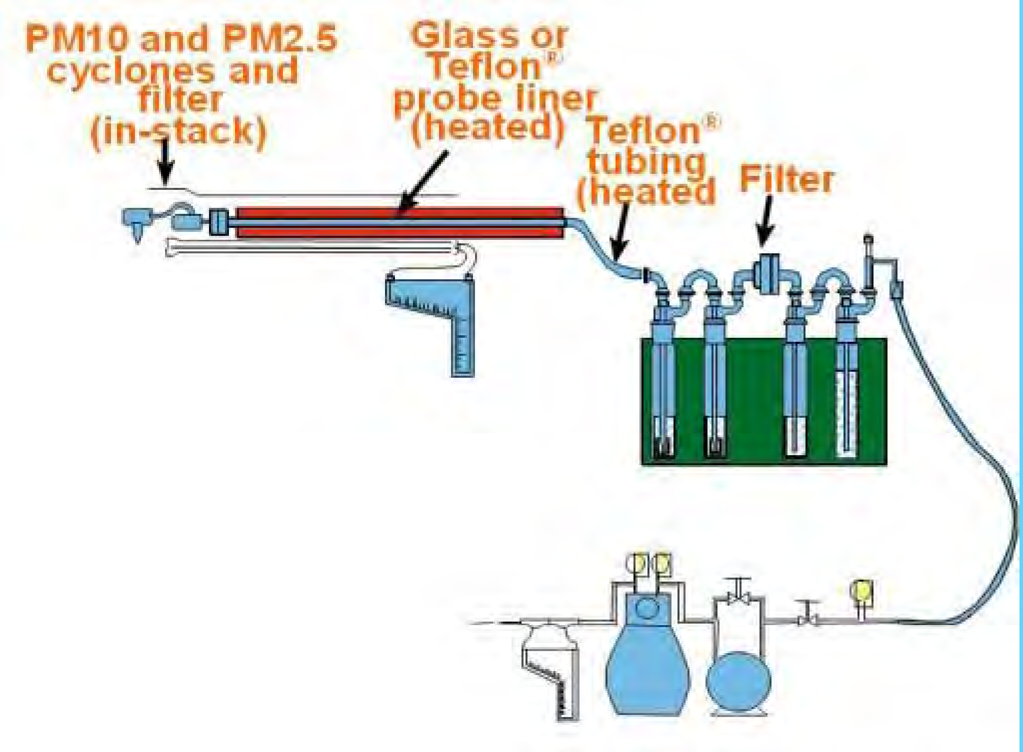
- **Emission Factor:**
  Amount emitted per unit time or unit of activity.
- **Particle Size:**
  Determines transport and deposition properties.
- **Chemical Composition:**
  Fractional abundance of gaseous and particulate chemical components in emissions. Used to speciate inventory and to apportion ambient concentrations to sources.
- **Temporal Variation:**
  Emissions change on daily, weekly, seasonal, and annual cycles. Timing of emissions affects atmospheric transport and dilution as well as human exposure to air pollution.

U.S. EPA’s stack emission certification and compliance tests are taken with 50+ year old technology

(Ducted emissions: hot stack sampling with filters and impingers)

Stationary source certification collects PM on a hot filter and bubbles exhaust through cold water impingers

This requires hauling glass impingers, clean reagents, and ice up and down dirty stacks



U.S. EPA, 1996, 1997

Mobile source certification requires dilution

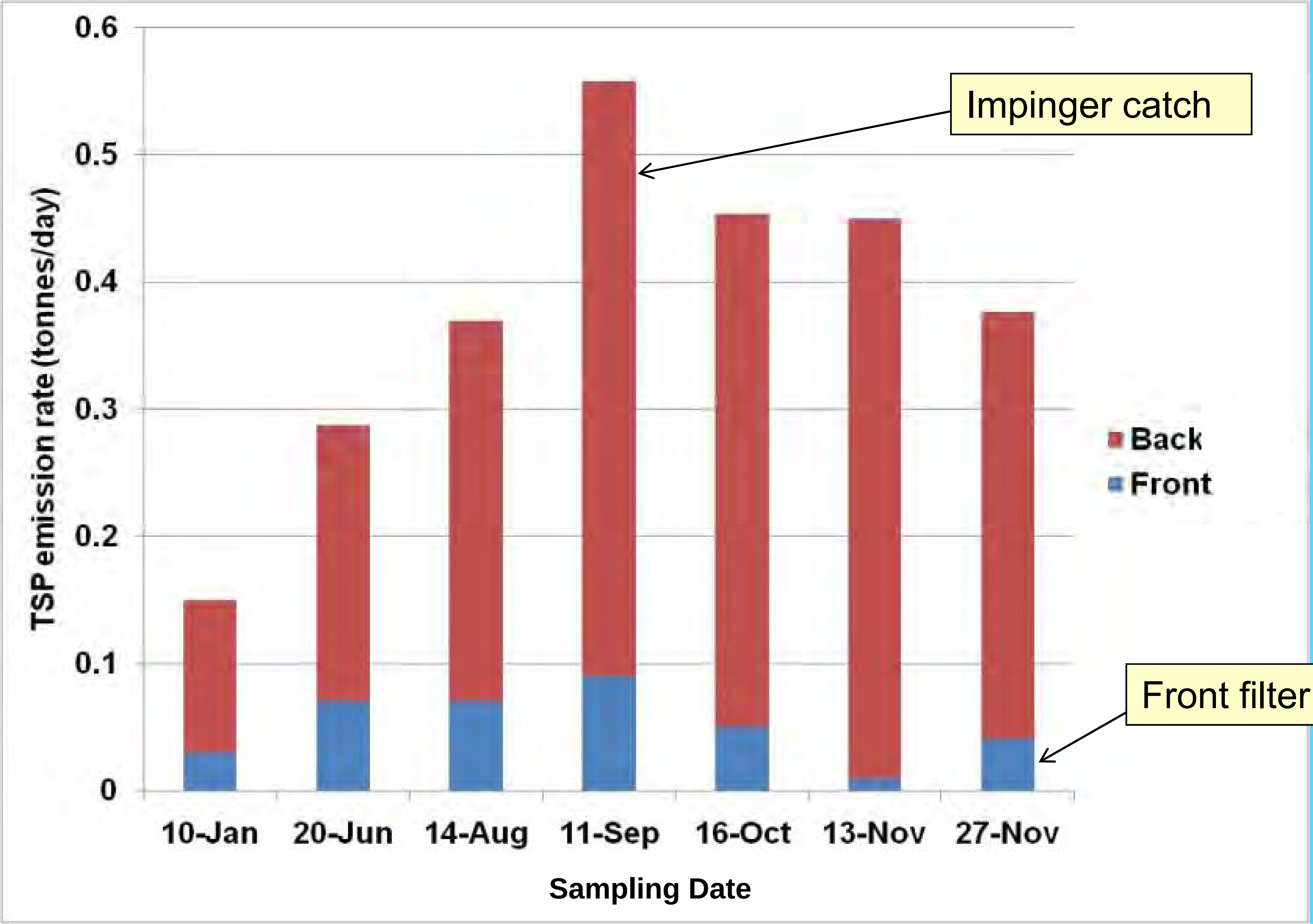
(Stationary sources require hot filters/impingers)

Dilution tunnel and sampling ports for vehicle exhaust

Put generator on wheels and move it and it is certified by dilution sampling

Install the generator permanently and it is certified by hot stack sampling and yields different emissions

Hot stack (filter/impinger) sampling measures too low for the hot filter and too high for the impingers

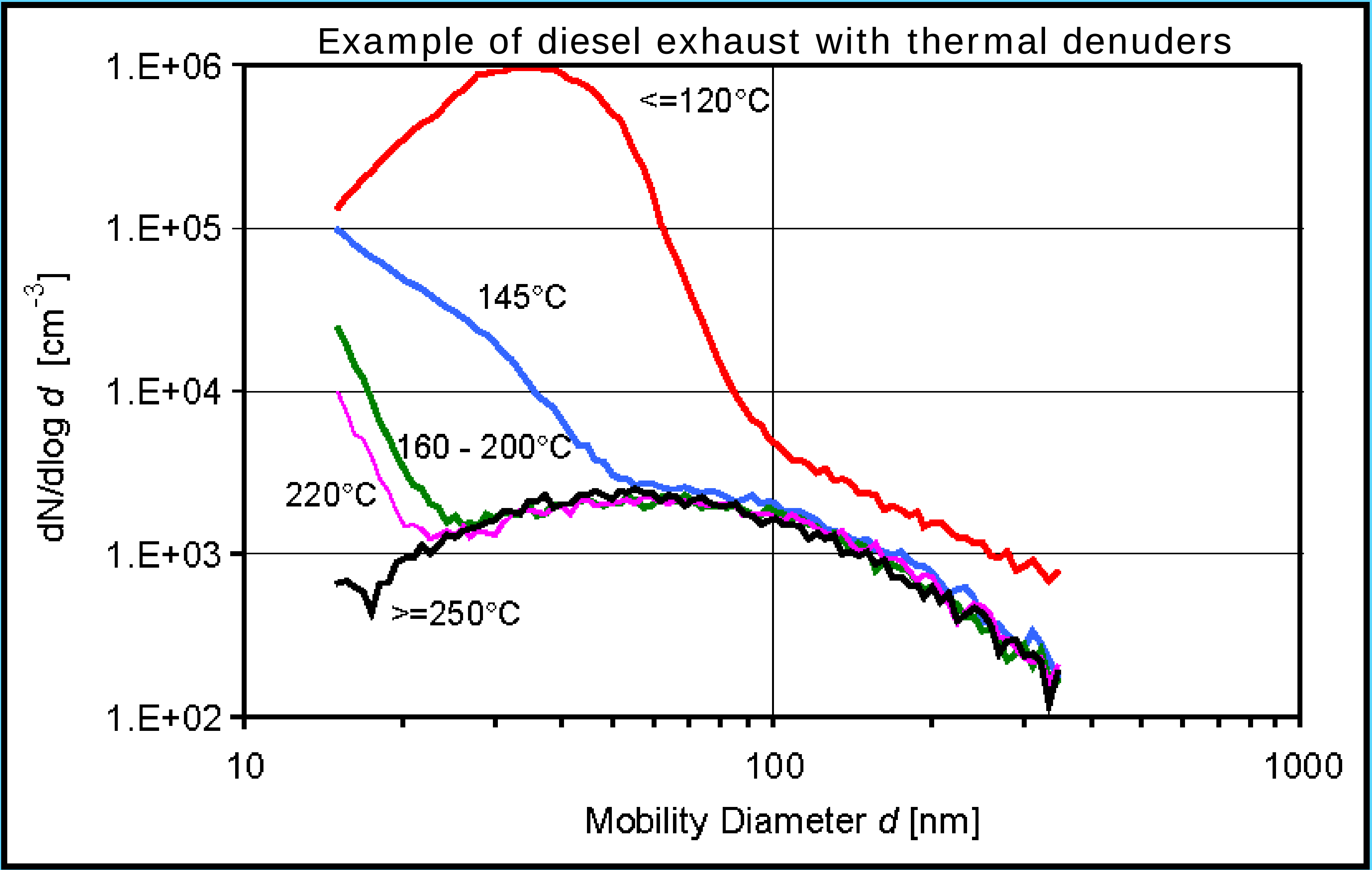


Impinger catch

Front filter catch

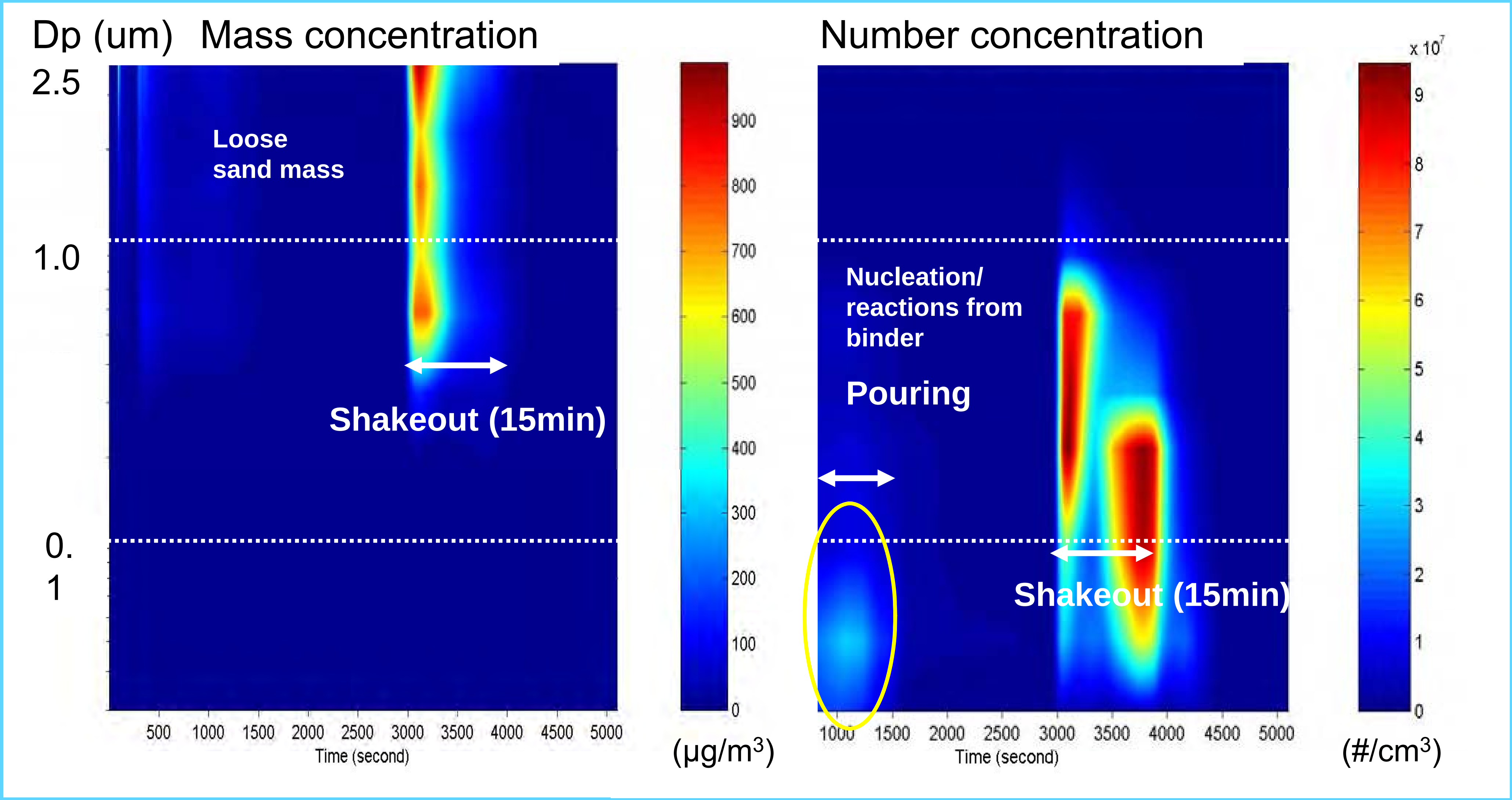
The hot filter does not collect condensable material, while the impingers collect soluble gases

(Preceding thermal denuders remove some ultrafine particles)



Burtscher, 2005, *J. Aerosol Sci.*

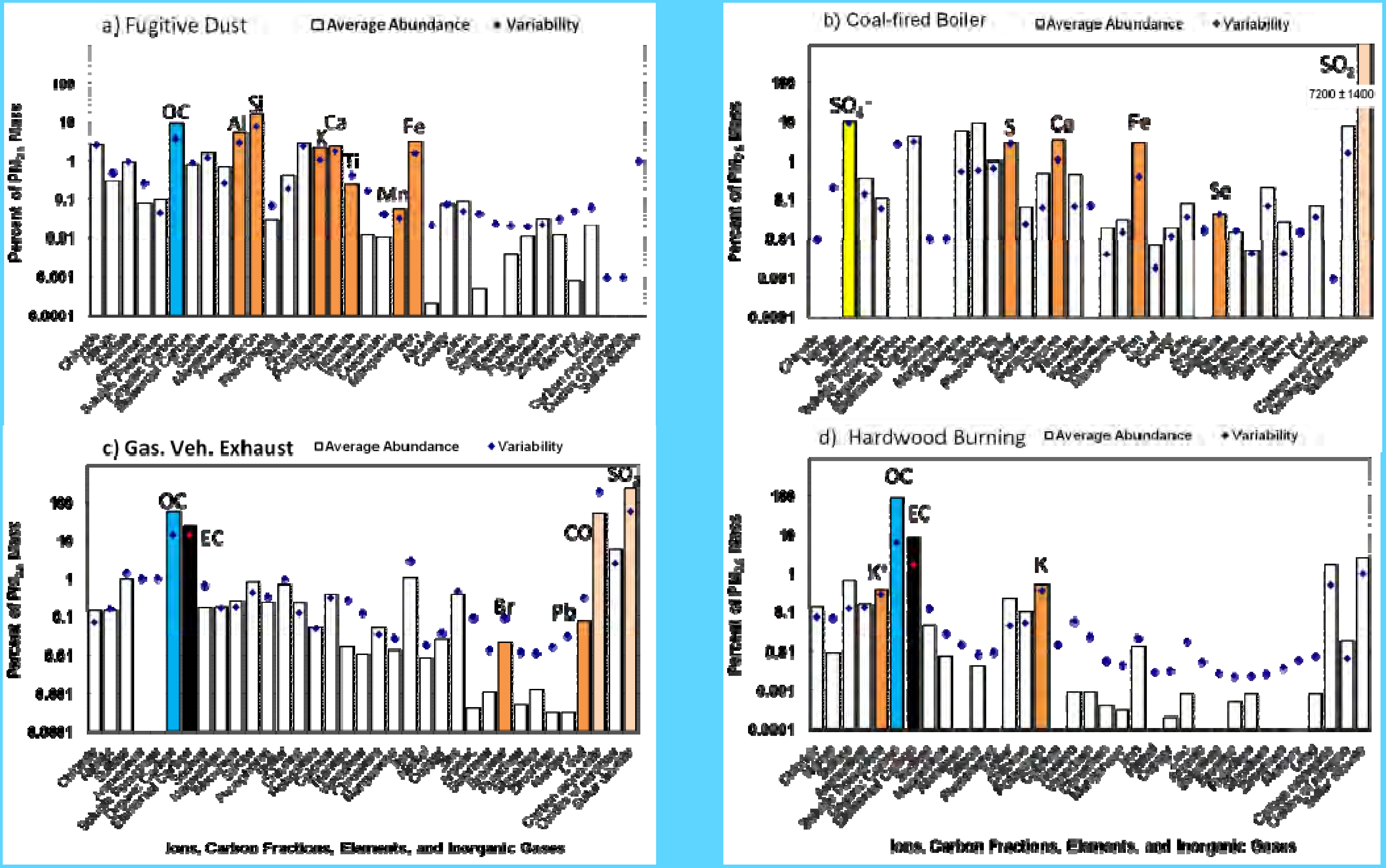
Particle characteristics* often vary during emission tests



