EVALUATION OF MOBILE SOURCE EMISSIONS AND TRENDS USING DETAILED CHEMICAL AND PHYSICAL MEASUREMENTS

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Mar 4, 2014

EPA STAR Project Meeting in Ann Arbor (OTAQ)

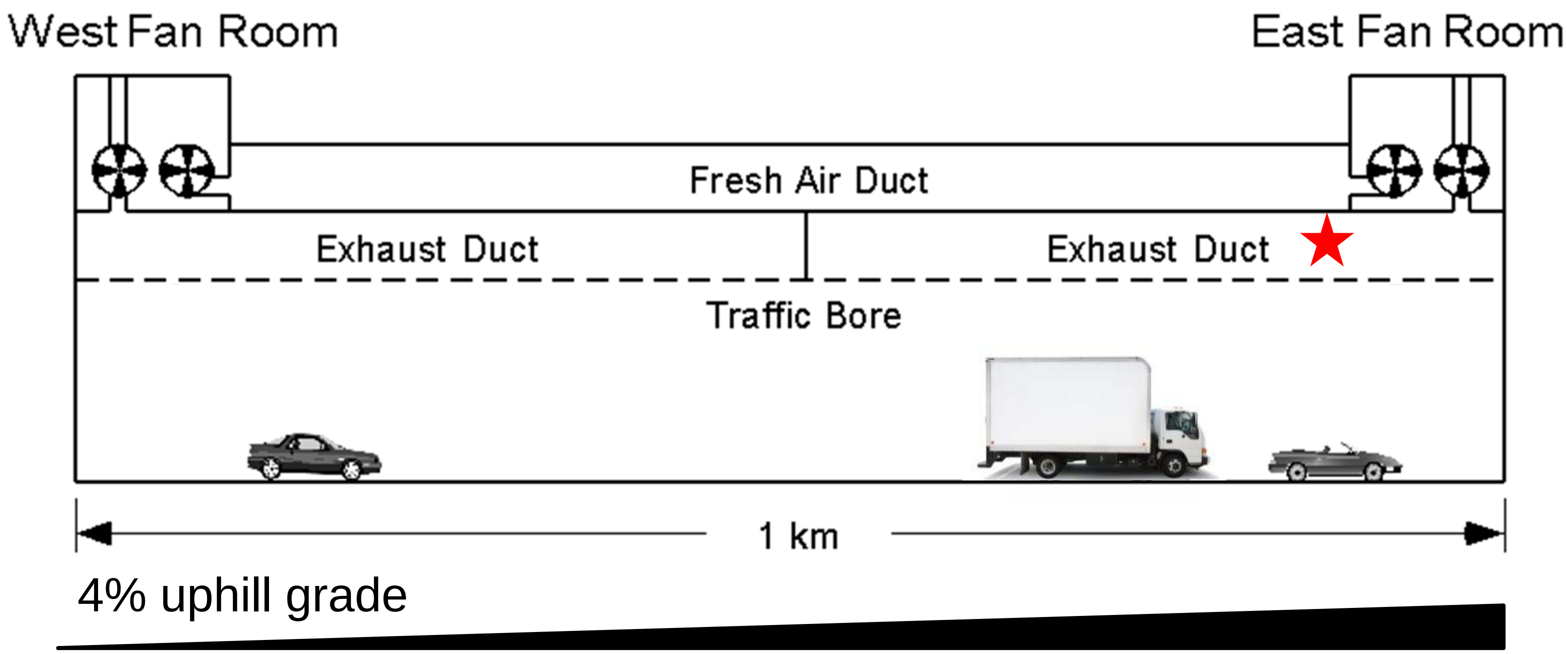
Acknowledgments

- UC Berkeley: Tim Dallmann, Drew Gentner, Arthur Chan, Allen Goldstein, Gabriel Isaacman, Steven DeMartini, Brian McDonald, and Dave Worton.
- Aerodyne: Ezra Wood, Tim Onasch, Scott Herndon, John Franklin, Ed Fortner, Doug Worsnop
- LBNL: Tom Kirchstetter, Kevin Wilson
- Research funding:
  - US Environmental Protection Agency (Grant # RD834553)

A Highway Tunnel Laboratory

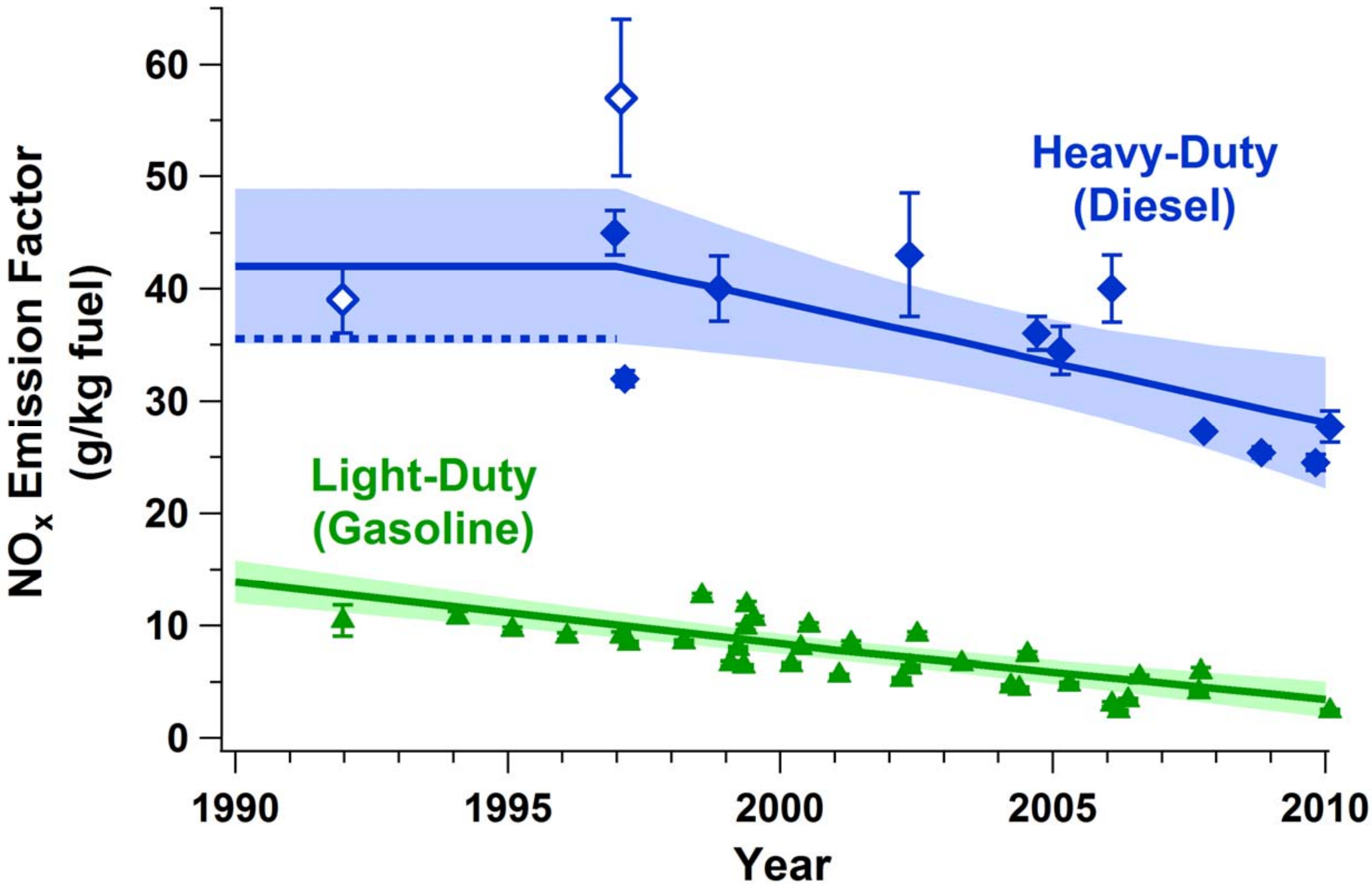
Vehicle emissions measured at Caldecott tunnel in SF Bay area:

- Light-Duty Gasoline: 1994-97, 1999, 2001, 2004, 2006, 2010
- Heavy-Duty Diesel Trucks: 1996-97, 2006, 2010



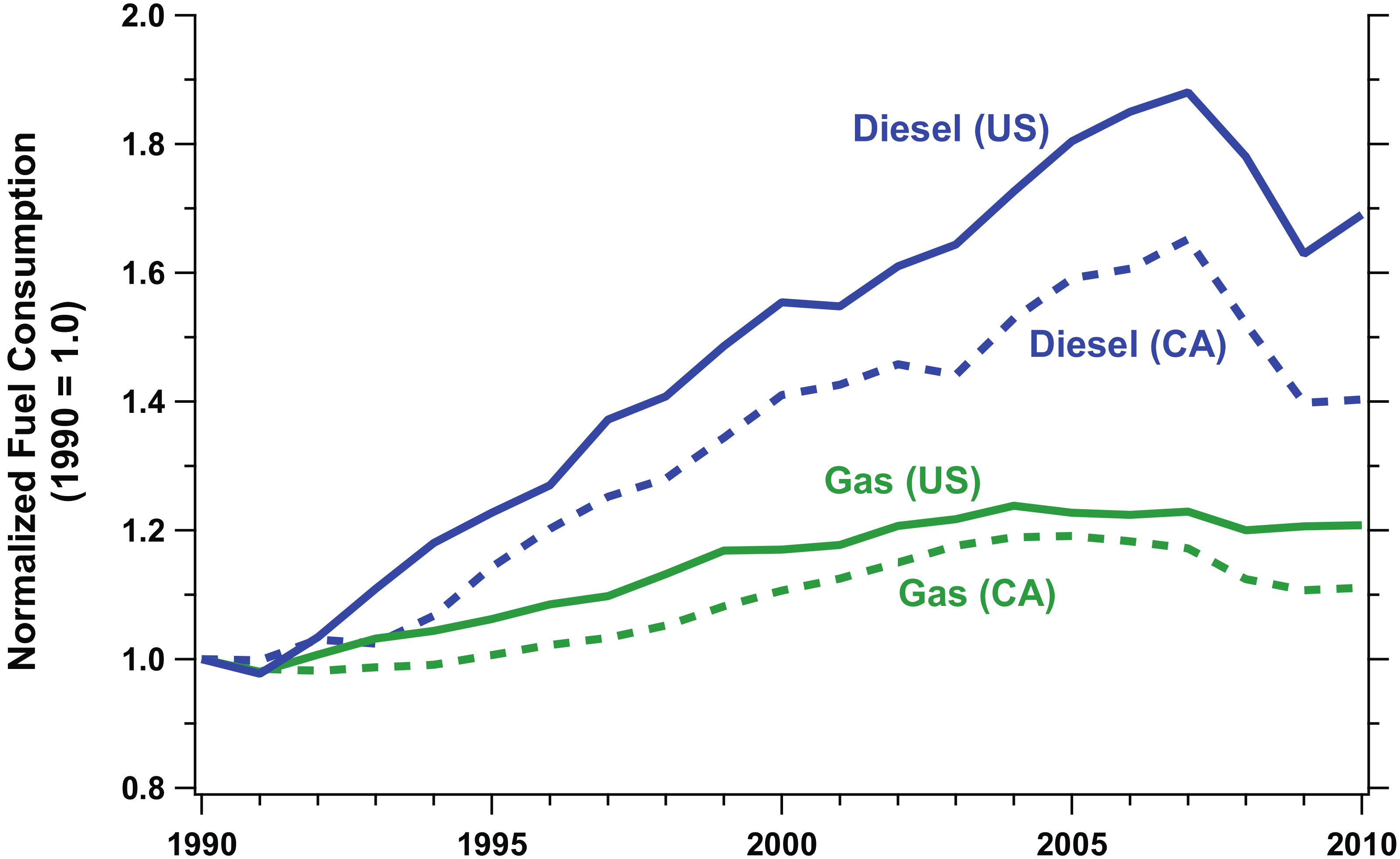
Pollutant	Tunnel Measurement Method
CO_2	Infrared absorption
Nitric Oxide (NO)	Chemiluminescense
NO_2, CO HCHO, C_2H_4	Tunable infrared laser spectroscopy
PM mass & composition	Aerosol mass spectrometer
Black Carbon (BC)	Aethalometer
Light absorption & scattering (532 nm)	Photoacoustic spectrometer and reciprocal nephelometer
Light absorption (630 nm)	Multi-angle absorption photometer
Light extinction (630 nm)	Cavity attenuation phase-shift

On-Road NO_x Emission Factor Trends



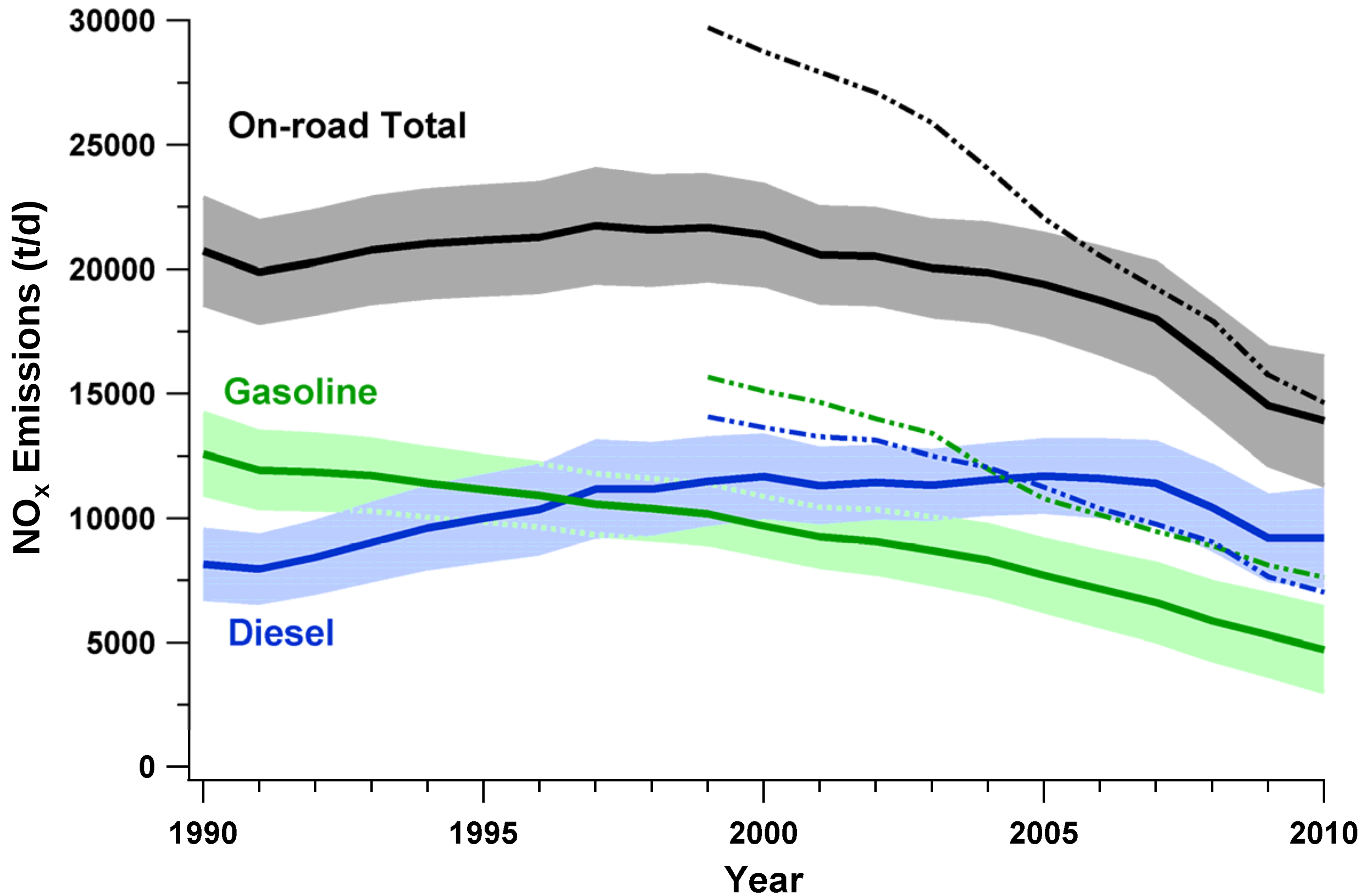
McDonald et al. (JGR 2012)

Fuel Sales Trends, 1990-2010



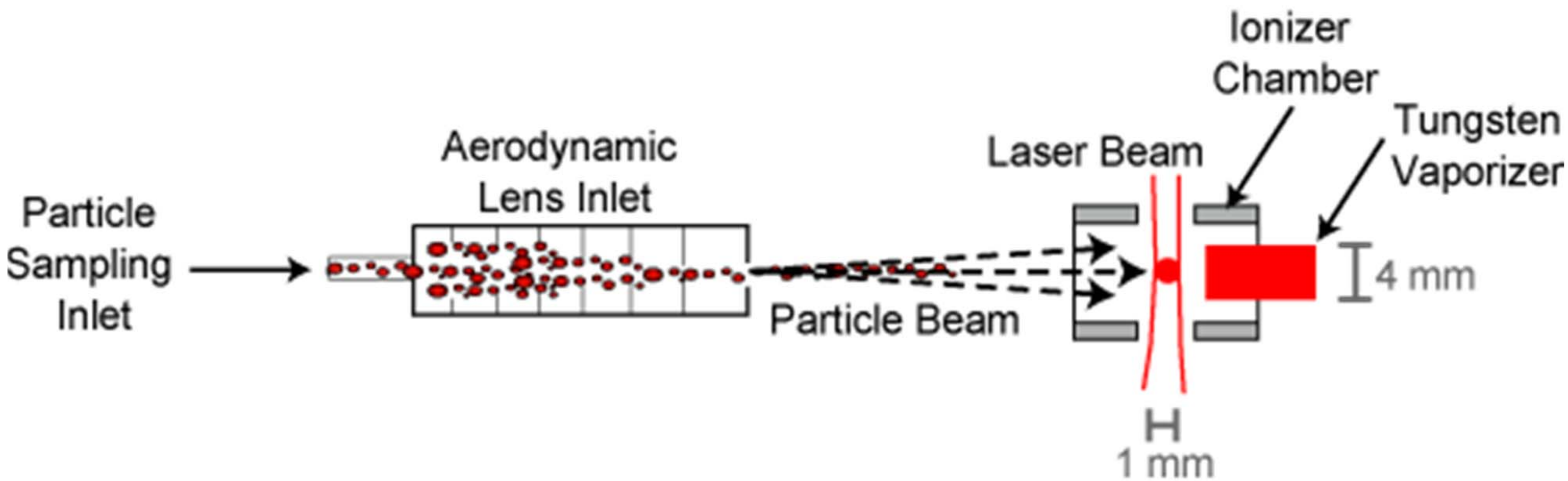
McDonald et al. (JGR 2012)