* ELPI and Grimm OPC Size Distributions from a casting foundry operation

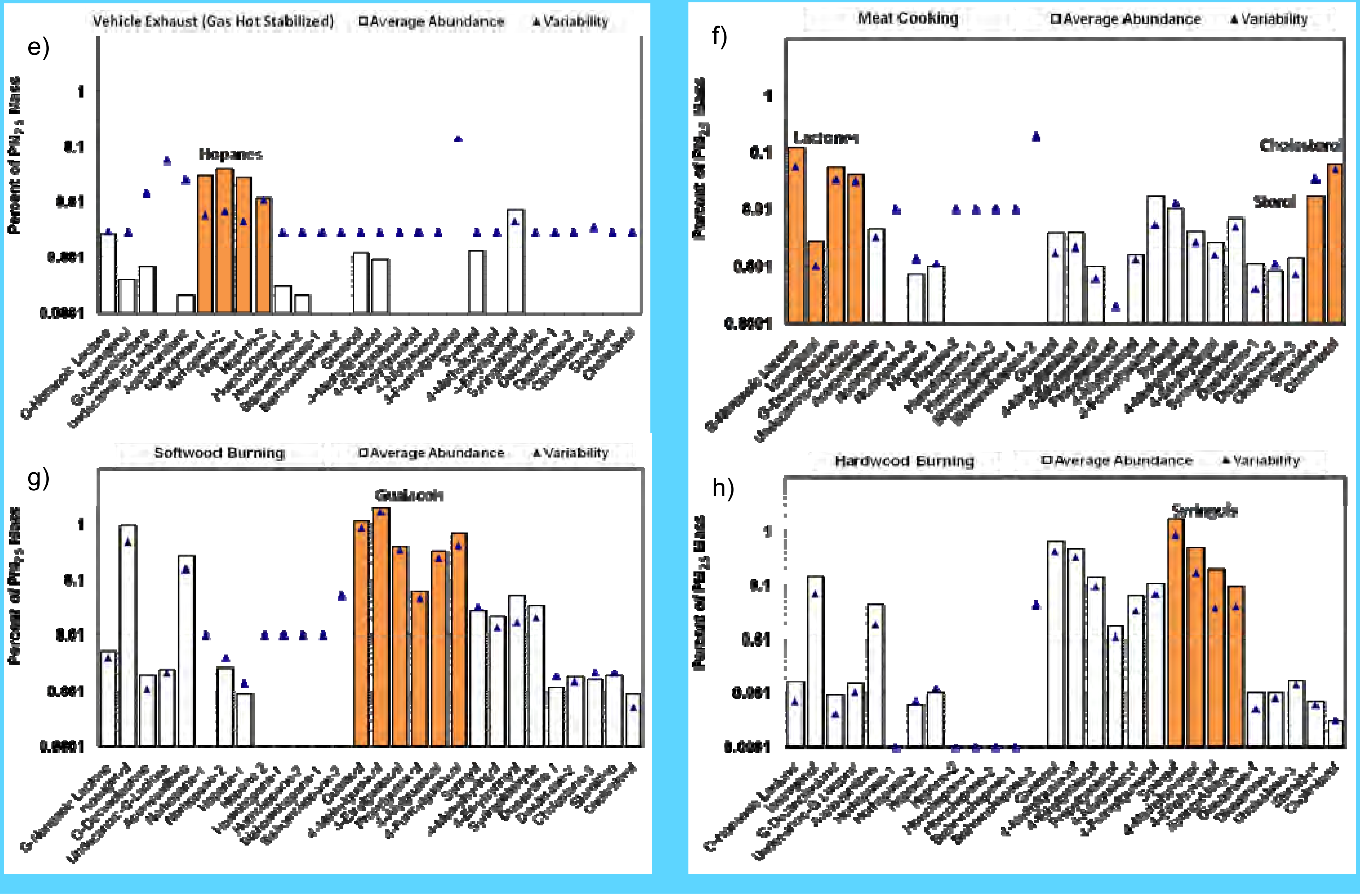
Chang et al., 2005, *AST*

Many of the chemical components in a source profile are condensable (commonly measured elements, ions, carbon, and gases)

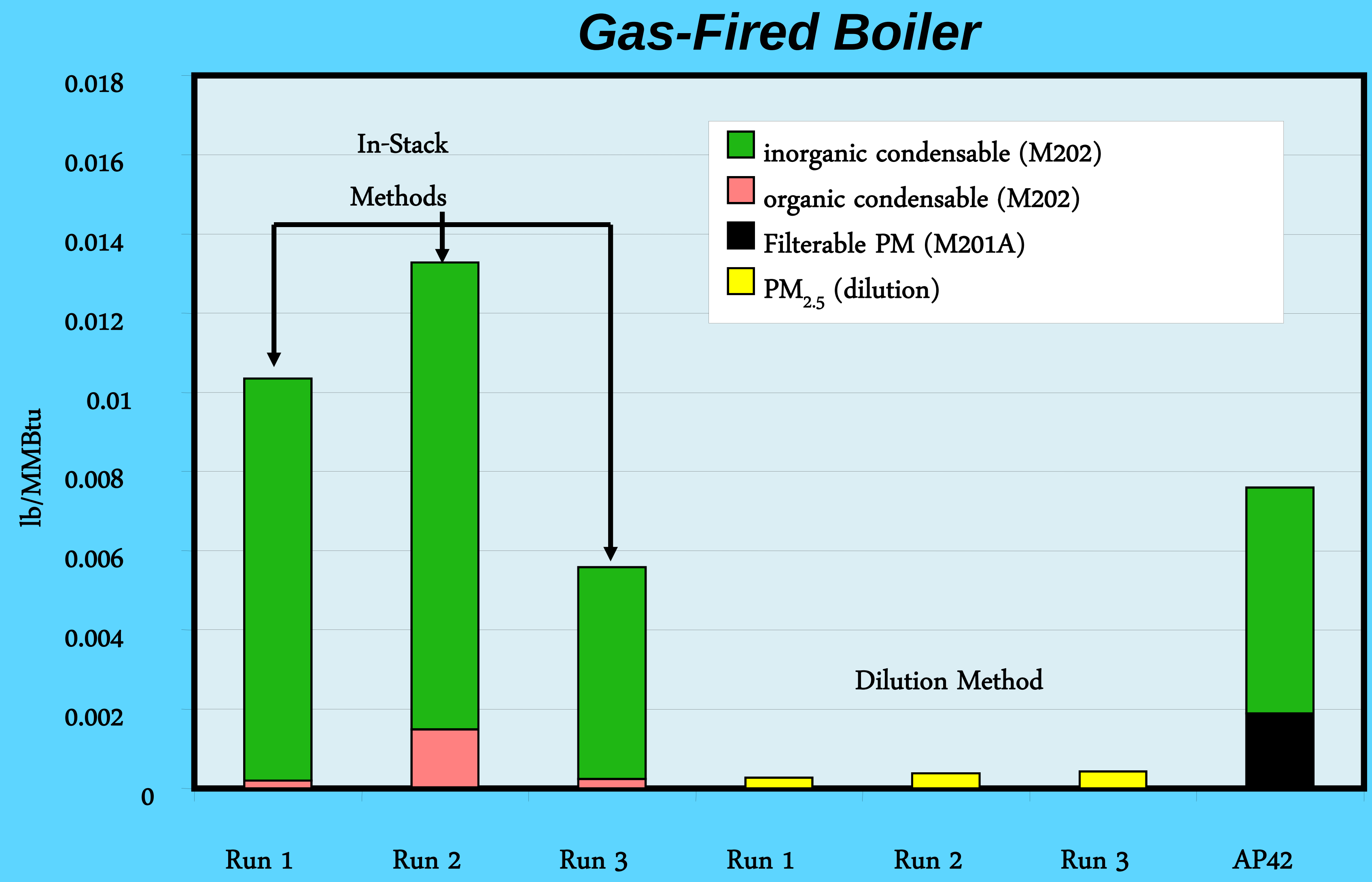


Watson and Chow, 2007

This is especially the case for organic compounds that are important source markers (e.g., lactones, hopanes, guaiacols, syringols, steranes, and sterols)



Dilution sampling provides a more realistic estimate of $PM_{2.5}$ emission rates than hot stack sampling



England et al., 2007a; 2007b, *JAWMA*

Specific pollution sources need to be tested with a dilution sampling system

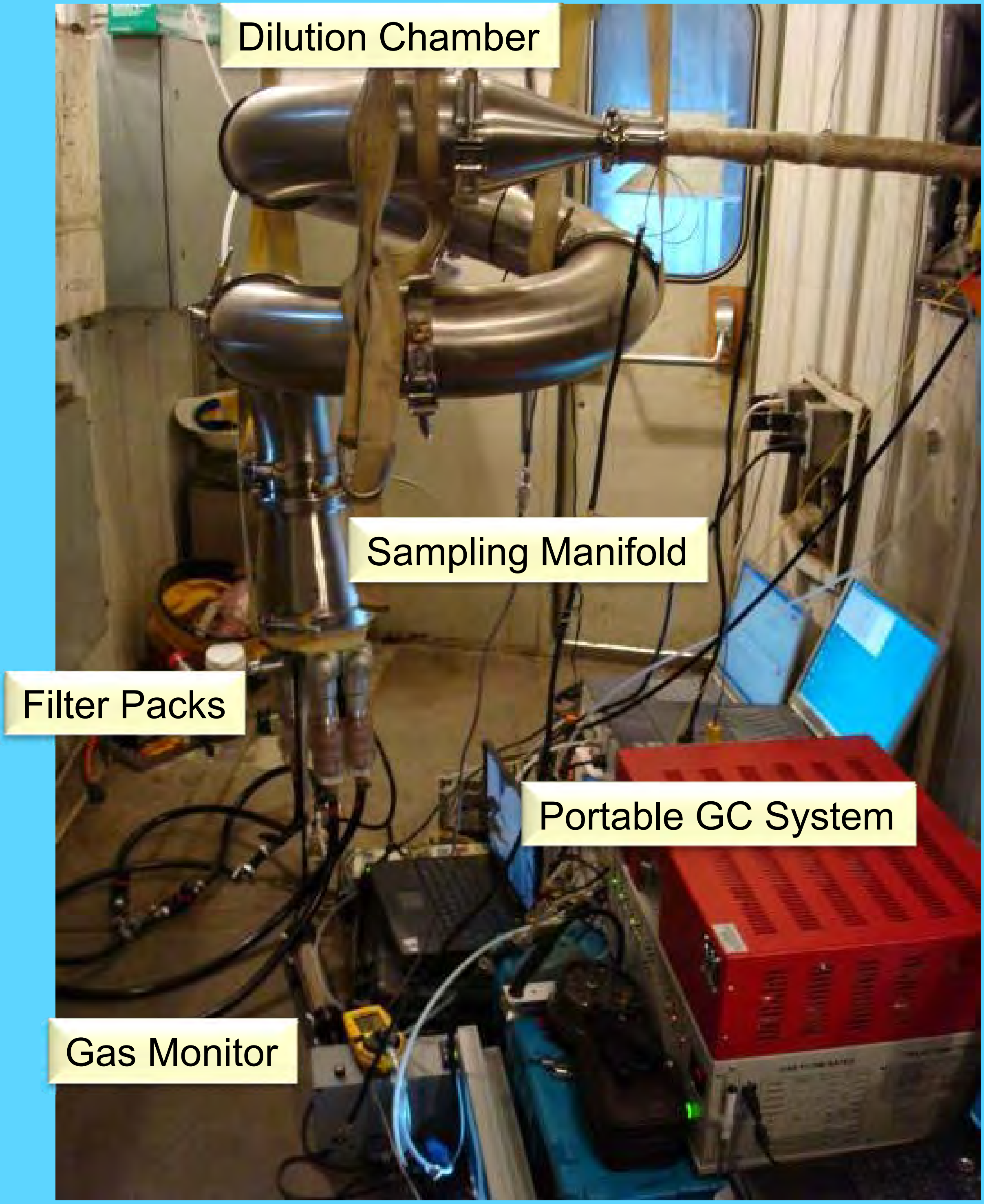
Casting foundry

Dilution sampling system

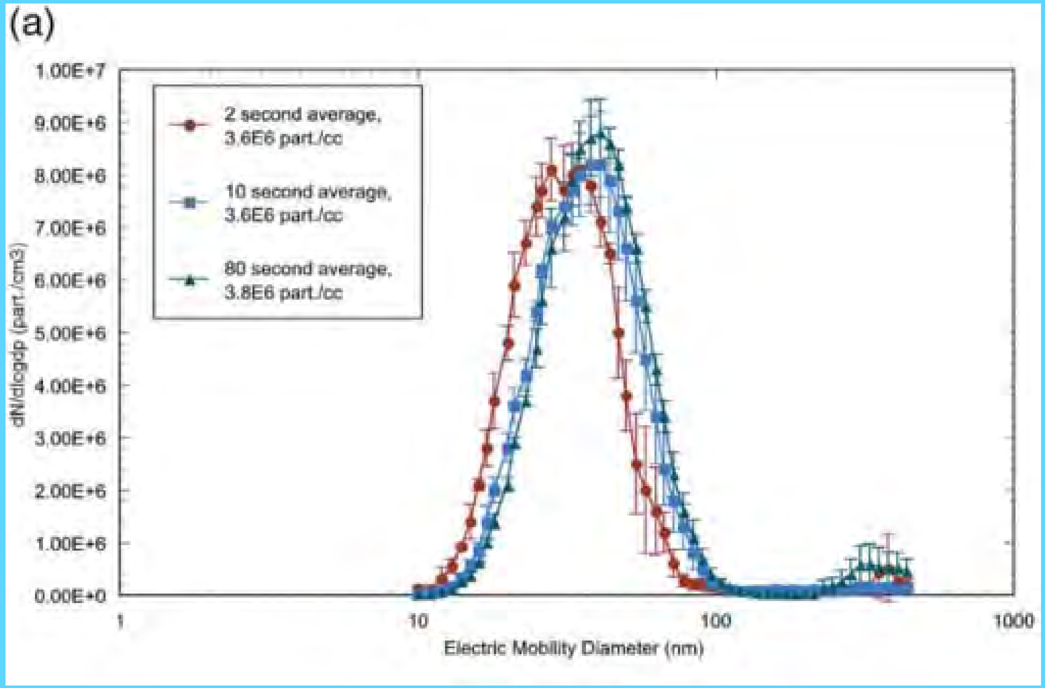
Dilution sampling collects condensables and allows for measurement of many chemical components

Six two-hour samples:

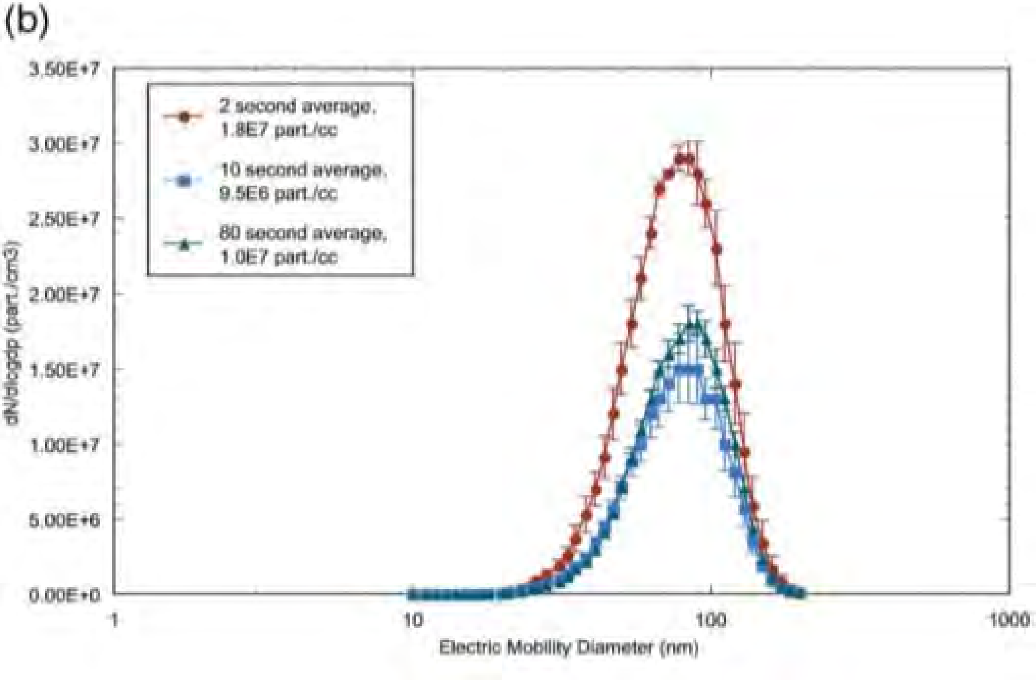
- Dilution ratio (22 – 45X)
- Residence time (28.2 sec)
- Stack and diluted temperatures (86-497 °F)
- Stack velocity (18.0-59 m/sec)