National On-Road NO_x Emission Trends



McDonald et al. (JGR 2012)

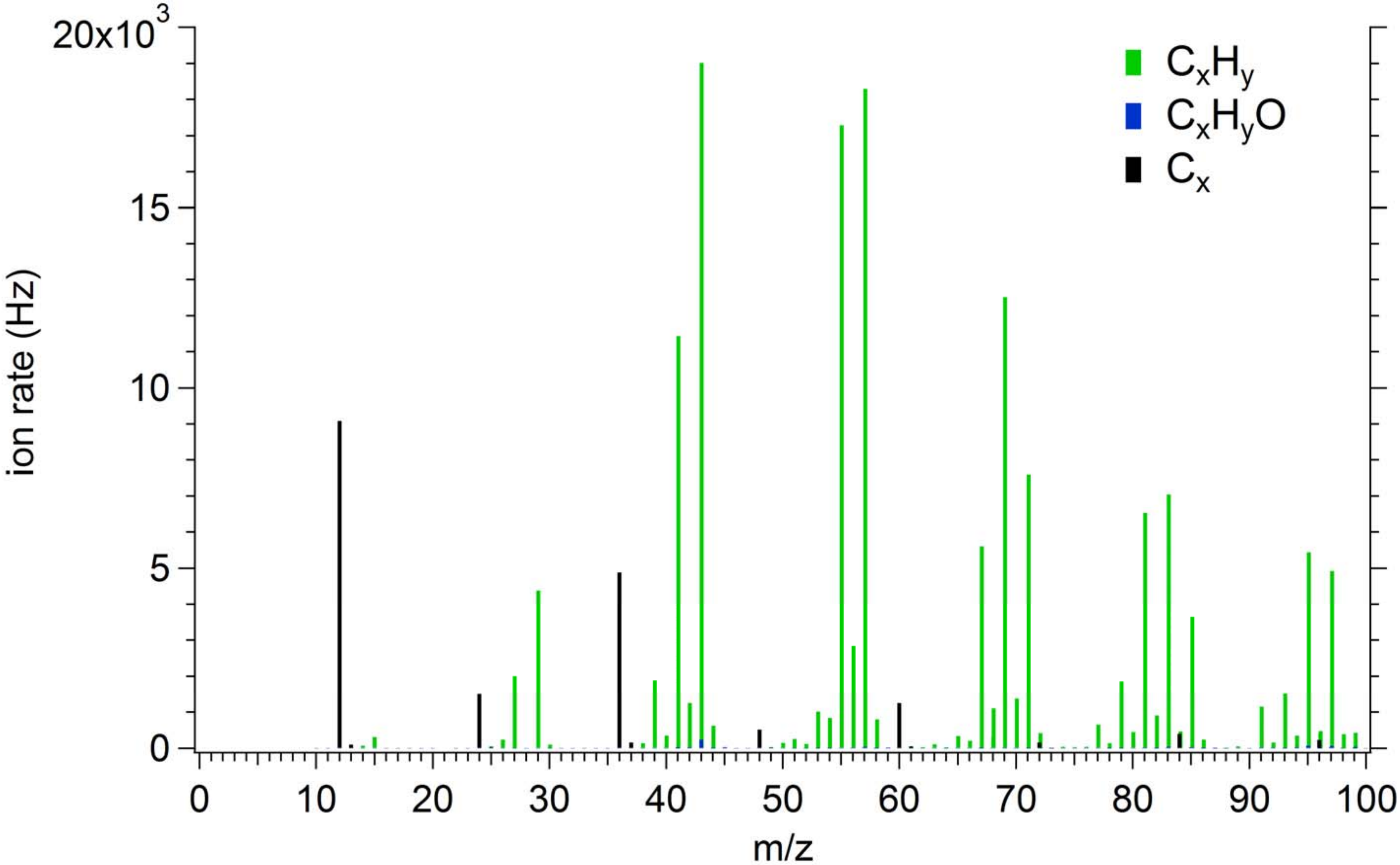
Aerosol Mass Spectrometer (SP-AMS)



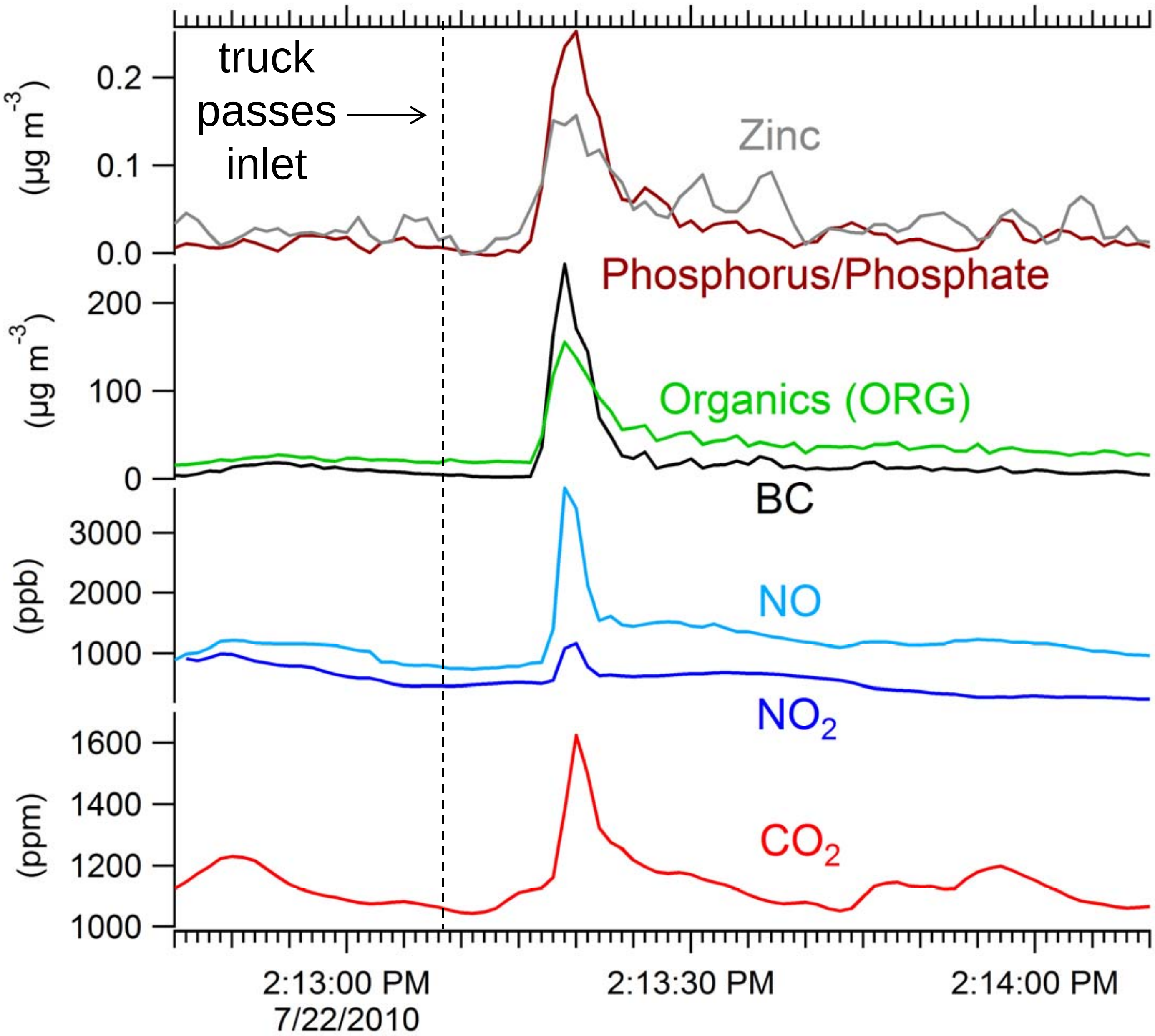
- Heated tungsten vaporizer combined with laser to vaporize organic *and* refractory aerosol (e.g., soot)
- Both vaporizers on at all times
- Operate in fast MS mode to capture individual truck plumes

Onasch et al. (AS&T 2012)

Sample AMS Data – Diesel Truck Plume



Capturing Individual Truck Exhaust Plumes

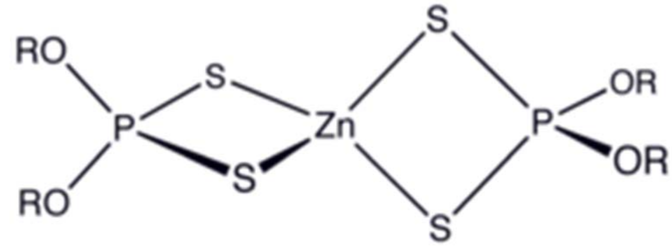


Chemical speciation of exhaust particles, including trace elements

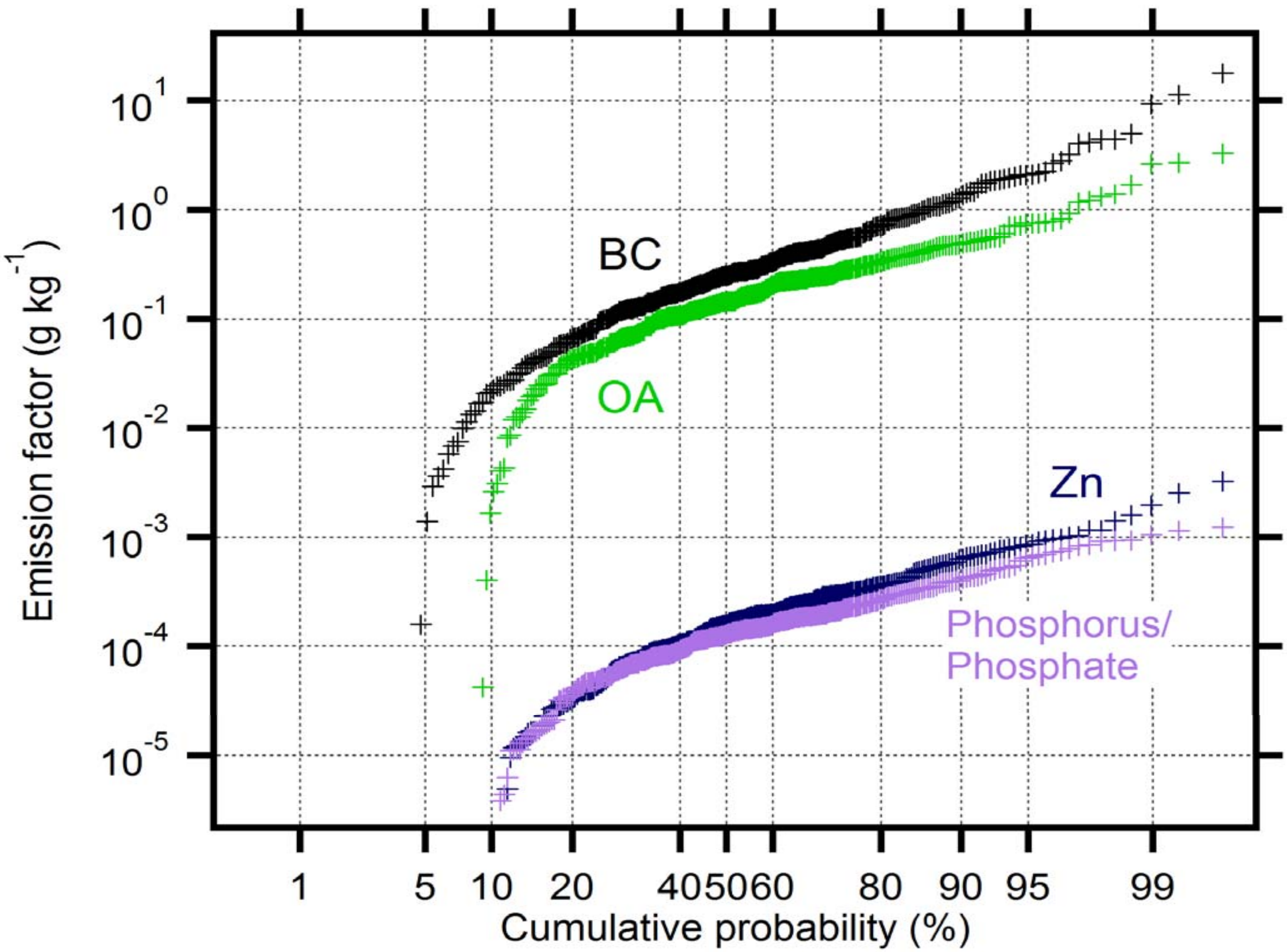
Independent measurements of NO and NO_2

Peak in CO_2 denotes capture of exhaust plume

HDDT Emission Factor Distributions

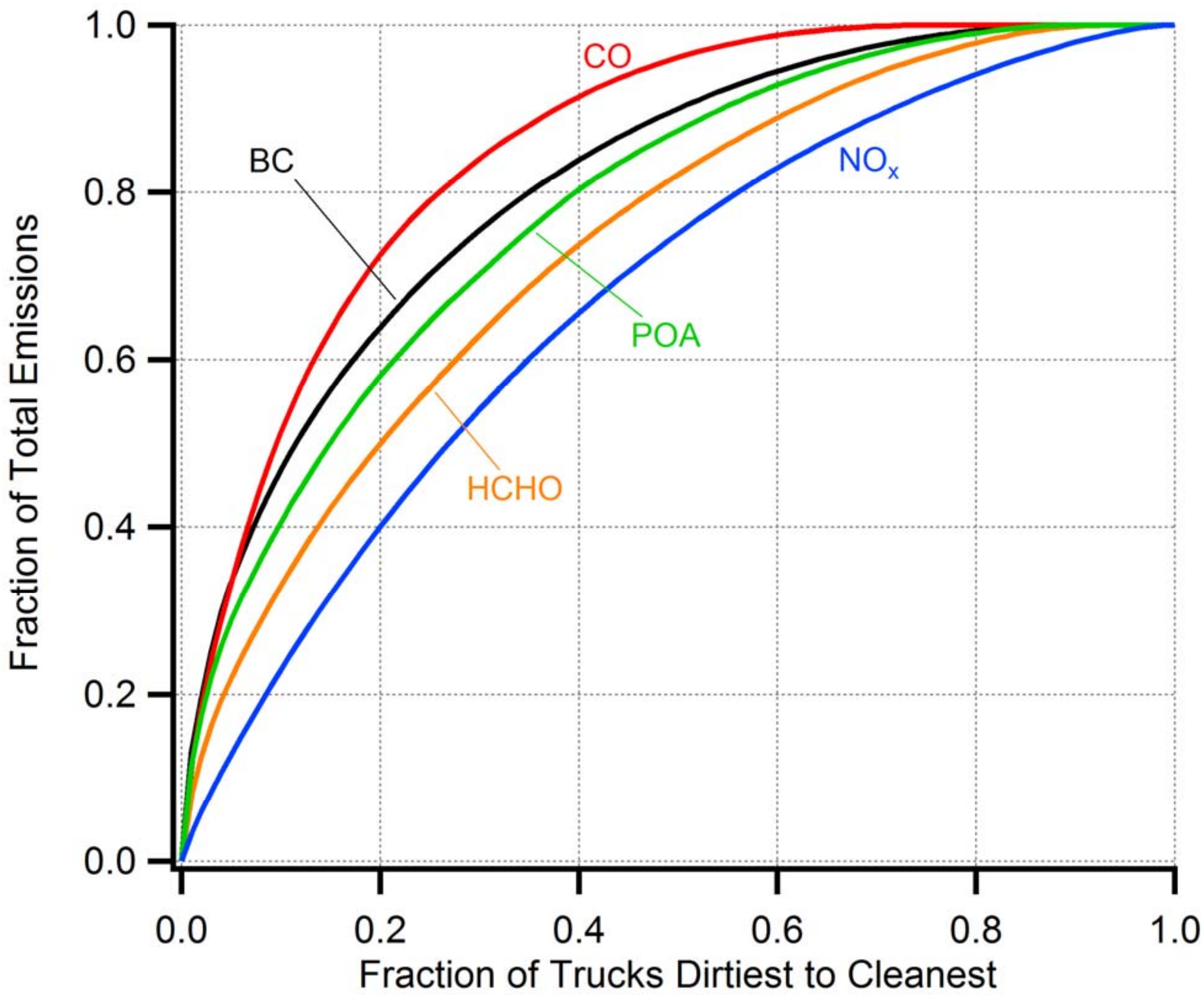


(R = alkyl)