A stable ultrafine size distribution indicates a sufficient residence time



Coal boiler



Residual oil boiler

Organic carbon and sulfates form at lower temperatures in diluted ship stack emissions

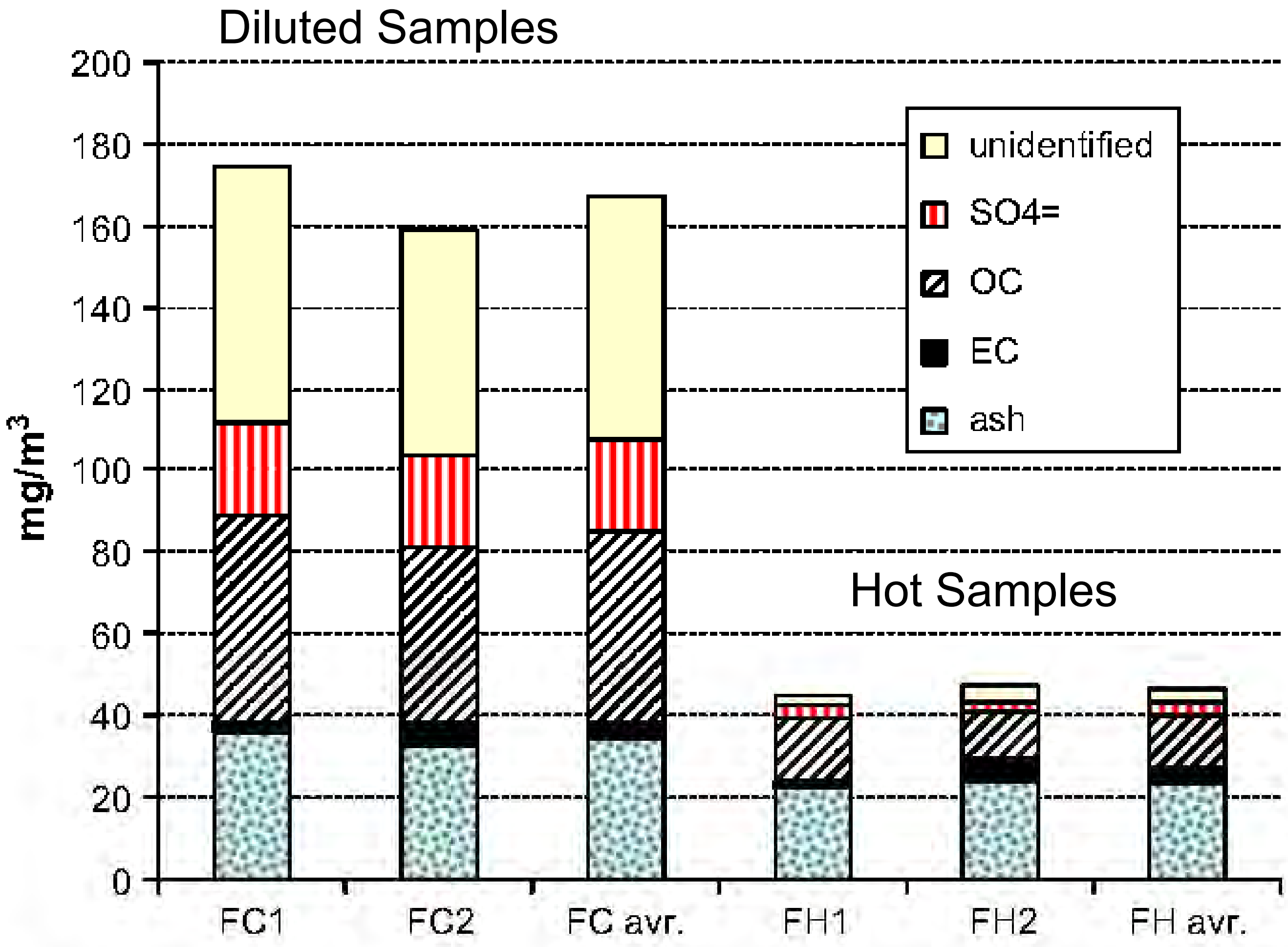


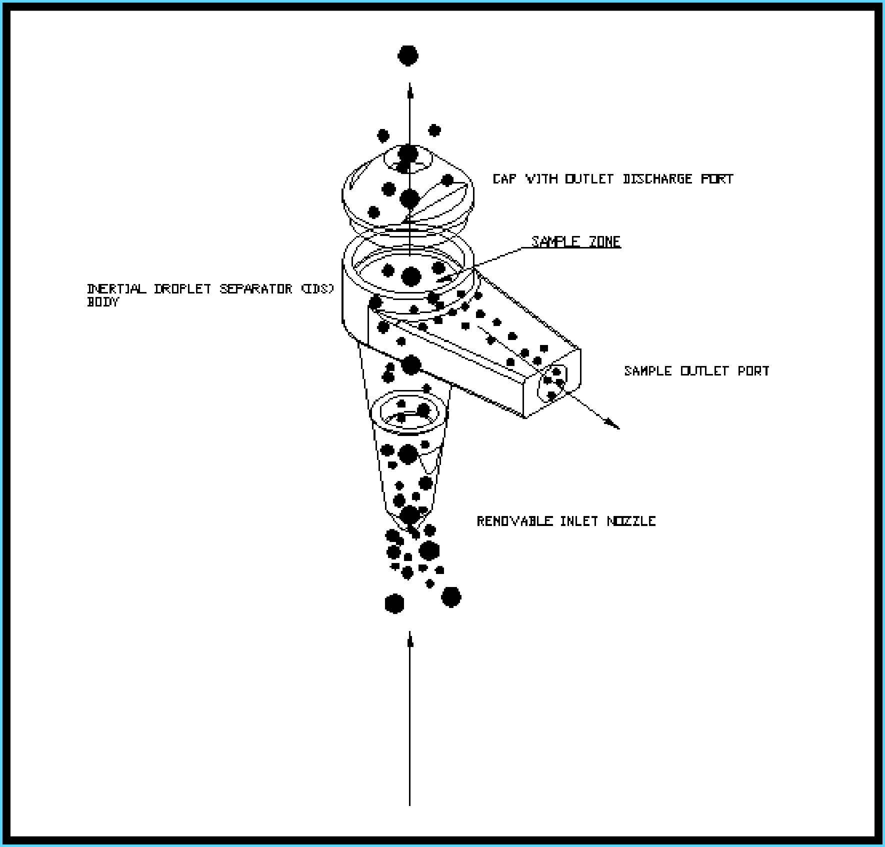
Fig. 3. Composition of PM (as mg m $^{-3}$ exhaust gas) collected on filters in the diluted (FC) and hot (FH) exhaust gas. FC1, FC2, FCavr. and FH1, FH2, FHavr. are individual filter samples and their average values collected in the diluted and hot exhaust, respectively.

Moldanova et al., 2009, *Atmos. Environ.*

Buttonhook nozzles in current stack tests do not pass many large particles

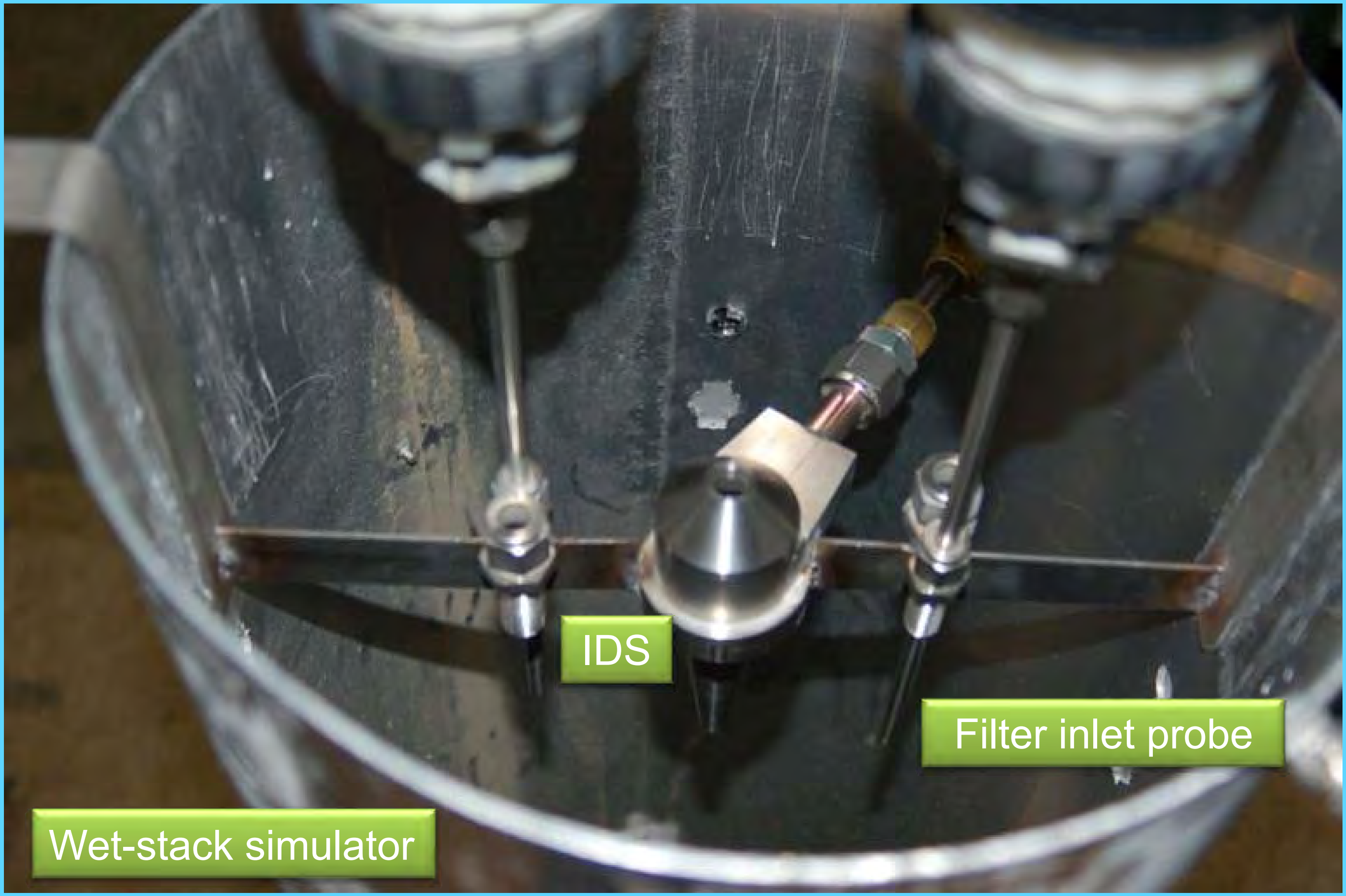
New nozzles are needed to measure large particle sizes such as droplets from wet scrubbers

(Inertial Droplet Separator [IDS])



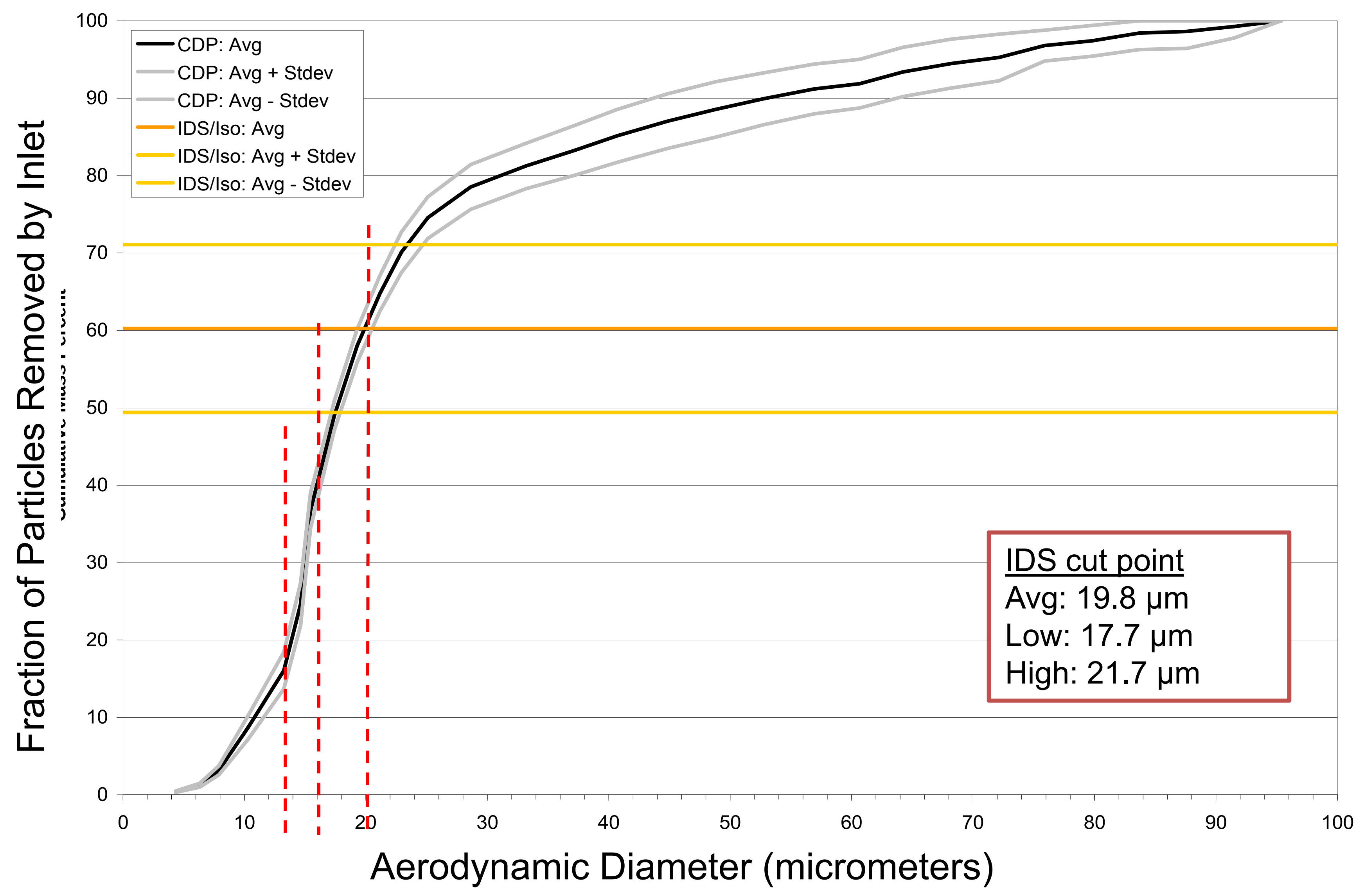
An IDS (Baldwin Environmental, Reno, NV, USA) has been designed to slow particles prior to extraction

IDS* is tested in a wet-stack simulator



*inertial droplet separator

Sampling effectiveness for IDS* using spherical glass beads



IDS cut point
Avg: 19.8 µm
Low: 17.7 µm
High: 21.7 µm

*inertial droplet separator

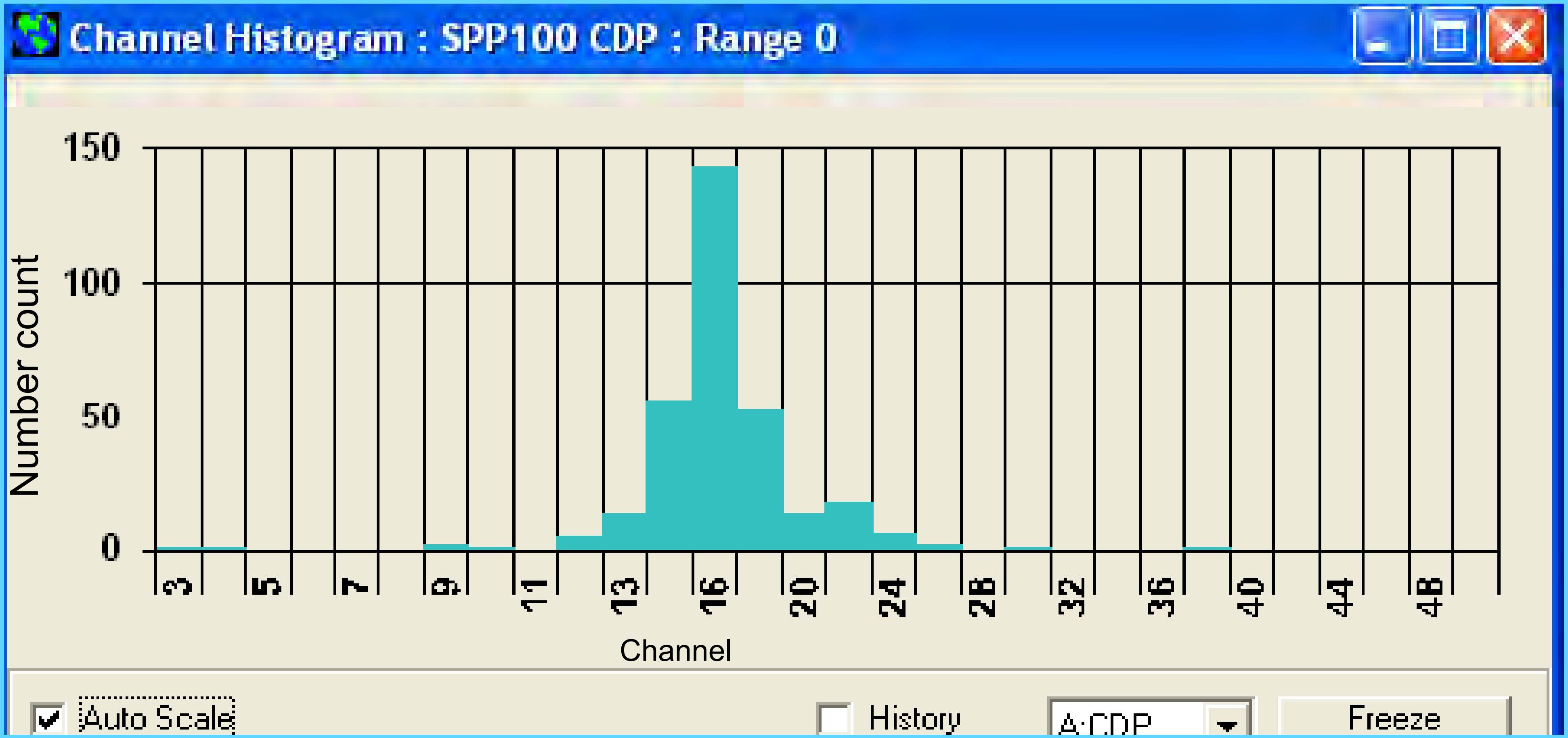
Testing such inlets requires an in-stack measurement of droplet size distributions


(DMT forward scattering cloud droplet probe [CDP])

The CDP* needs to be reconfigured for wet stack applications

*cloud droplet probe

The CDP* can be adapted to determine typical droplet size distributions in a stack at the extraction point



☑ Auto Scale

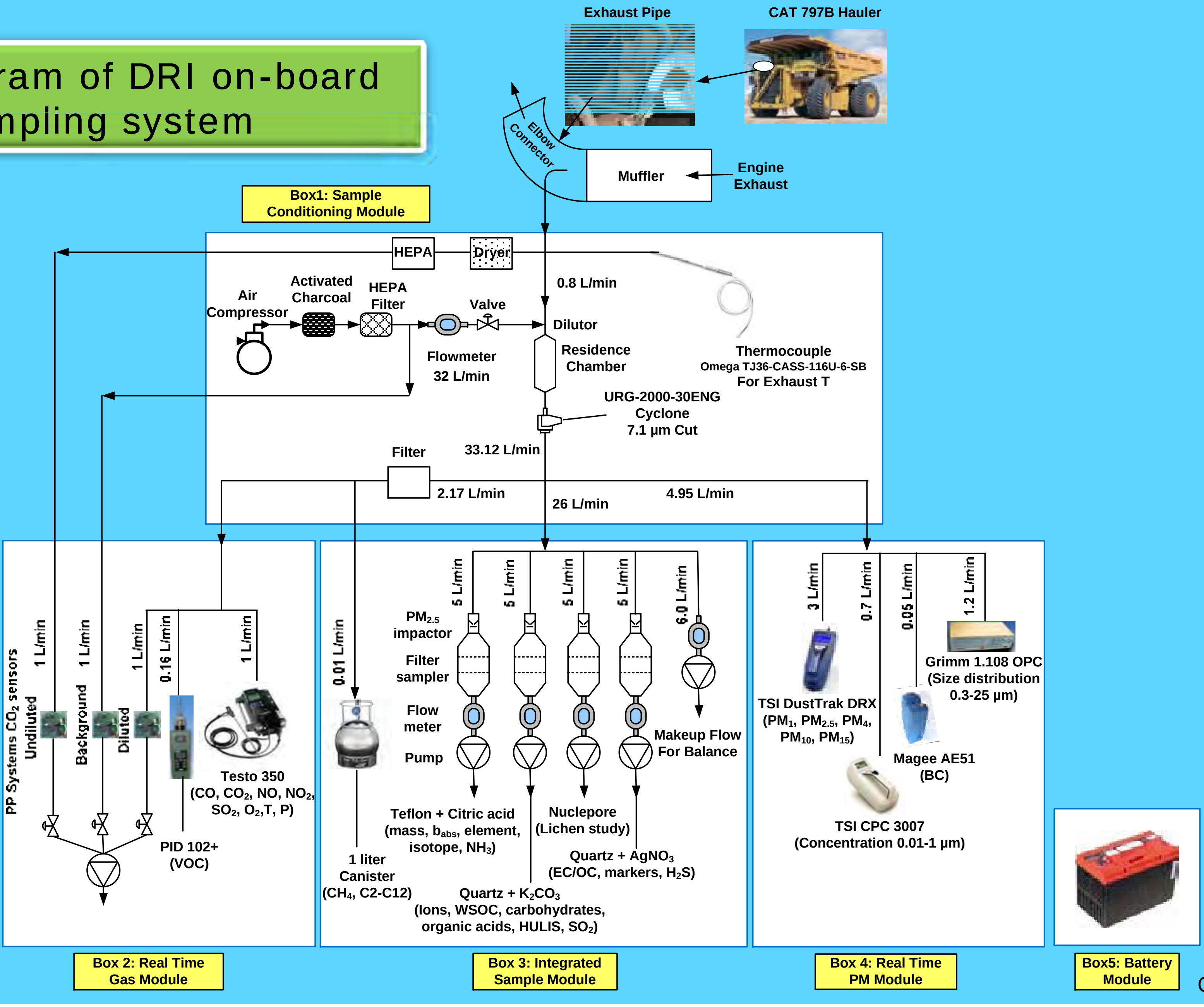
☐ History

A:CDP

*cloud droplet probe

More complex detection systems are needed to obtain a full range of measurements with dilution sampling system

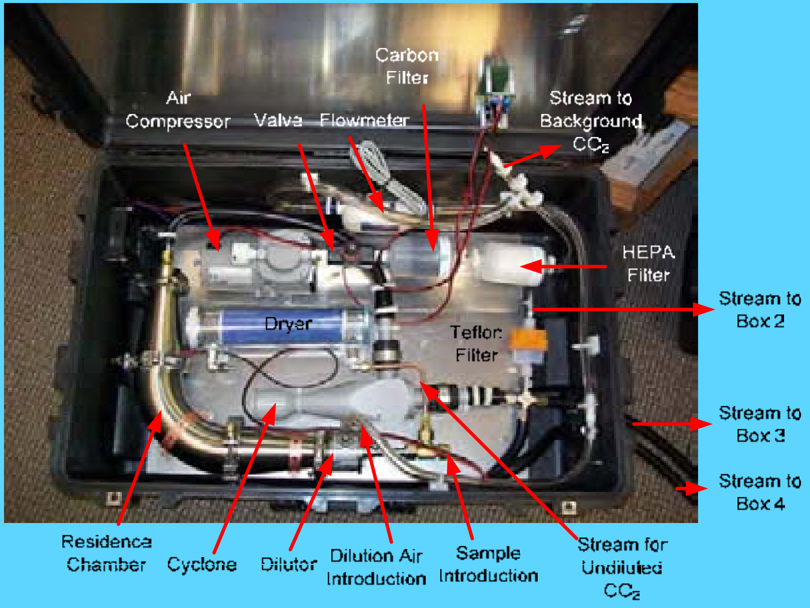
Flow diagram of DRI on-board sampling system



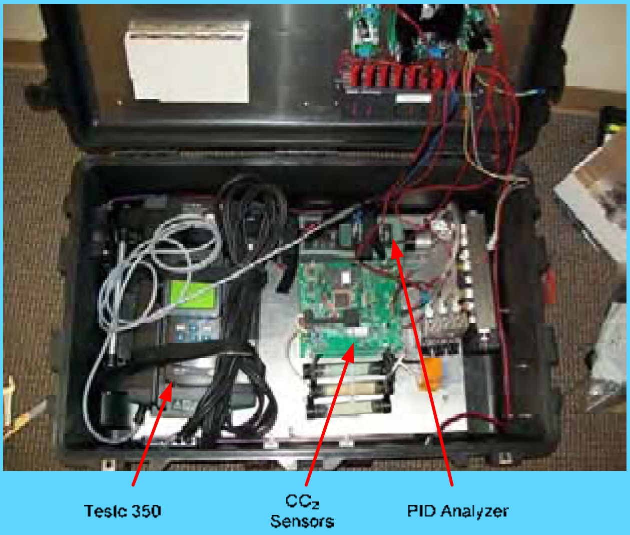
Chow et al., 2010

More compact and continuous in situ sensors are desired

Sample Conditioning Module (#1)

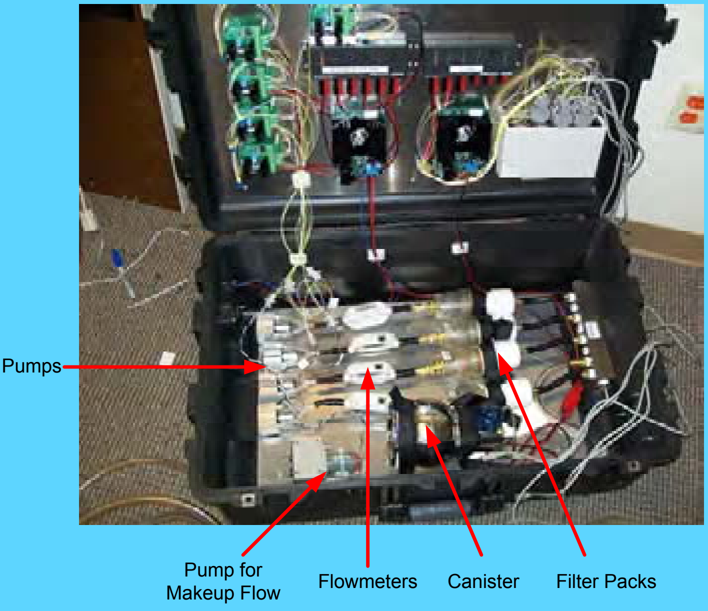


Real-time Gas Module (#2)

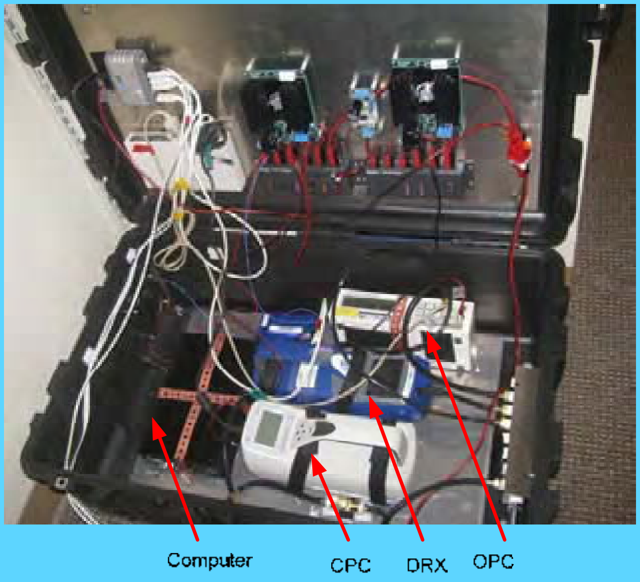


Caterpillar 797B Heavy Hauler (345 tons)

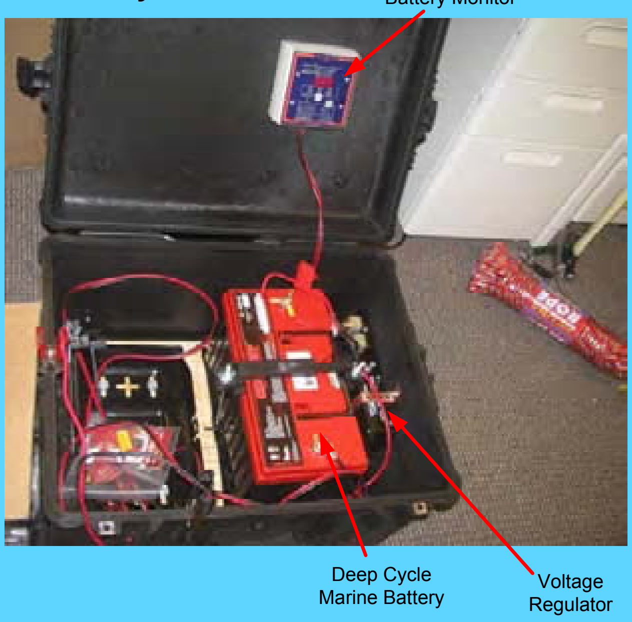
Integrated Sample Module (#3)



Real-time PM Module (#4)



Battery (#5)



Each module measures = 80 cm L × 52 cm W × 32 cm H

Real-world sampling uses on-board instruments to sample plumes and normalize concentrations to CO_2 and fuel carbon content to obtain emission factor in g-pollutant/kg-fuel

Caterpillar 797B Heavy Hauler (345 tons)

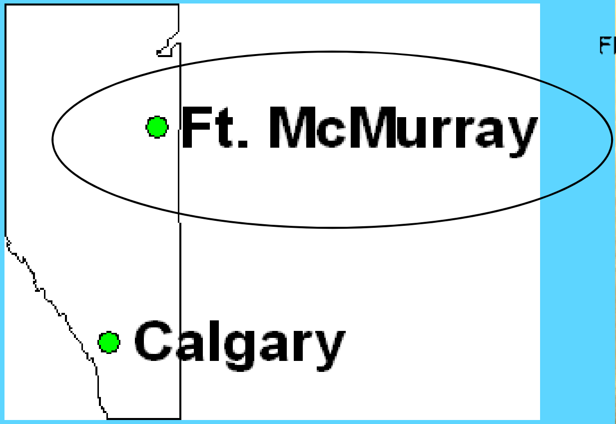
Samples drawn from exhaust pipe.
No interference with vehicle operations.

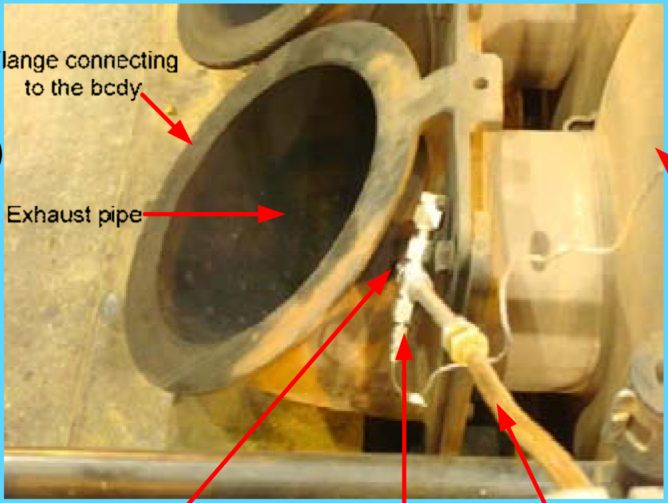
- Battery powered
  - Particle light scattering (b$_{scat}$; normalized to filter mass)
  - Particle size distribution
  - Black carbon (two wavelengths)
  - Volatile organic compounds (VOCs)
  - Gases
    - O_2
    - CO_2
    - CO
    - NO
    - NO_2
    - SO_2
    - H_2S
  - Filter-based samples

Chow et al., 2010; Watson et al., 2010

Sampling port is connected to the exhaust pipe

(muffler outlet)





Athabasca Oil Sands Region

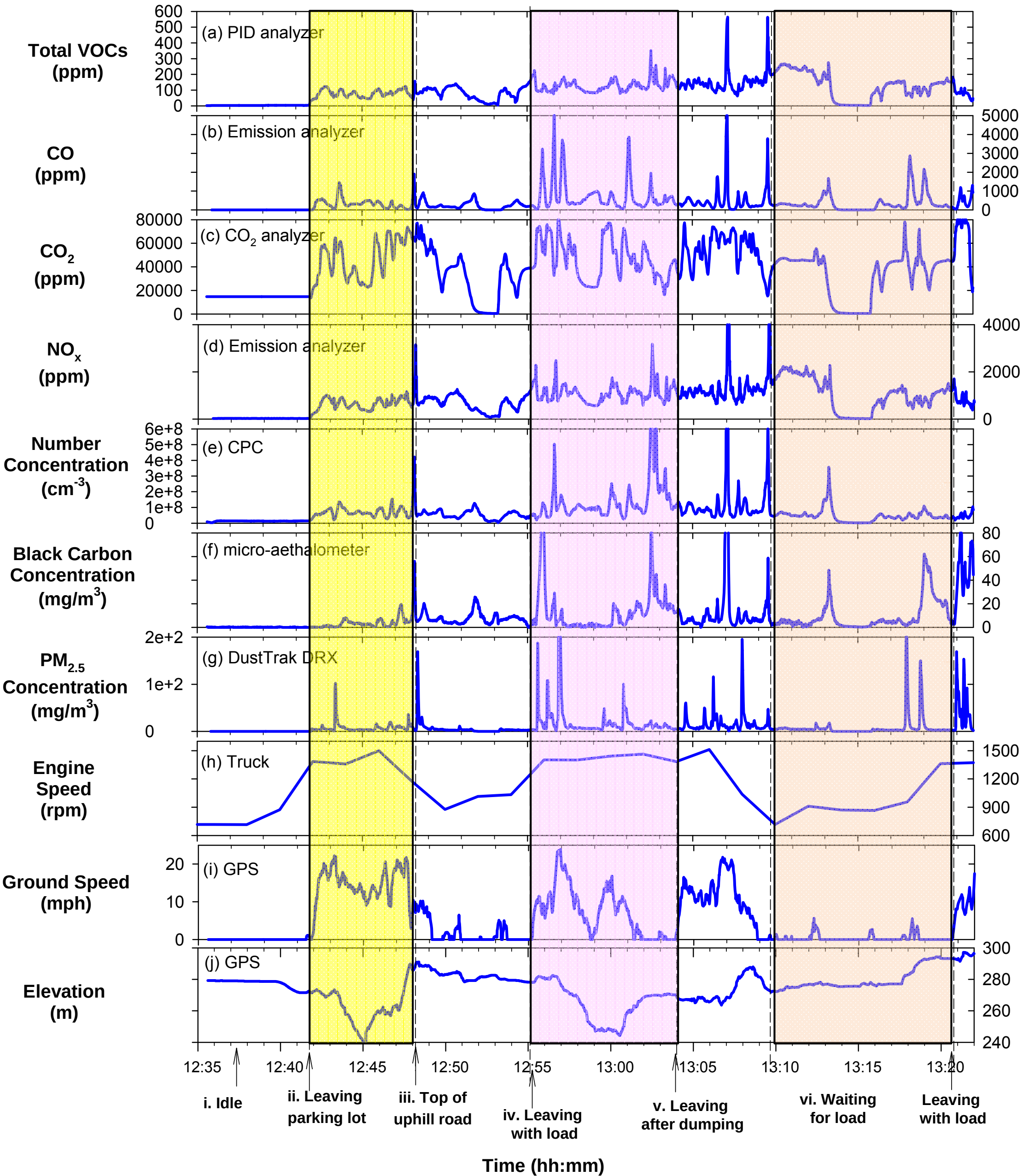
Sampling Modules

Sampling Platform

Driver Cabin

Emission concentrations varied by operating conditions

(time series)



i. Idling: Concentration stable and low.

ii. Leaving parking lot: All concentrations increase.