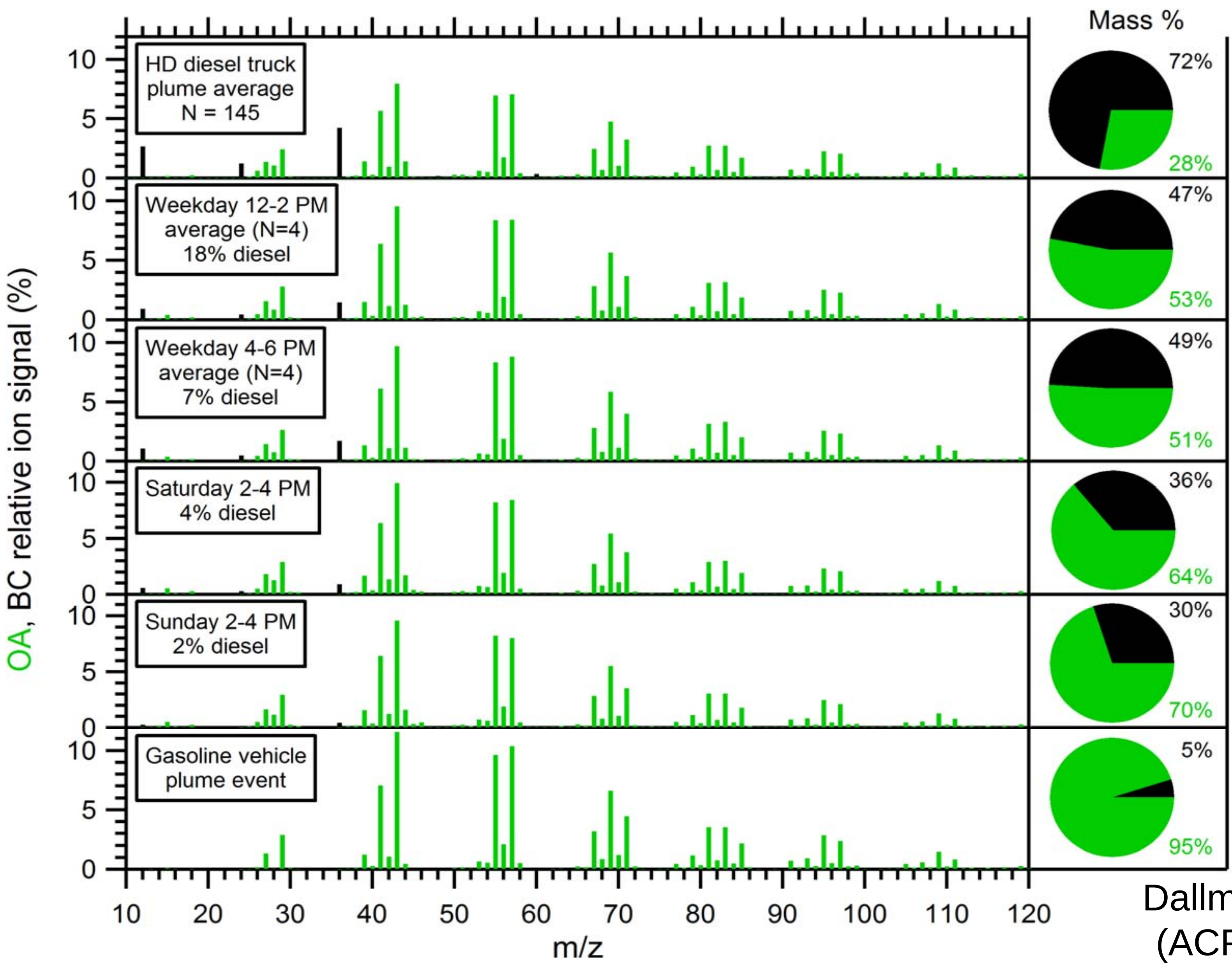
Dallmann et al.
(ACPD 2014)

Cumulative Contributions to Total Emissions from Heavy-Duty Diesel Trucks



Dallmann et al. (ES&T 2012)

OA mass spectra similar for Gasoline and Diesel

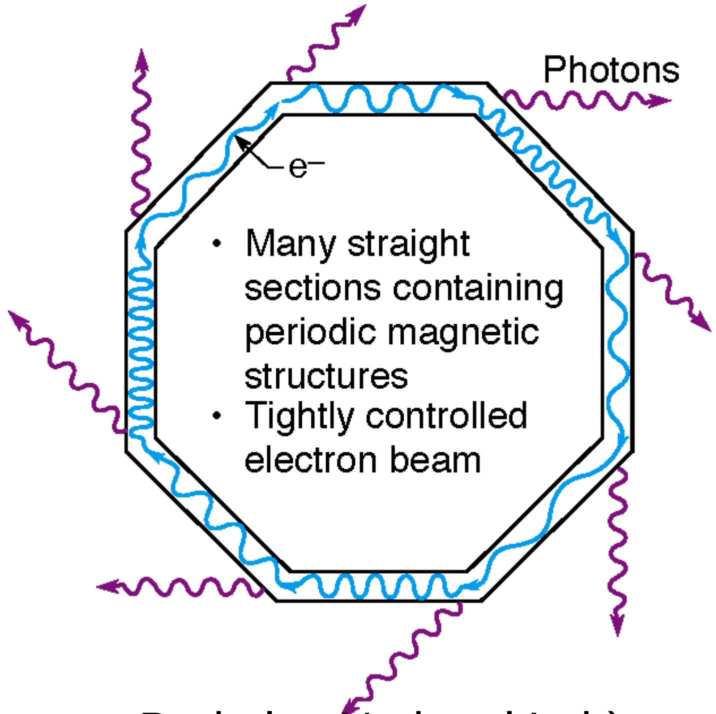


Dallmann et al.
(ACPD 2014)

GC-MS Analysis of Organic Aerosol

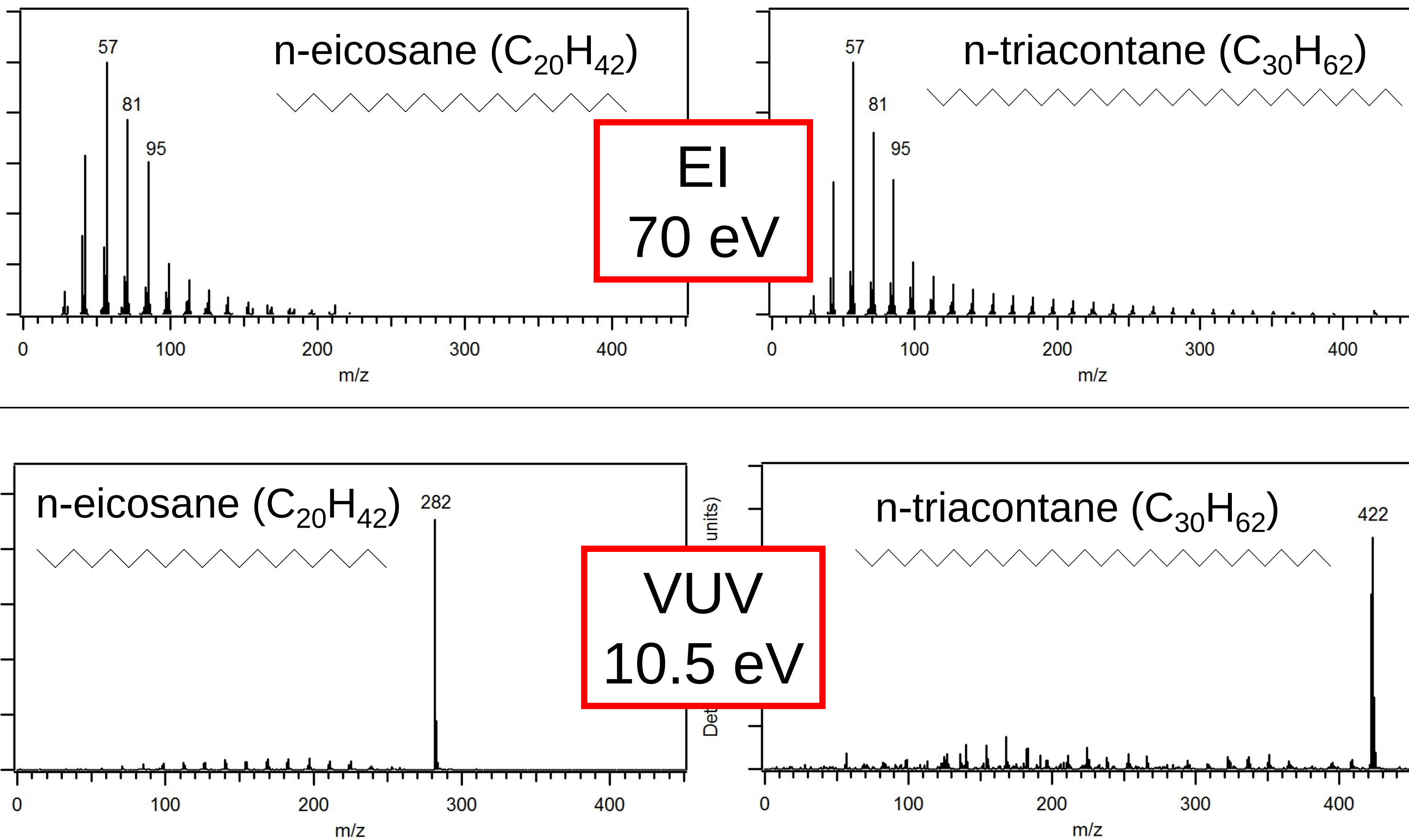
Previous GC-MS analyses of vehicular OA emissions typically identify only a small fraction (~5%) of total mass.