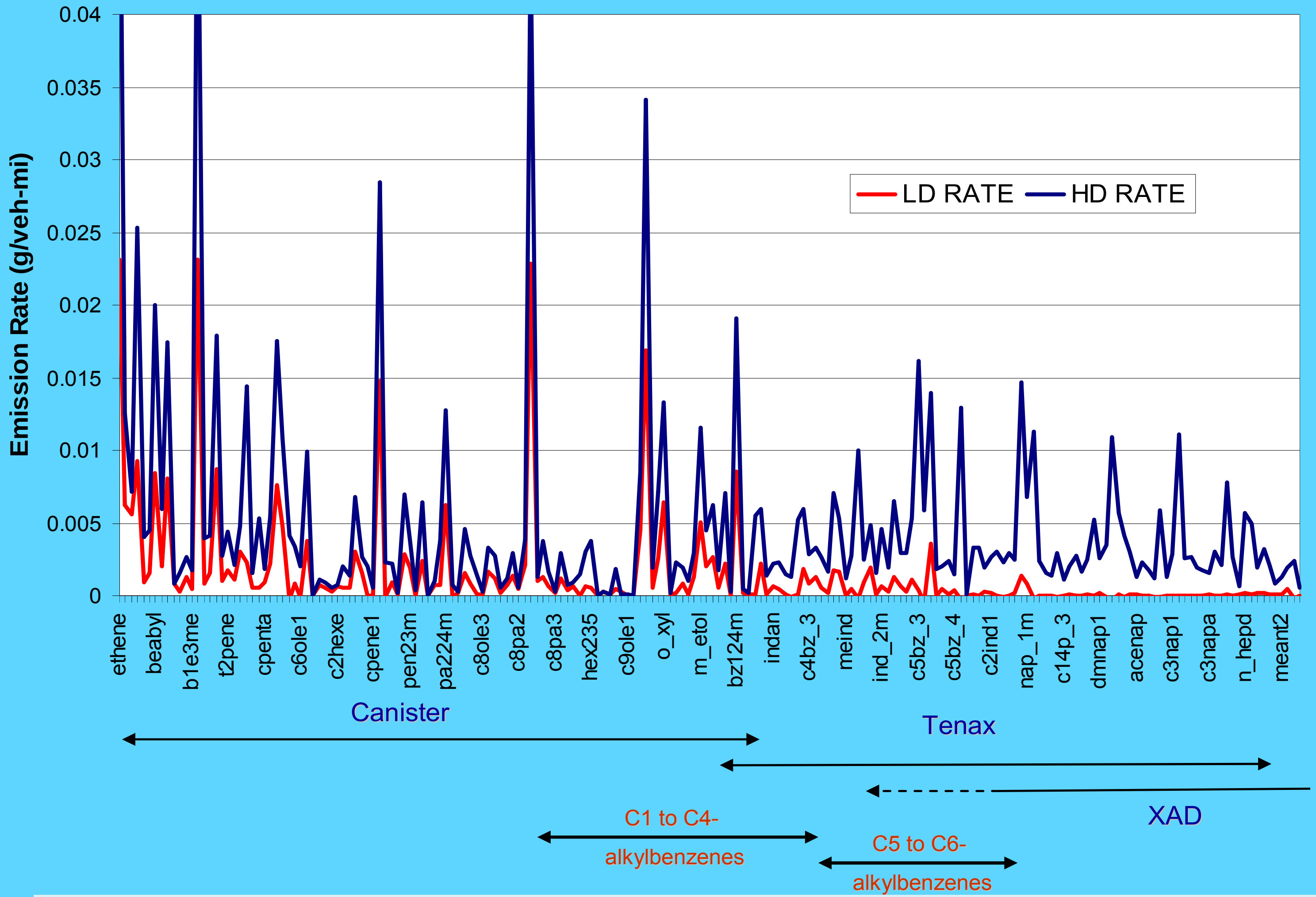
iii. Top of uphill: Spikes of concentrations.

iv. Leaving with load: high concentration spikes when accelerating.

v. Leaving after dumping: concentration spikes when climbing uphill.

vi. Waiting for load: low concentration except when moving forward in line.

Distributions of VOC and SVOC varied between LDGV[a] and HDDV[b] Exhaust (Ft. McHenry Tunnel, Baltimore, MD)



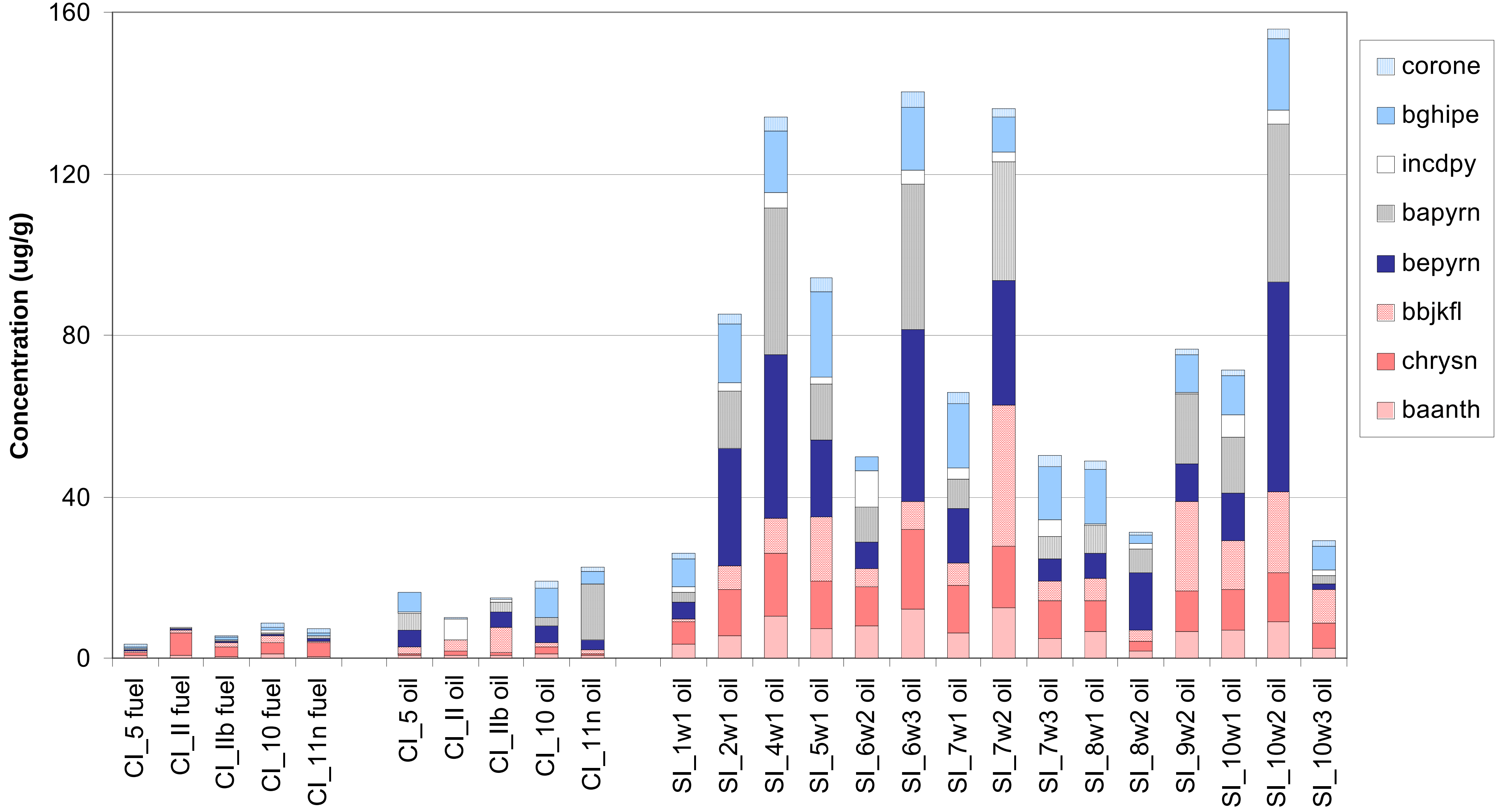
Measured by combination of canisters and Tenax adsorbent cartridges (Sagebiel et al., 1996).
Also shown is the analytical range for XAD cartridges used in the Kansas City Study to capture SVOC downstream of the filter sample.

---

[a] LDGV: Light Duty Gasoline Vehicle

[b] HDDV: Heavy Duty Diesel Vehicle

Large Particulate PAH variations found in lubrication oil (Gasoline/Diesel PM Split Study)



Fujita et al., 2005

Combustion sources can be characterized in the laboratory

Diesel Generator

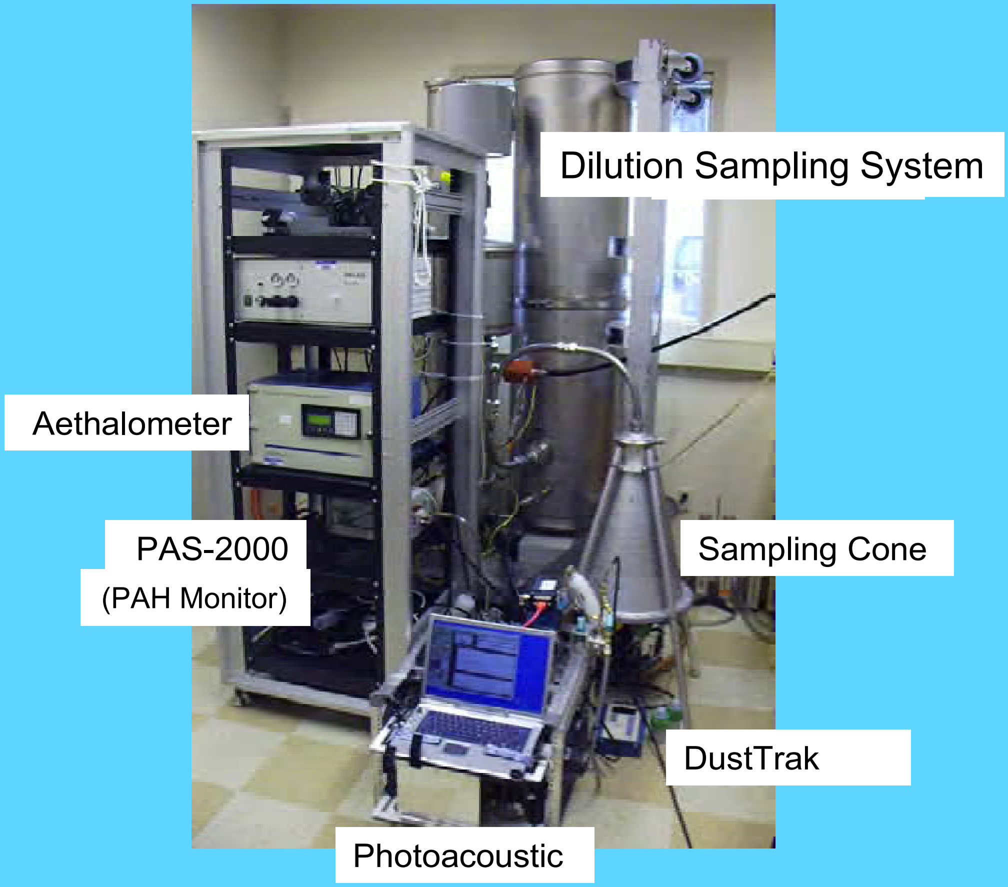
Wood Stove

Acetylene Flame in a hood

- Electric Arc Generator (PALAS)

- Carbon Black and Graphite Powder

Many instruments are needed for source characterization

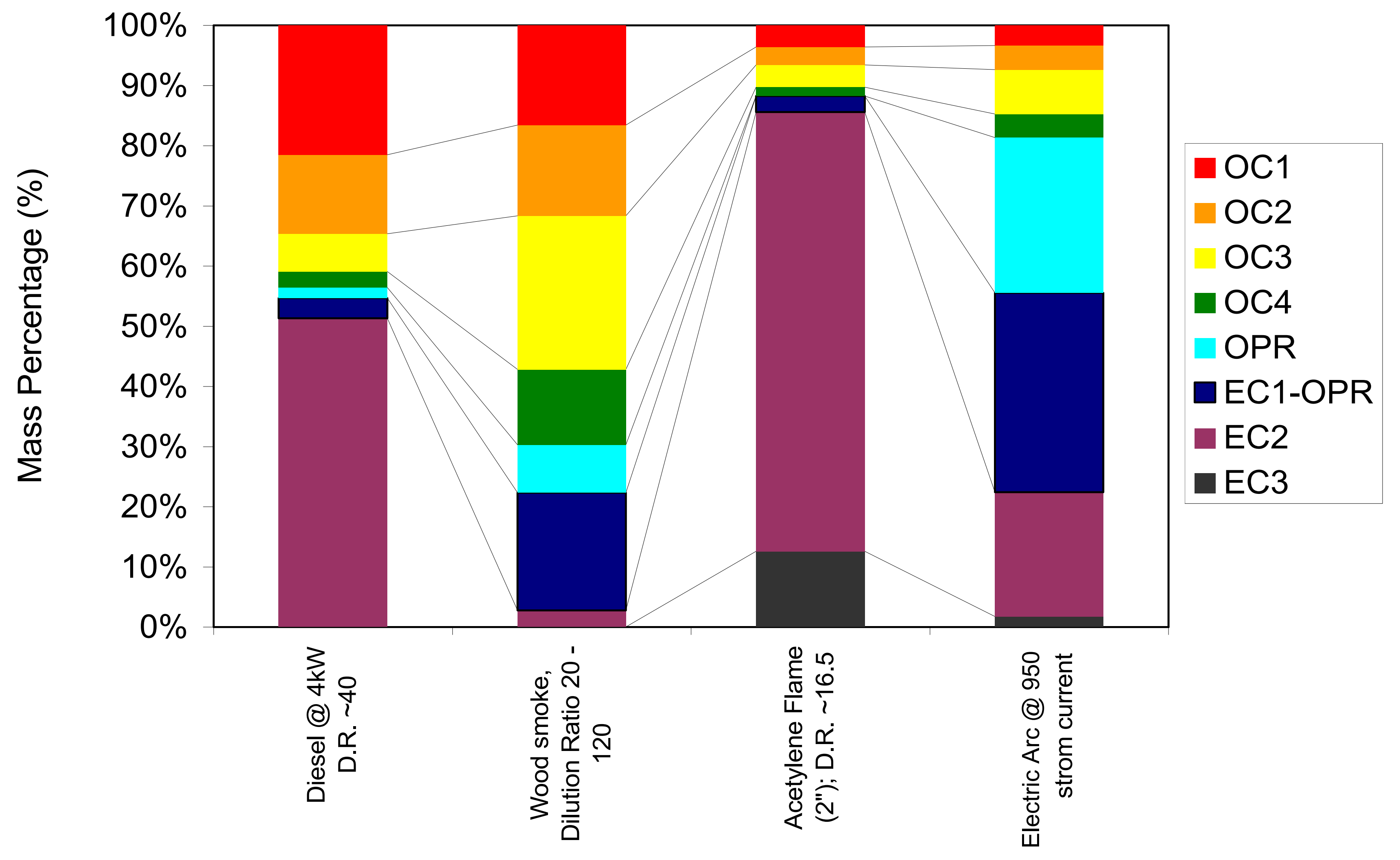


Particle Sizing Instruments
(3 nm to 10 µm)

- TSI Nano-SMPS
  (TSI, St. Paul, MN)
- Grimm SMPS+C
  (Grimm, Ainring, Germany)
- MSP Wide Range Spectrometer
  (MSP; St. Paul, MN)

Abundances of different carbon fractions vary by source

(reproducibility is ± 15% for all except for wood burning)



OC1 – OC4 at 140, 280, 480, and 580 °C in a 100% He atmosphere

EC1 – EC3 at 580, 740, and 840 °C in a 98% He/2% O_2 atmosphere

Chow et al., 2006, Report to ARB

Characterizing biomass burning is most challenging

Flaming Phase: hot and dark; high combustion efficiency

Smoldering Phase: not-so-hot and white; low combustion efficiency
(Waterfall Fire near Carson City, NV; 14 July 2004)

- Optical Properties
- Size Distribution
- Emission Factors

} Phase Specific?

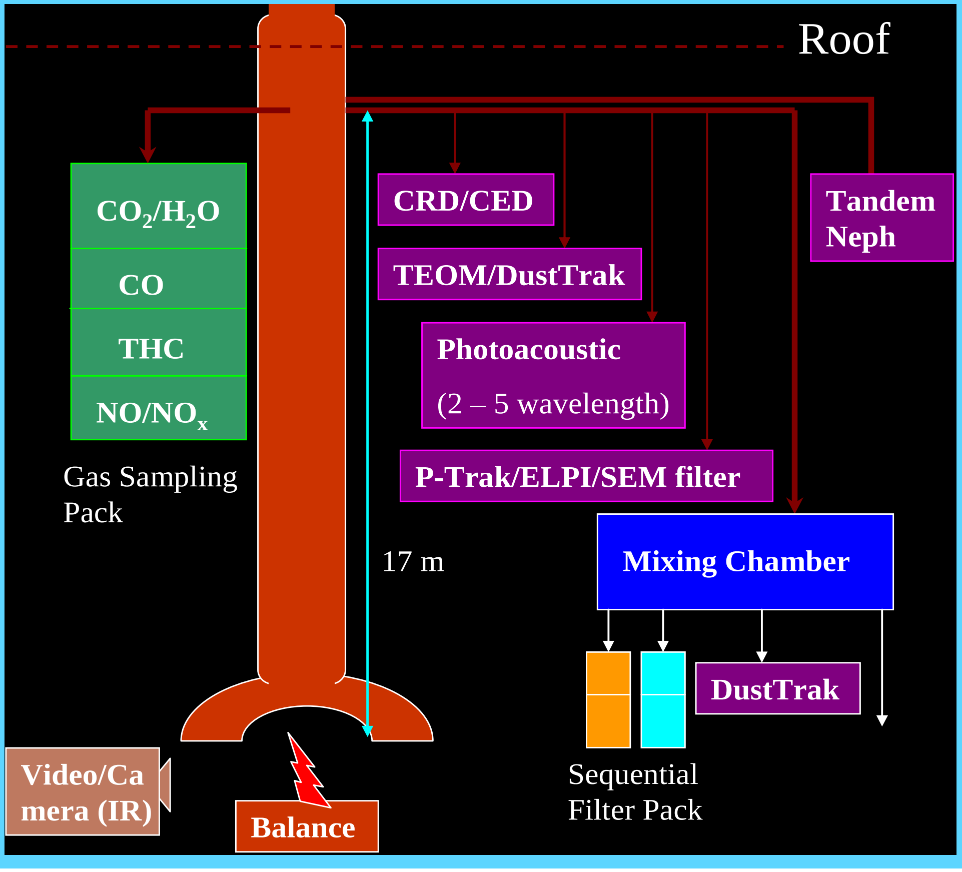
Experimental set-up for vegetative burning

(U.S. Forest Service Fire Science Laboratory; Missoula, MT, U.S.A)

Wildland Fuel

Controlled vegetative burning;
Smoke Jumper Base

Sampling system →



Roof

CO_2/H_2O

CO

THC

NO/NO_x

Gas Sampling Pack

17 m

CRD/CED

TEOM/DustTrak

Tandem Neph

Photoacoustic

(2 – 5 wavelength)

P-Trak/ELPI/SEM filter

Mixing Chamber

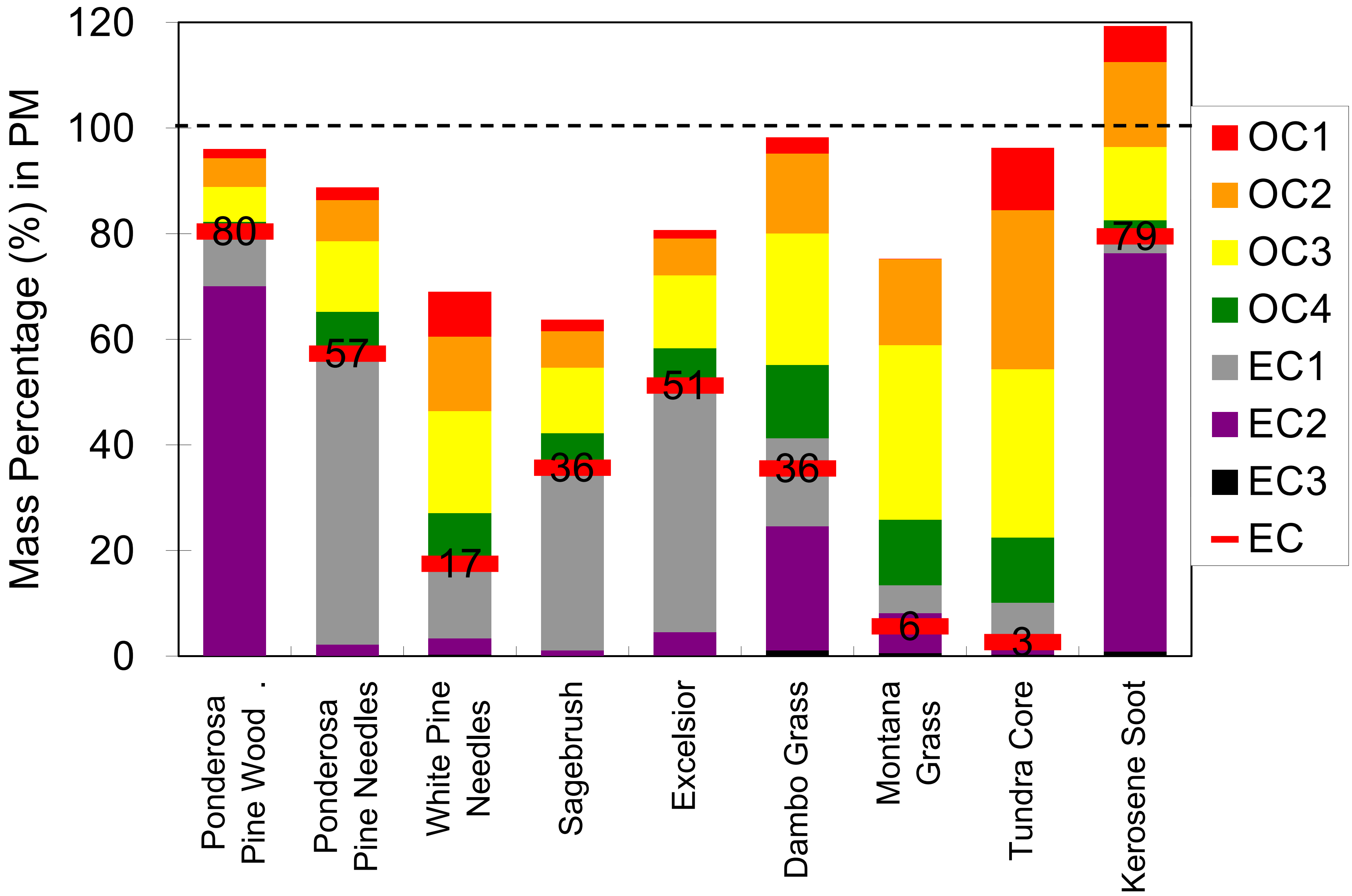
DustTrak

Sequential Filter Pack

Video/Camera (IR)

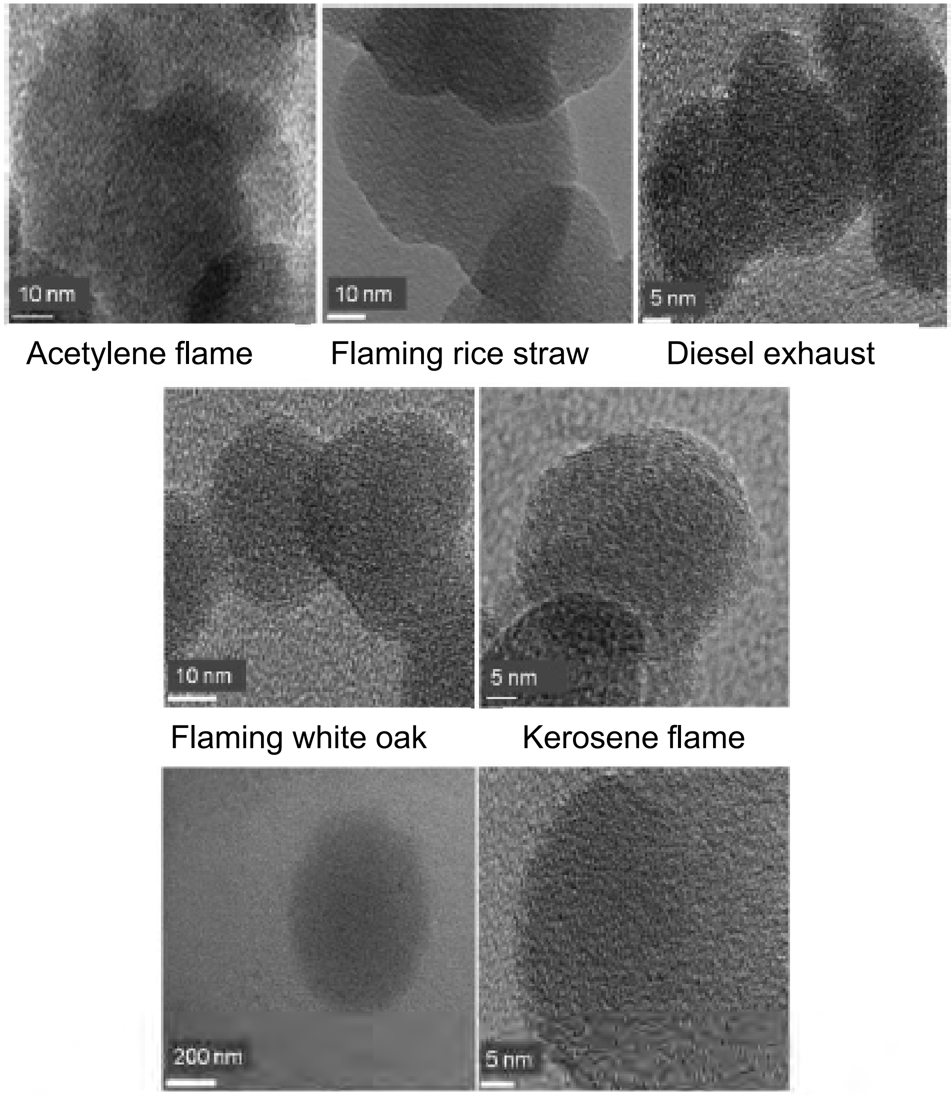
Balance

Carbon fractions in biomass burning varied by fuel and combustion conditions (EC varied from 3% to 80% in $PM_{2.5}$)



Chen et al., 2007, *Environ. Sci. Technol.*

Transmission Electron Microscope (TEM) shows degree of carbonization varies by source



Acetylene flame　Flaming rice straw　Diesel exhaust

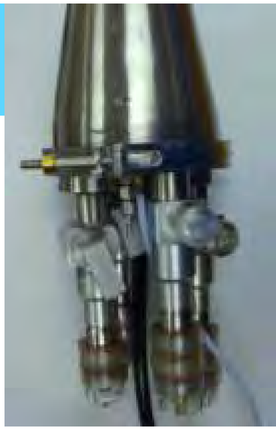
Flaming white oak　Kerosene flame

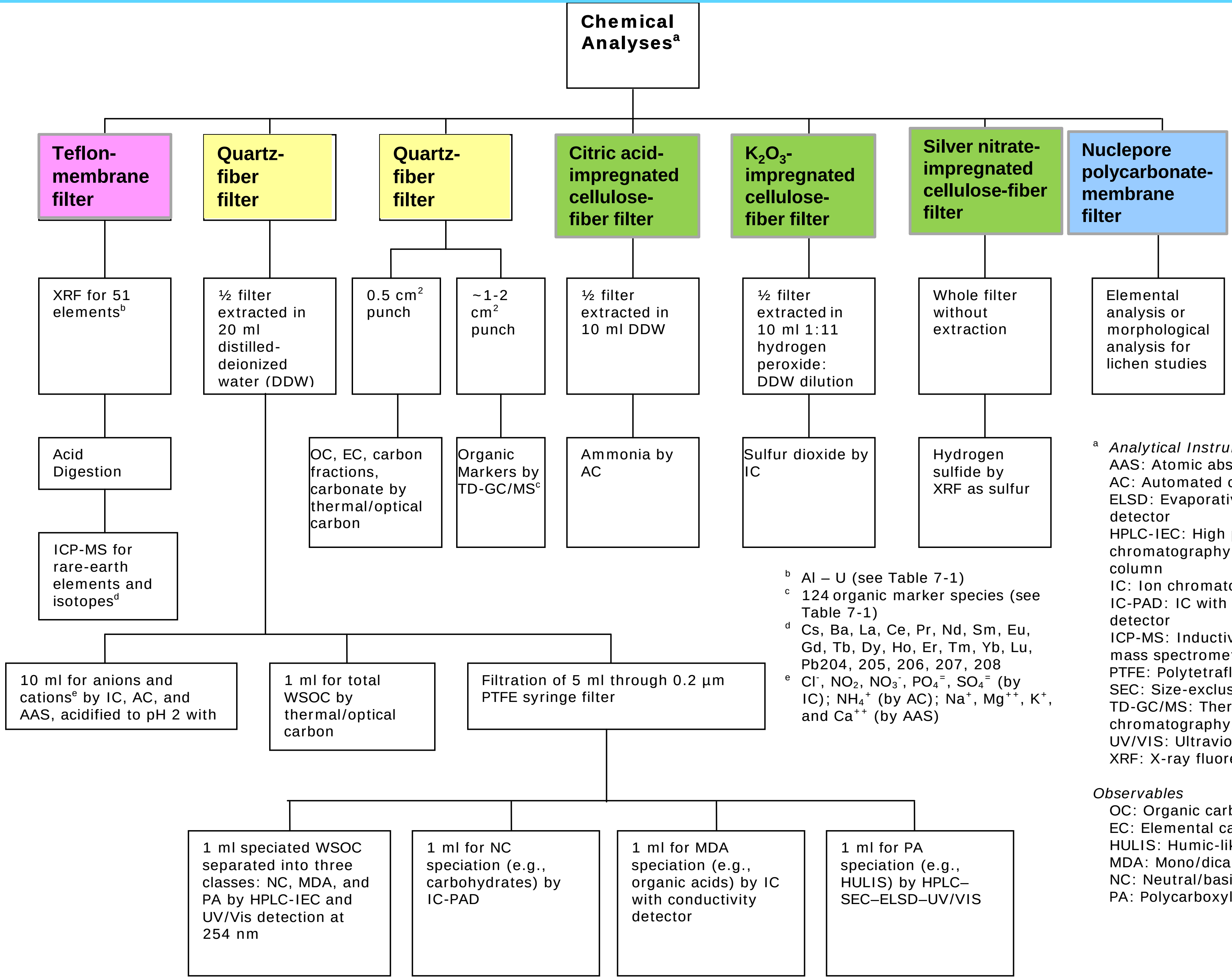
Smoldering pine bark　Burned plastic

FIG. 5. Microstructure of soot or carbonaceous particles from: (a) acetylene flame, (b) rice straw burning in the flaming phase, (c) diesel exhaust, (d) white oak burning in the flaming phase, (e) kerosene flame, (f) pine bark burning in the smoldering phase, and (g) plastic burning.

Tumolva et al., 2010, *Aerosol Sci.Tech.*

Complete characterization of filter samples allows markers to be identified





Chemical Analyses[a]

Teflon-membrane filter

XRF for 51 elements[b]

Acid Digestion

ICP-MS for rare-earth elements and isotopes[d]

Quartz-fiber filter

½ filter extracted in 20 ml distilled-deionized water (DDW)

10 ml for anions and cations[e] by IC, AC, and AAS, acidified to pH 2 with

1 ml for total WSOC by thermal/optical carbon

Filtration of 5 ml through 0.2 µm PTFE syringe filter

1 ml speciated WSOC separated into three classes: NC, MDA, and PA by HPLC-IEC and UV/Vis detection at 254 nm

1 ml for NC speciation (e.g., carbohydrates) by IC-PAD

1 ml for MDA speciation (e.g., organic acids) by IC with conductivity detector

1 ml for PA speciation (e.g., HULIS) by HPLC–SEC–ELSD–UV/VIS

Quartz-fiber filter

0.5 cm^2 punch

OC, EC, carbon fractions, carbonate by thermal/optical carbon

~1-2 cm^2 punch

Organic Markers by TD-GC/MS[c]

Citric acid-impregnated cellulose-fiber filter

½ filter extracted in 10 ml DDW

Ammonia by AC

K_2O_3-impregnated cellulose-fiber filter

½ filter extracted in 10 ml 1:11 hydrogen peroxide: DDW dilution

Sulfur dioxide by IC

Silver nitrate-impregnated cellulose-fiber filter

Whole filter without extraction

Hydrogen sulfide by XRF as sulfur

Nuclepore polycarbonate-membrane filter

Elemental analysis or morphological analysis for lichen studies

[b] Al – U (see Table 7-1)

[c] 124 organic marker species (see Table 7-1)