We analyzed tunnel OA by photo-ionization mass spectrometry using vacuum ultraviolet (VUV) photons instead of electron ionization (EI).

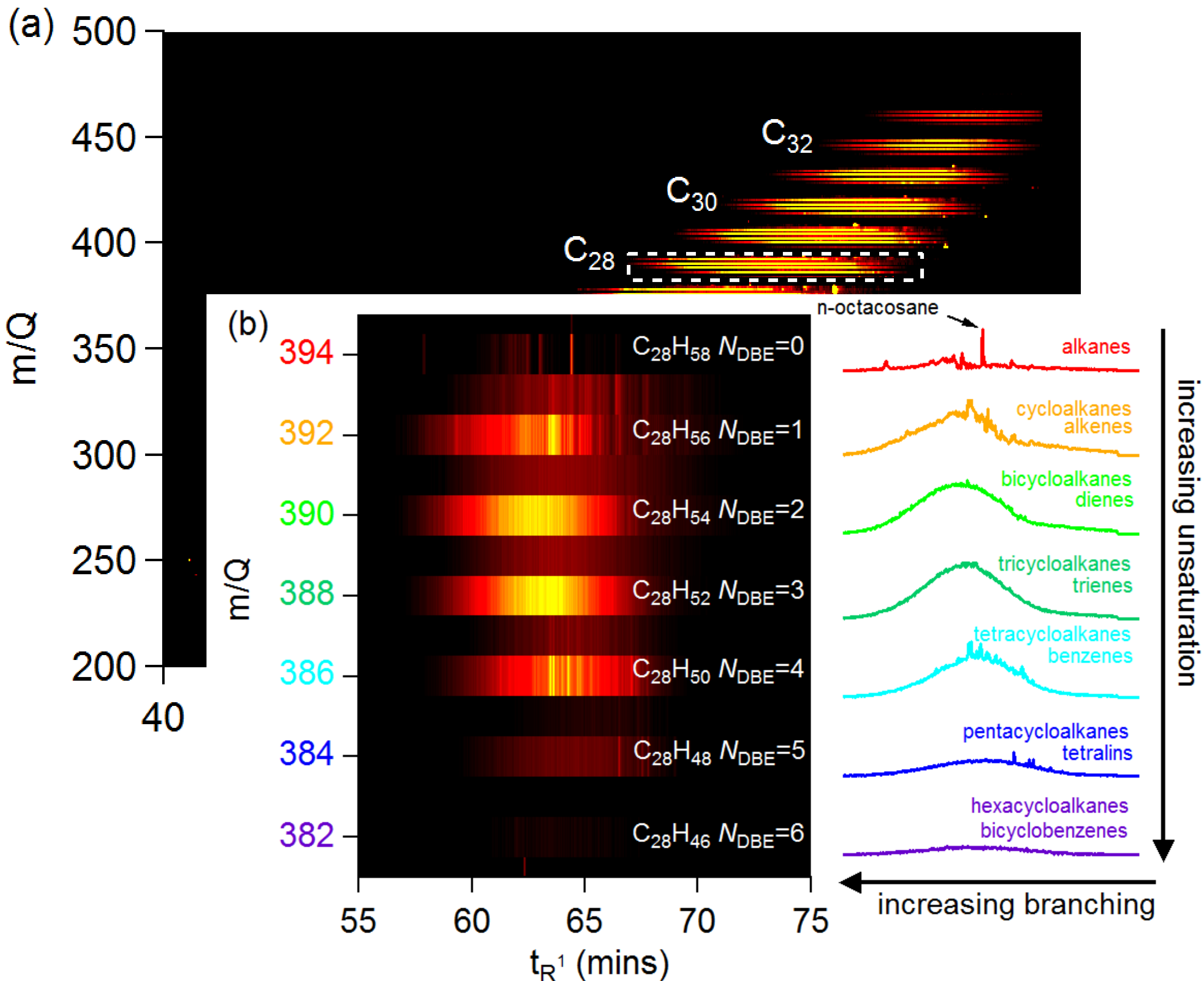


Contacts: Allen Goldstein (UCB) & Kevin Wilson (Lawrence Berkeley National Lab)

Electron Ionization (EI) versus Vacuum Ultraviolet (VUV) Ionization

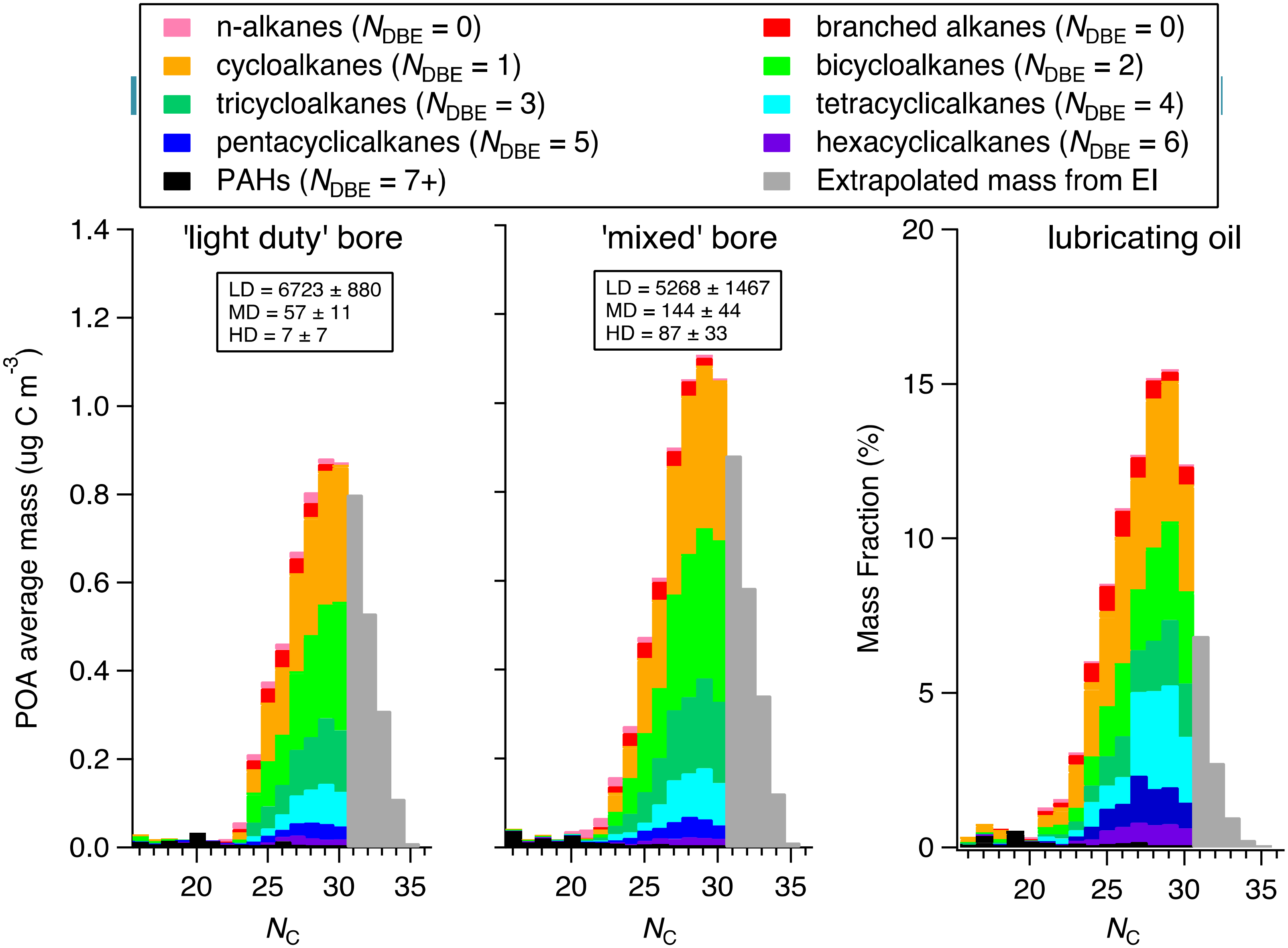


Sample GC-MS Results for Tunnel OA



Worton et al. (ES&T, in review)