[d] Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb204, 205, 206, 207, 208

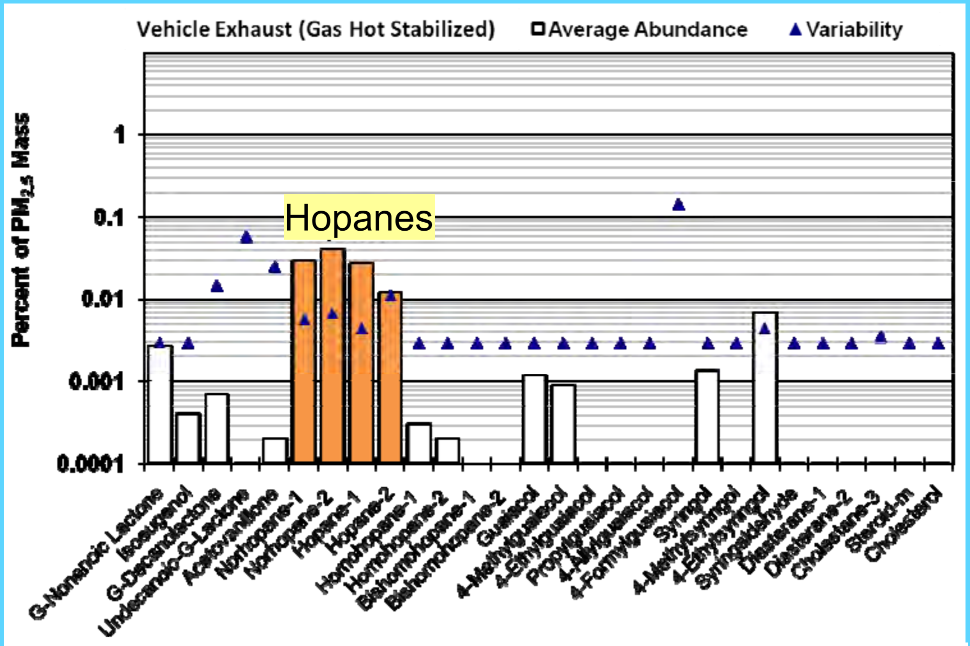
[e] Cl^-, NO_2, NO_3^-, $PO_4^=$, $SO_4^=$ (by IC); NH_4^+ (by AC); Na^+, Mg^{++}, K^+, and Ca^{++} (by AAS)

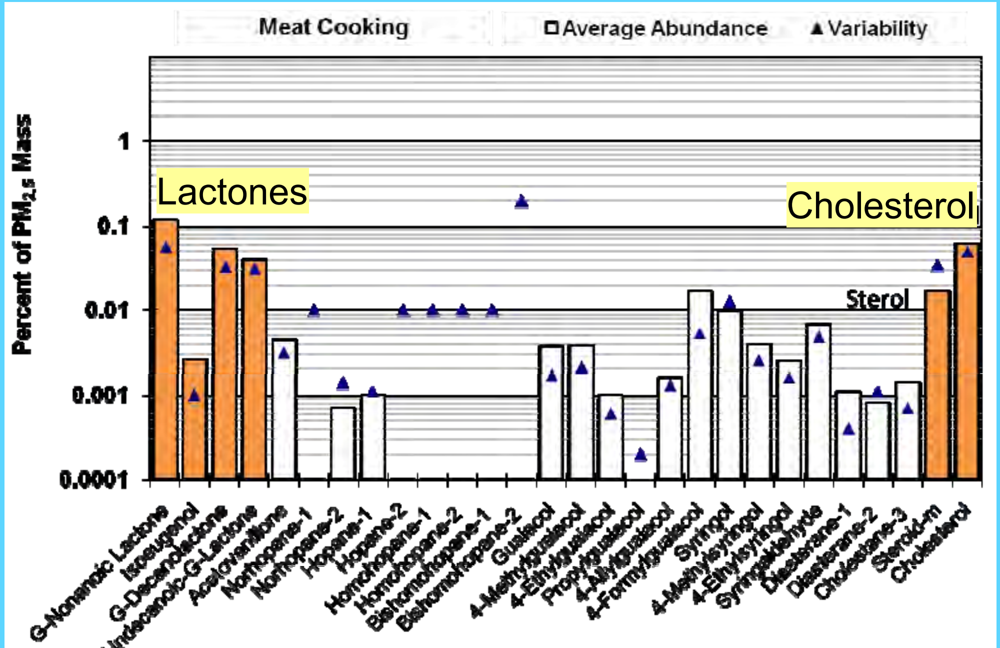
[a] *Analytical Instruments:*
AAS: Atomic absorption spectroscopy
AC: Automated colorimetry
ELSD: Evaporative light scattering detector
HPLC-IEC: High performance liquid chromatography with an ion exchange column
IC: Ion chromatography
IC-PAD: IC with pulsed amperometric detector
ICP-MS: Inductively coupled plasma – mass spectrometry
PTFE: Polytetrafluoroethylene
SEC: Size-exclusion chromatography
TD-GC/MS: Thermal desorption-gas chromatography/mass spectrometry
UV/VIS: Ultraviolet detector
XRF: X-ray fluorescence

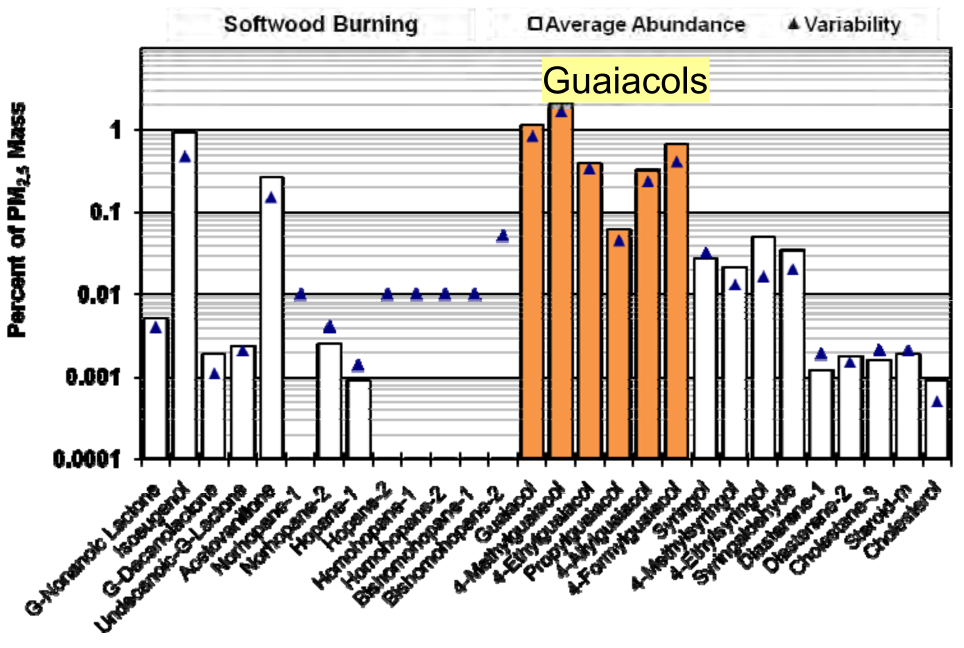
Observables
OC: Organic carbon
EC: Elemental carbon
HULIS: Humic-like substances
MDA: Mono/dicarboxylic acids
NC: Neutral/basic compounds
PA: Polycarboxylic acids

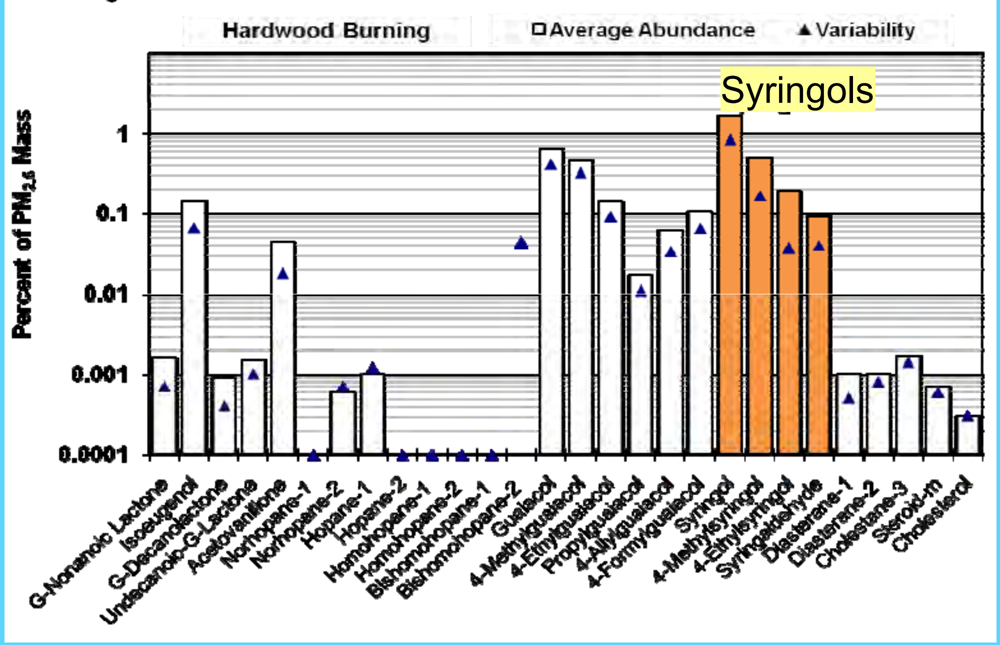
Organic speciation allows better quantification of combustion sources

(Lactones, hopanes, guaiacols, syringols, steranes, and sterols)

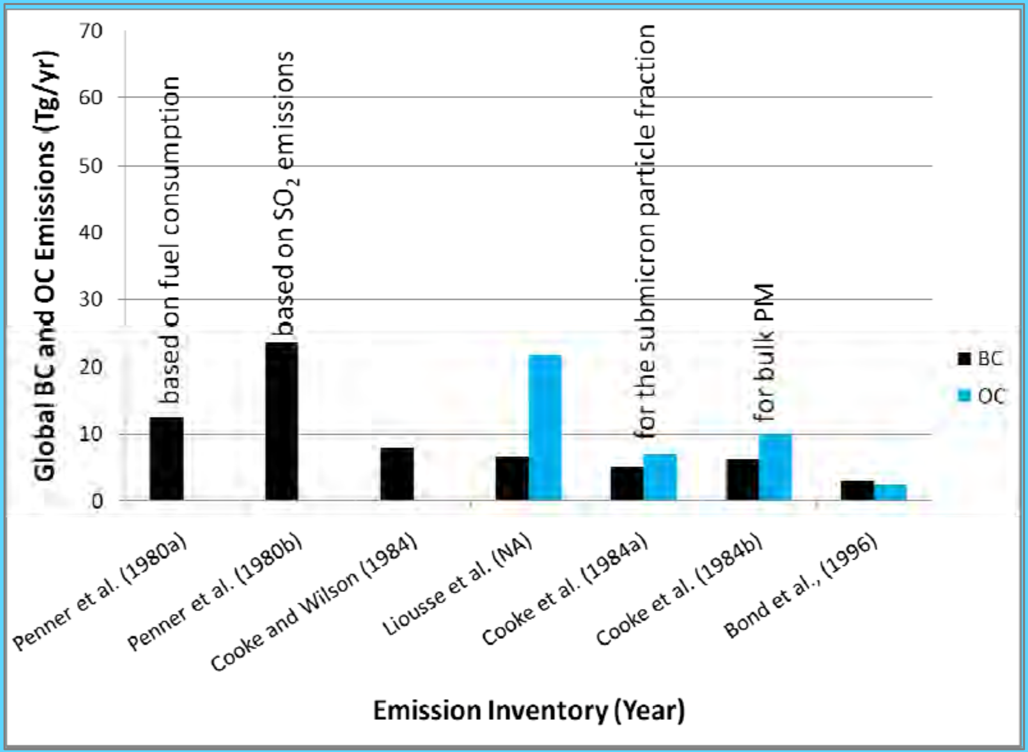




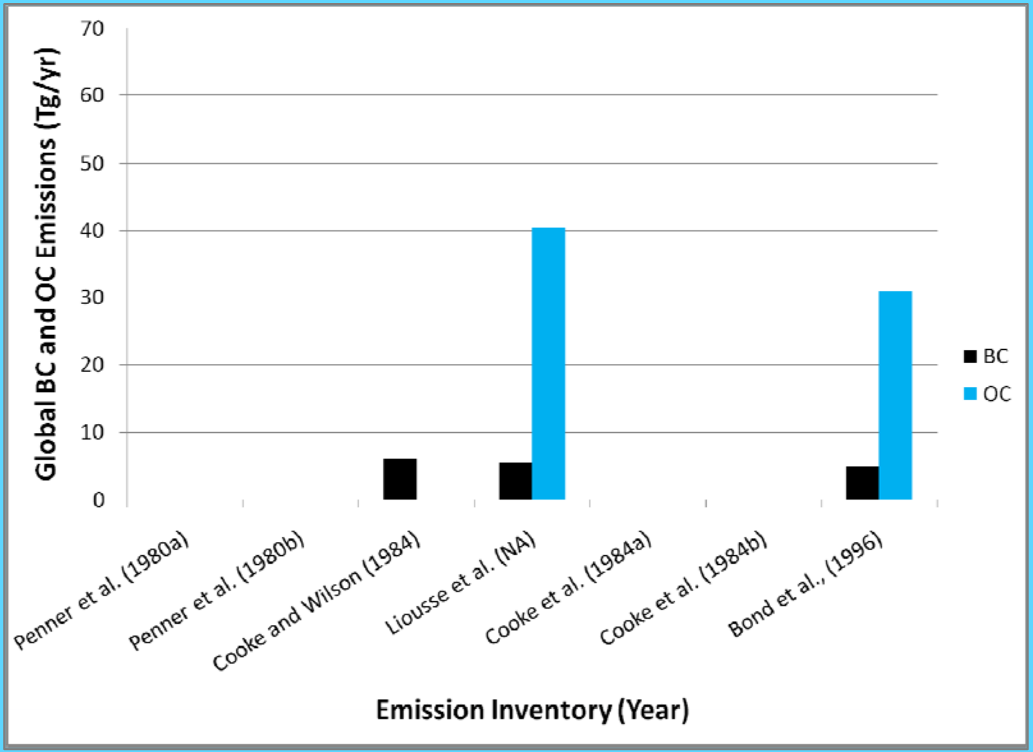




Global carbon inventories are uncertain



Anthropogenic Fossil Fuels



Biomass Burning

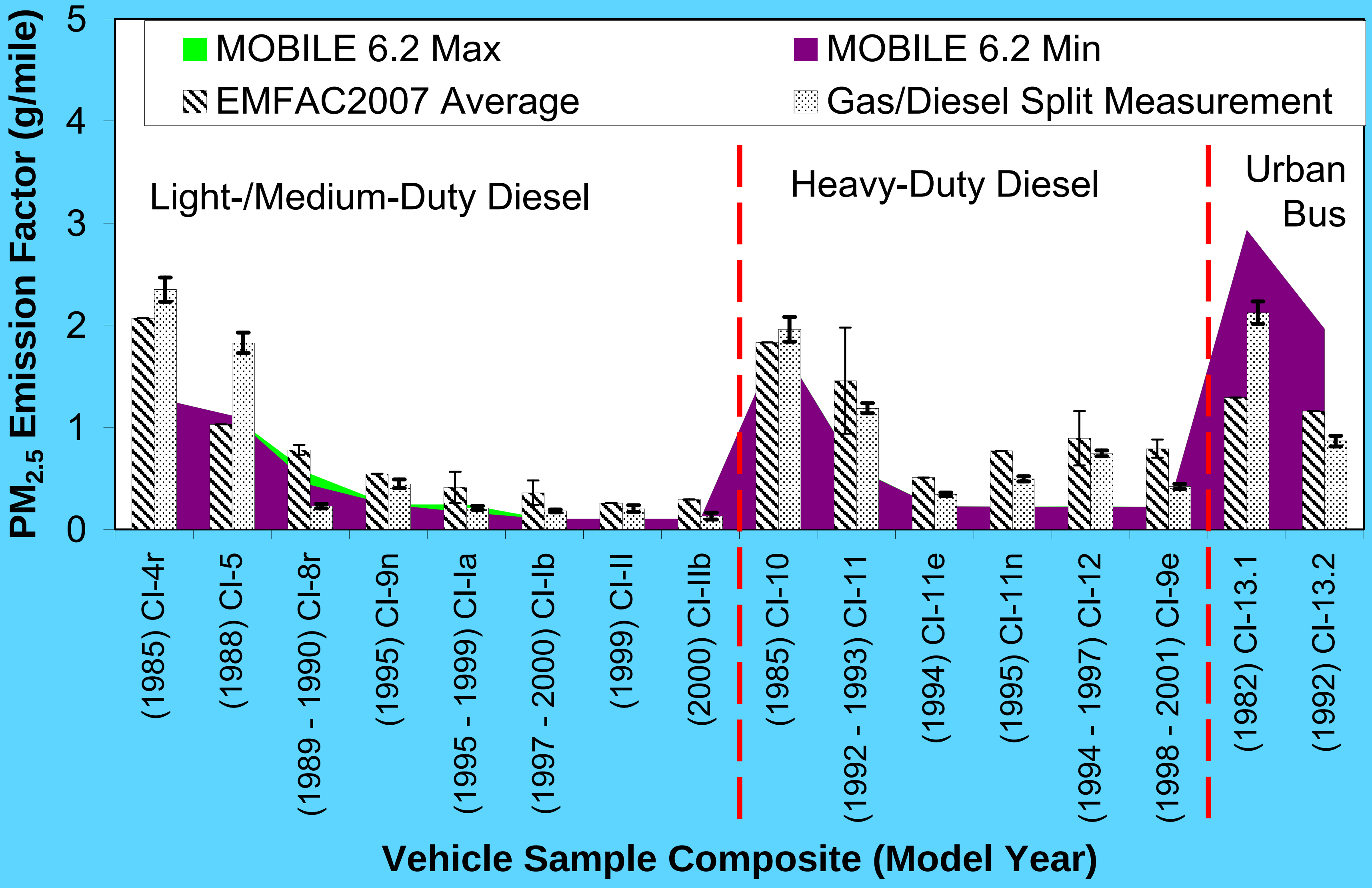
Sum of fossil fuel and biomass burning

BC: 8 – 14 Tg/yr

OC: 33.4 – 62.2 Tg/yr

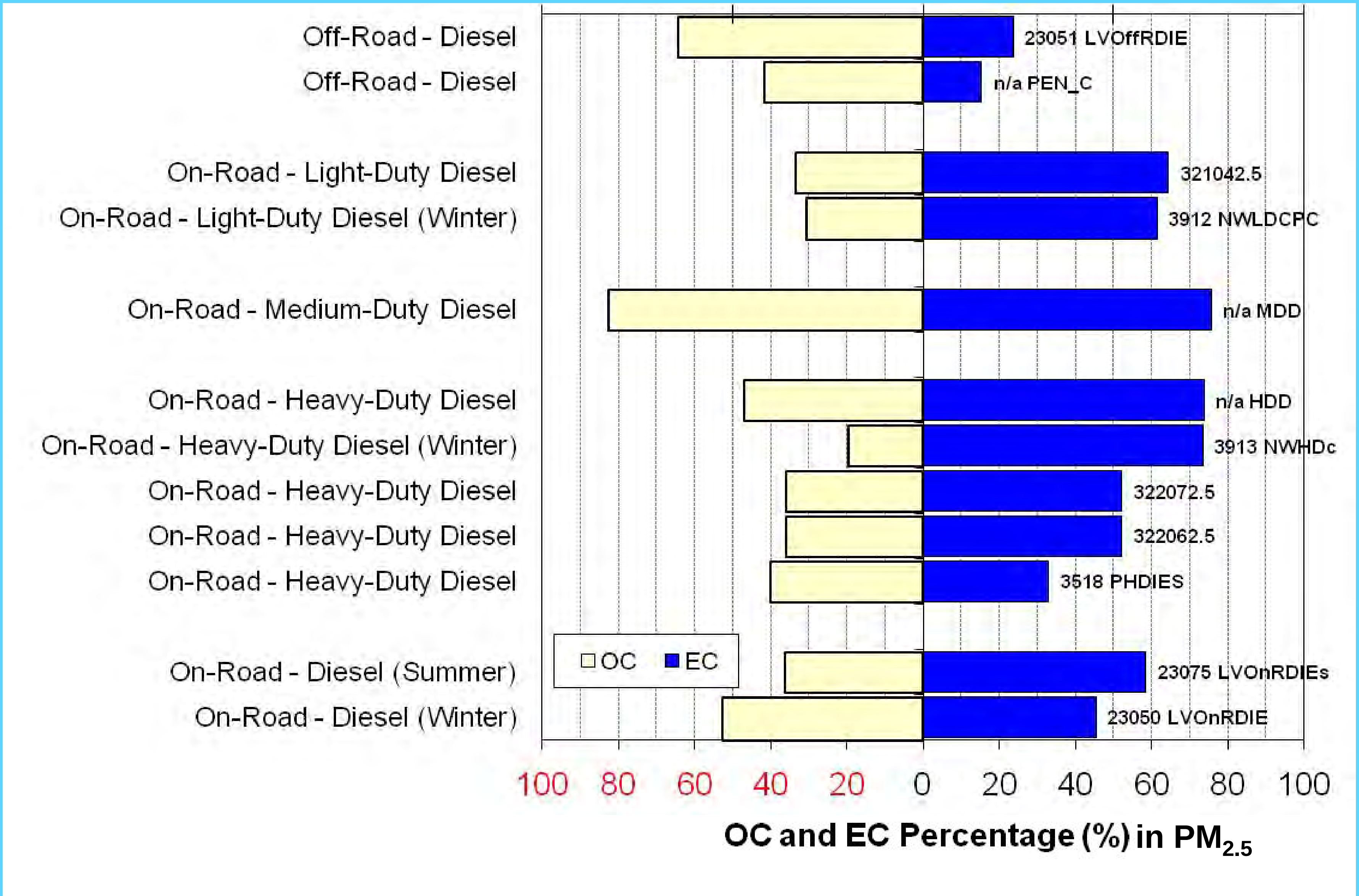
Tg/yr = teragrams/year

PM emission models for on-road engines are improving, but these become less important emitters with engine improvements



Hot City-Suburban route (HCS) driving cycle during the Gas/Diesel Split Study with MOBILE 6.2 and EMFAC 2007 model estimates for the Federal Test Procedure (FTP) cycle.

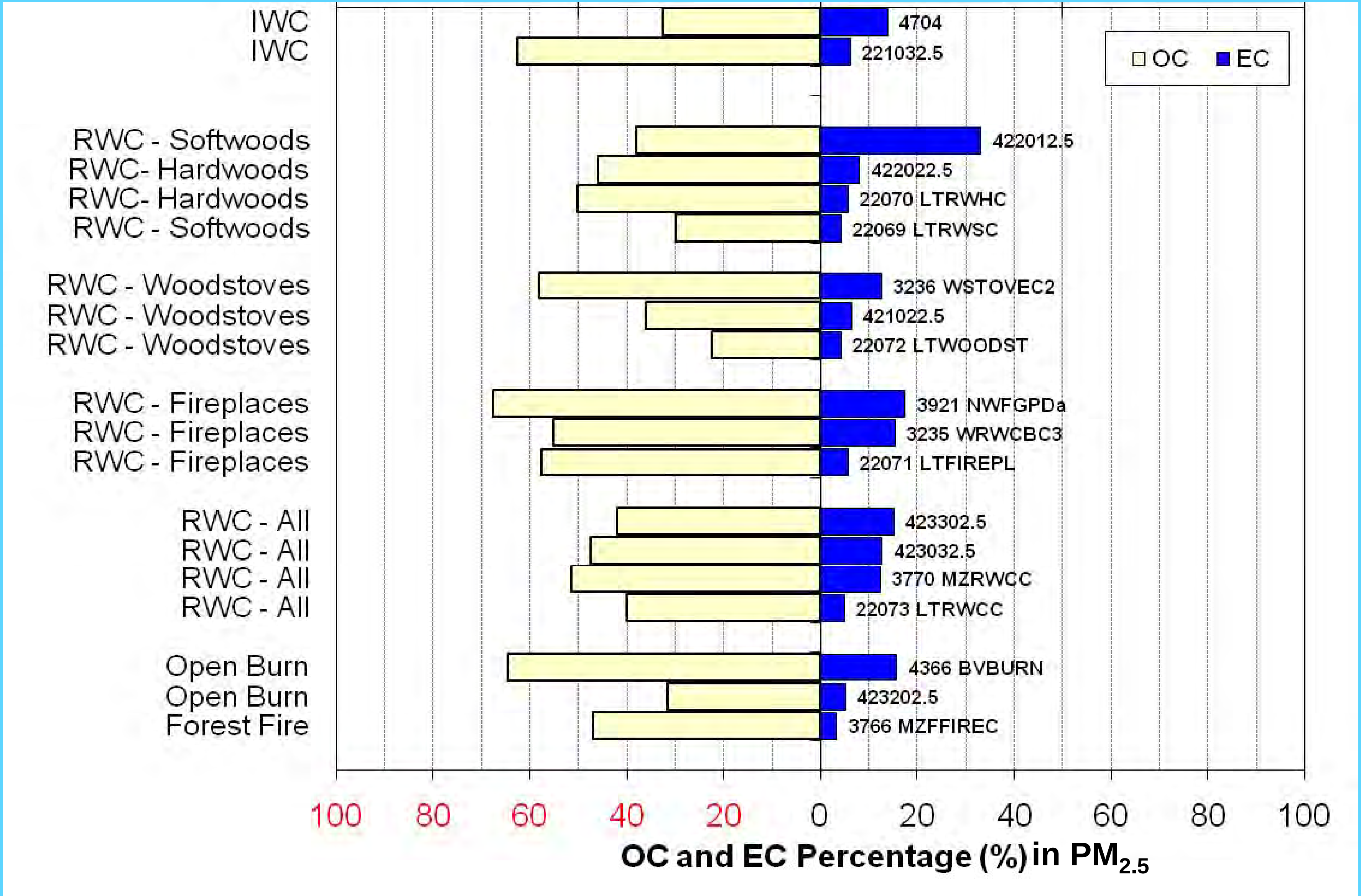
OC and EC abundances in $PM_{2.5}$ are highest in diesel exhaust from older engines



OC abundances: 20–83% of $PM_{2.5}$
EC abundances: 15–74% of $PM_{2.5}$

Chow et al., 2011, *Atmos. Environ.*

OC and EC abundance in $PM_{2.5}$ are viable for biomass burning



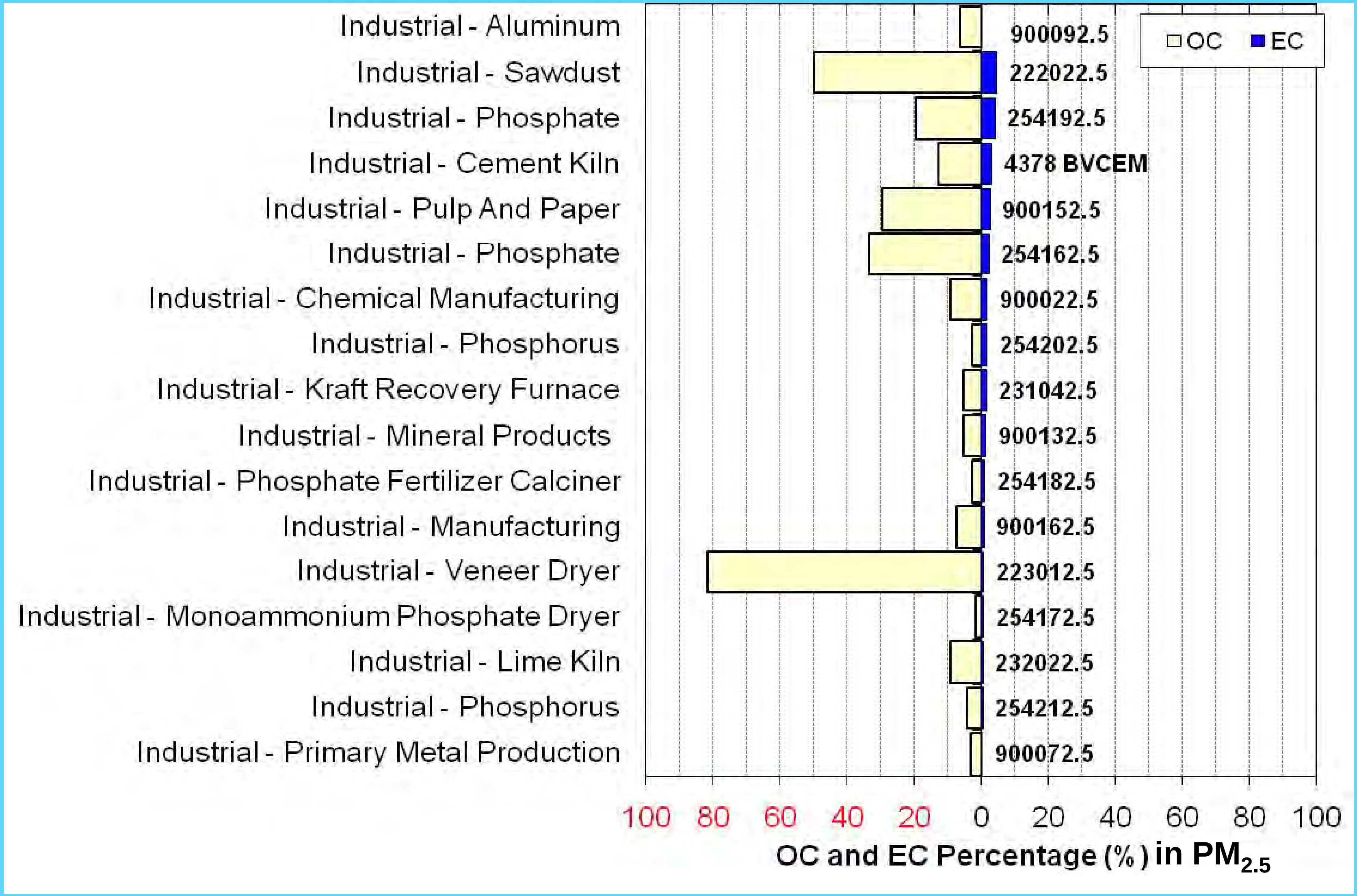
OC abundances: 22–67% of $PM_{2.5}$

EC abundances: 3–33% of $PM_{2.5}$

IWC: Industrial Wood Combustion; RWC: Residential Wood Combustion

Chow et al., 2011, *Atmos. Environ.*

OC and EC abundances in PM$_{2.5}$ are generally low in industrial stack emissions with efficient control measures



OC abundances: 2–82% of PM$_{2.5}$
EC abundances: below minimum detectable limit–0-5% of PM$_{2.5}$

Chow et al., 2011, *Atmos. Environ.*

Improvements are needed for real-world emission source testing

- Replace hot filter/impinger stack testing method with dilution sampling
- Reconcile test methods among stationary and mobile sources
- Ensure comparability between emission testing and ambient sampling methods

- Integrate multiple gas/ particle measurements with a single source test

Conclusions

- U.S. EPA certification methods are costly to apply and do not represent real-world emissions
- Resources used for certification and compliance tests would yield more useful results if they were directed toward more real-world emission testing
- A variety of modern emission characterization methods exist that can practically obtain real-world emission factors, profiles, and activity levels for global emission inventories
- Black Carbon (BC) or elemental carbon (EC) abundances vary by an order of magnitude among pollution sources, especially for vehicle exhaust and biomass burning

References

- Burtscher, H. (2005). Physical characterization of particulate emissions from diesel engines: A review. *J. Aerosol Sci*., **36**(7): 896-932.
- Chang, M.-C.O.; Chow, J.C.; Watson, J.G.; Glowacki, C.; Sheya, S.A.; Prabhu, A. (2005). Characterization of fine particulate emissions from casting processes. *Aerosol Sci. Technol*., **39**(10): 947-959.
- Chen, L.-W.A.; Moosmüller, H.; Arnott, W.P.; Chow, J.C.; Watson, J.G.; Susott, R.A.; Babbitt, R.E.; Wold, C.E.; Lincoln, E.N.; Hao, W.M. (2007). Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. *Environ. Sci. Technol*., **41**(12): 4317-4325.
- Chow, J.C.; Watson, J.G.; Doraiswamy, P.; Chen, L.-W.A.; Sodeman, D.A.; Ho, S.S.H.; Tropp, R.J.; Kohl, S.D.; Trimble, D.L.; Fung, K.K. (2006). Climate change - Characterization of black carbon and organic carbon air pollution emissions and evaluation of measurement methods, Phase I. Report Number DRI 04-307; prepared by Desert Research Institute, Reno, NV, for California Air Resources Board, Sacramento, CA; http://www.arb.ca.gov/research/apr/past/04-307_v1.pdf
- Chow, J.C.; Wang, X.L.; Kohl, S.D.; Gronstal, S.; Watson, J.G. (2010). Heavy-duty diesel emissions in the Athabasca Oil Sands Region. In Proceedings, 103rd Annual Meeting of the Air & Waste Management Association, Tropp, R. J., Legge, A. H., Eds.; Air & Waste Management Association: Pittsburgh, PA, 1-5.
- Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Lowenthal, D.H.; Motallebi, N. (2011). Source profiles for black and organic carbon emission inventories. *Atmos. Environ.*, accepted.
- England, G.C.; Watson, J.G.; Chow, J.C.; Zielinska, B.; Chang, M.-C.O.; Loos, K.R.; Hidy, G.M. (2007a). Dilution-based emissions sampling from stationary sources: Part 1. Compact sampler, methodology and performance. *J. Air Waste Manage. Assoc.,* **57**(1): 65-78.
- England, G.C.; Watson, J.G.; Chow, J.C.; Zielinska, B.; Chang, M.-C.O.; Loos, K.R.; Hidy, G.M. (2007b). Dilution-based emissions sampling from stationary sources: Part 2. Gas-fired combustors compared with other fuel-fired systems. *J. Air Waste Manage. Assoc.,* **57**(1): 79-93.
- Fujita, E.M.; Campbell, D.E.; Centric, A.; Arnott, W.P.; Chow, J.C.; Zielinska, B. (2005). Exposure to air toxics in mobile source dominated microenvironments, year-2 annual report. Report Number HEI contract 4704-RFA03-1/03-16; prepared by Desert Research Institute, Reno, NV, for Health Effects Institute, Boston, MA.
- Moldanova, J.; Fridell, E.; Popovicheva, O.B.; Demirdjian, B.; Tishkova, V.; Faccinetto, A.; Focsa, C. (2009). Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. *Atmos. Environ*., **43**(16): 2632-2641.

References

- Sagebiel, J.C.; Zielinska, B.; Pierson, W.R.; Gertler, A.W. (1996). Real-world emissions and calculated reactivities of organic species from motor vehicles. *Atmos. Environ.*, **30**(12):2287-2296.
- Tumolva, L.; Park, J.Y.; Kim, J.S.; Miller, A.L.; Chow, J.C.; Watson, J.G.; Park, K. (2010). Morphological and elemental classification of freshly emitted soot particles and atmospheric ultrafine particles using the TEM/EDS. *Aerosol Sci. Technol.*, **44**(3): 202-215.
- U.S. EPA (1996). Method 202. Condensible Particulate Matter - Determination of condensible particulate emissions from stationary sources. prepared by U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Technical Support Division, Research Triangle Park, NC, http://www.epa.gov/ttn/emc/promgate/m-202.pdf
- U.S. EPA (1997). Compilation of air pollutant emission factors. Volume I: Stationary point and area sources. prepared by U. S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- Watson, J.G.; Chow, J.C. (2007). Receptor models for source apportionment of suspended particles. In Introduction to Environmental Forensics, 2nd Edition, 2; Murphy, B., Morrison, R., Eds.; Academic Press: New York, NY, 279-316.
- Watson, J.G.; Chow, J.C.; Wang, X.L.; Kohl, S.D. (2010). Emission characterization plans for the Athabasca Oil Sands Region. In Proceedings, 103rd Annual Meeting of the Air & Waste Management Association, Tropp, R. J., Legge, A. H., Eds.; Air & Waste Management Association: Pittsburgh, PA, 1-6.