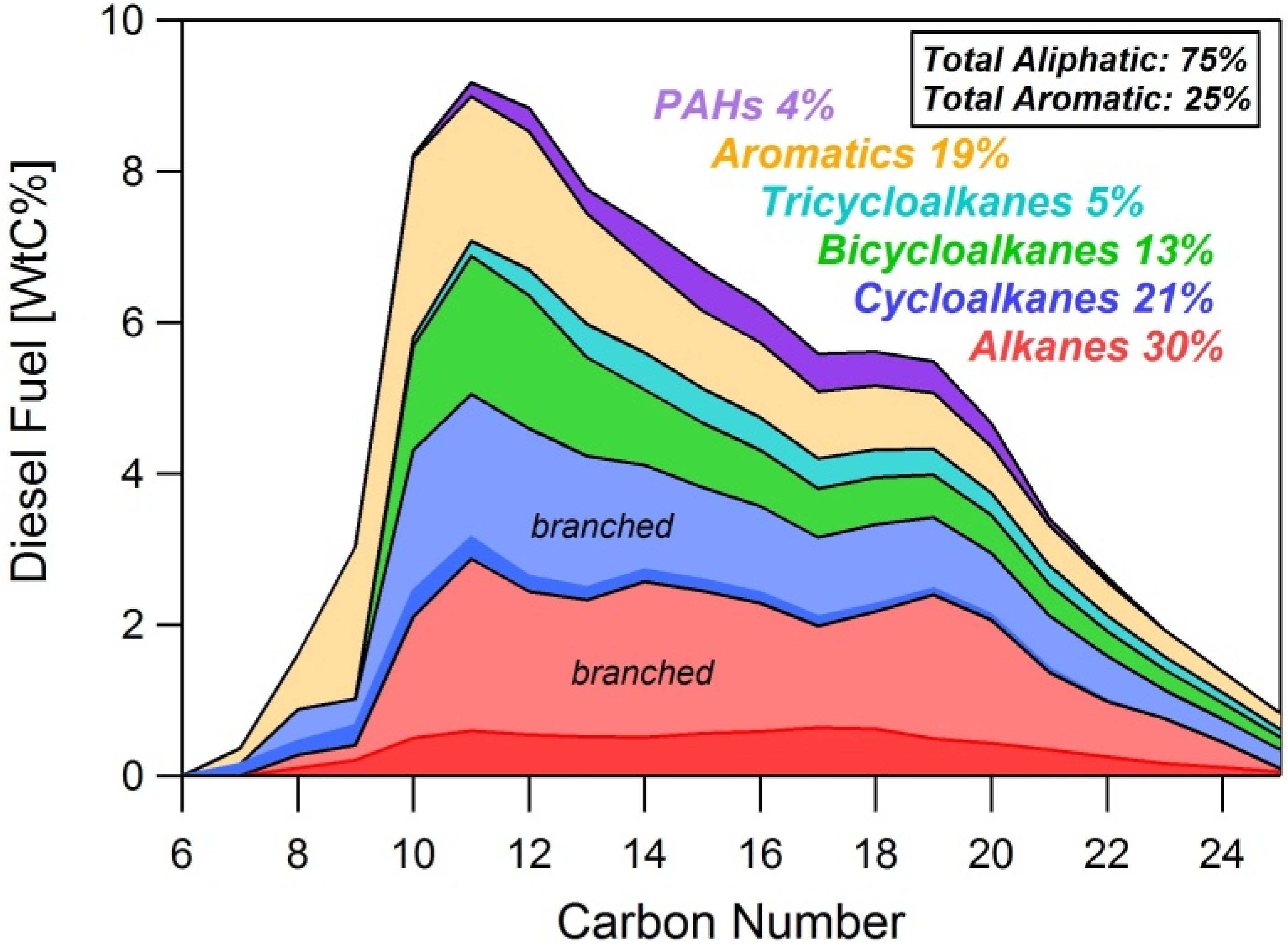
Chemical Composition of Tunnel OA



Worton et al. (ES&T, in review)

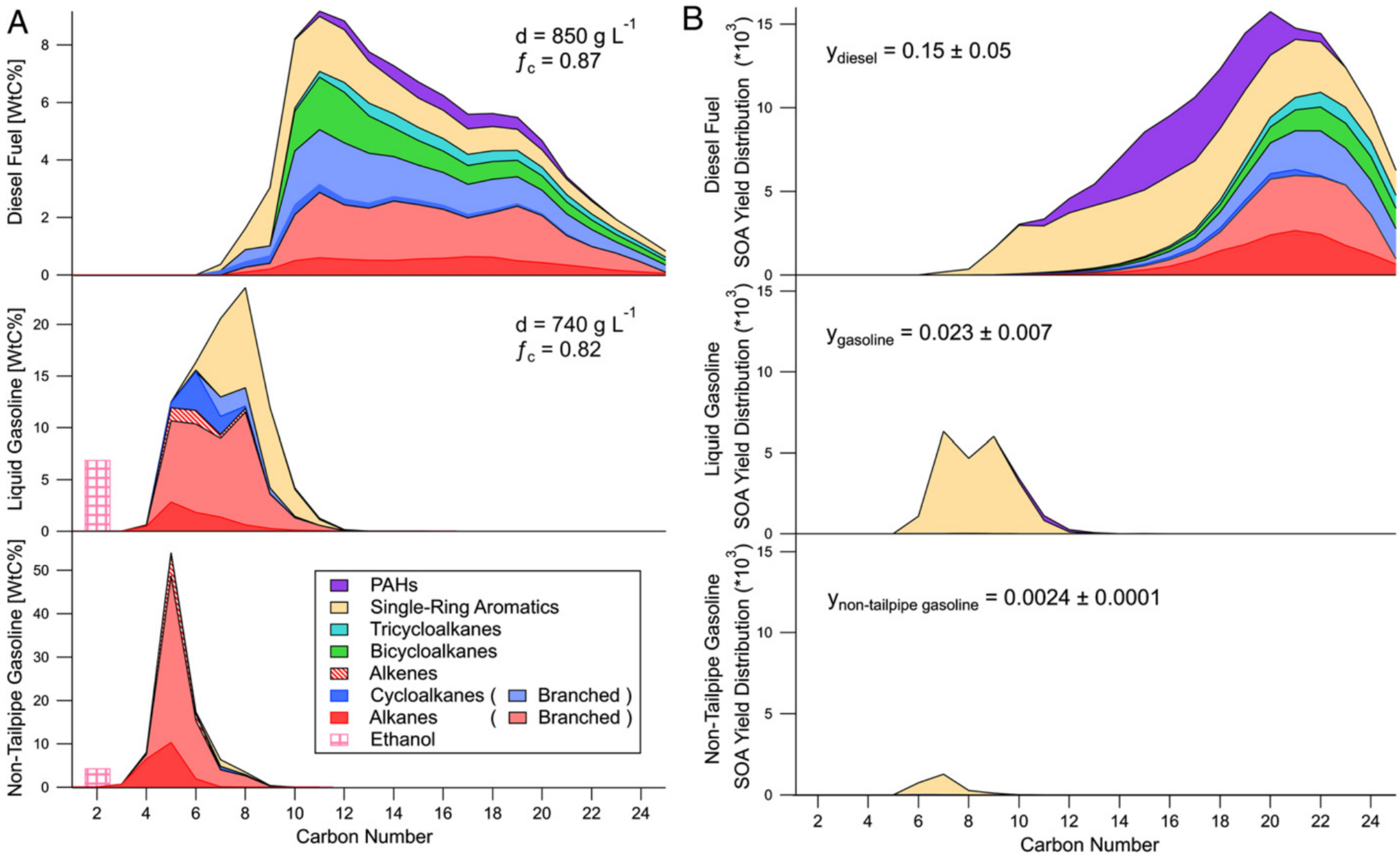
Diesel Fuel Speciation

(Gentner et al. PNAS 2012)



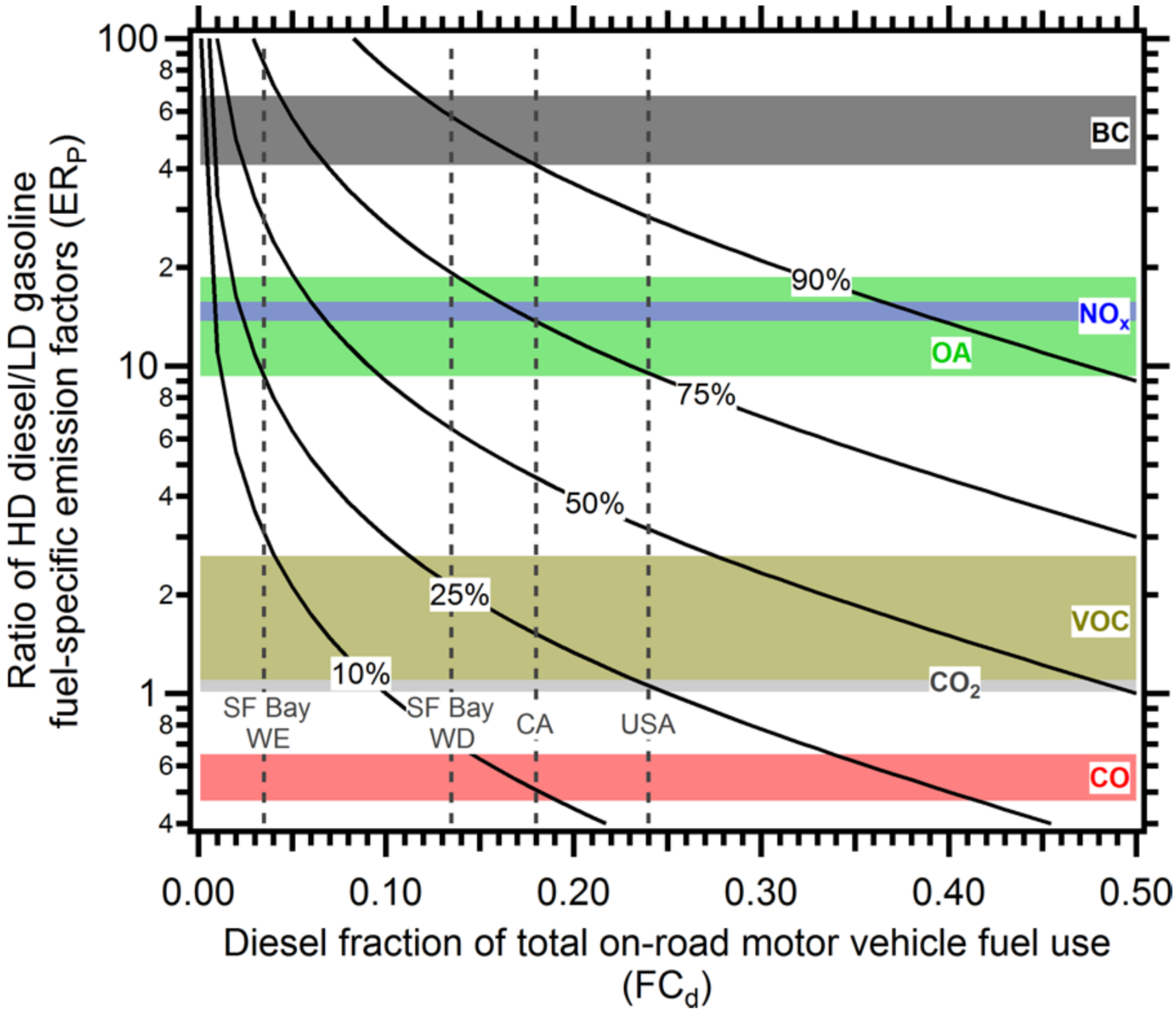
Gasoline and Diesel and SOA Yields

(Gentner et al. PNAS 2012)



Diesel Contribution to On-Road Emissions

Stabilized Running Emissions – as of 2010



Dallmann et al. (ES&T 2013)

Summary

- On-road engines are important air pollution source
  - In 2010, diesel was dominant on-road source of BC, POA, and NO_x
  - Emission factor distributions are becoming **increasingly** skewed
    - High-emitting tail of distribution responsible for majority of running emissions

- Novel approaches used to characterize emissions
  - Aerosol Mass Spectrometer (SP-AMS)
    - BC, OA, zinc and phosphorus (lube oil additives) measured in individual truck plumes
    - POA mass spectra **very similar** for gasoline & diesel engine emissions & lube oil
  - GC-MS analysis using Vacuum Ultraviolet (VUV) photons
    - EI analysis (70 eV) of diesel and lube oil leads to near-total fragmentation of parent molecular ions, and leaves most of the emitted HC mass unidentified (“UCM”)
    - use of softer (9-10.5 eV) photo-ionization preserves molecular ions; **greatly enhances** ability to identify and quantify organics present in diesel fuel and vehicle emissions
    - SOA yield per unit mass of diesel fuel emitted is ~6X higher than gasoline yield

Publications

- Dallmann et al. (2012). On-Road Measurements of Gas and Particle Phase Pollutant Emission Factors for Individual Heavy-Duty Diesel Trucks. *Environ. Sci. Technol.* **46**, 8511–8518.

- Dallmann et al. (2013). Quantifying On-Road Emissions from Gasoline-Powered Motor Vehicles: Accounting for the Presence of Medium- and Heavy-Duty Diesel Trucks. *Environ. Sci. Technol.* **47**, 13873-13881.

- Dallmann et al. (2014). Characterization of particulate matter emissions from on-road gasoline and diesel vehicles using a soot particle aerosol mass spectrometer. *Atmos. Chem. Phys. Disc.* **14**, 4007-4049.

- Gentner et al. (2012). Elucidating Secondary Organic Aerosol from Diesel and Gasoline Vehicles Through Detailed Characterization of Organic Carbon Emissions. *PNAS* **109**, 18318-18323.

Publications

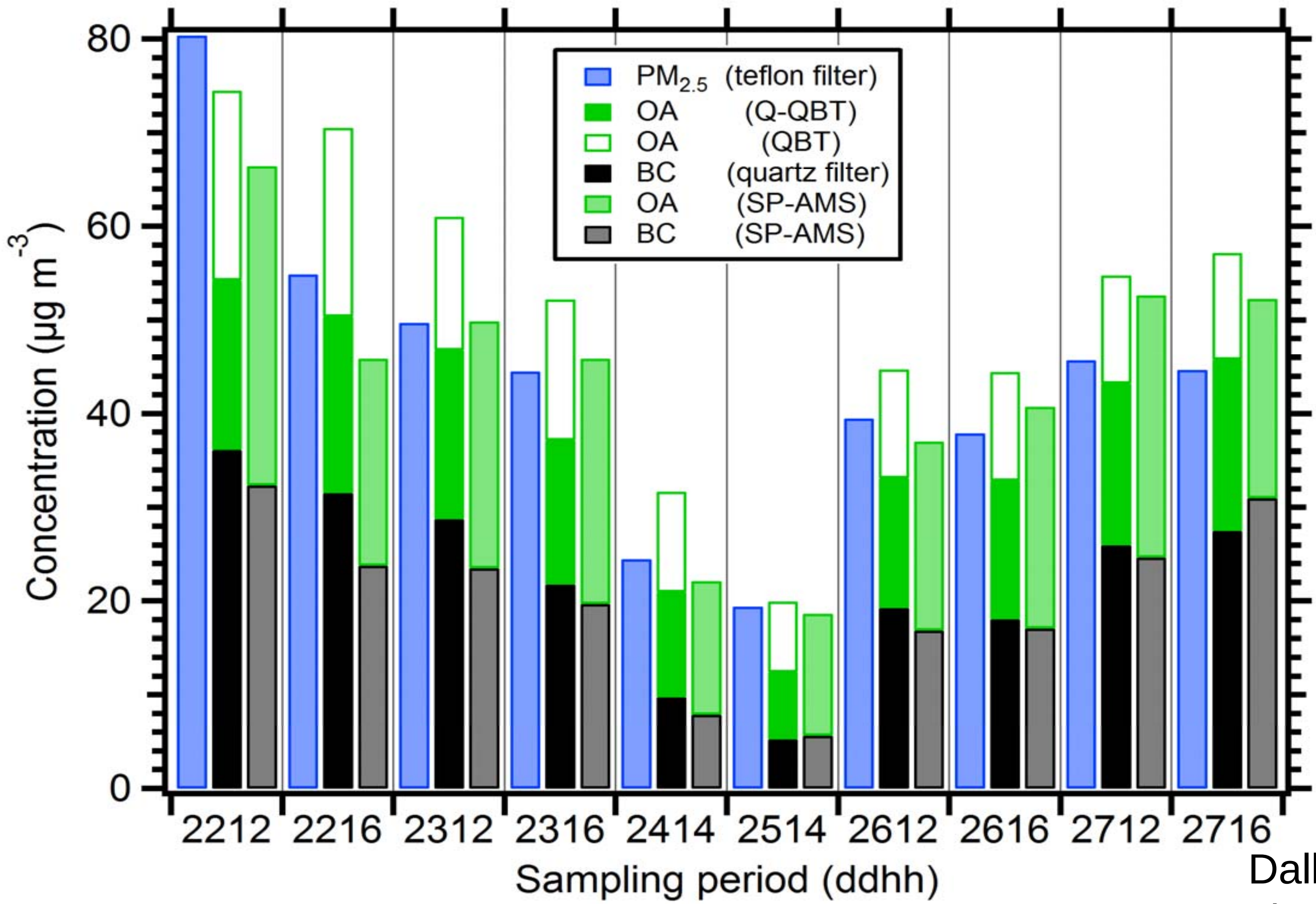
- Gentner et al. (2013). Chemical Composition of Gas-Phase Organic Carbon Emissions from Motor Vehicles and Implications for Ozone Production. *Environ. Sci. Technol.* **47**, 11837-11848.

- McDonald et al. (2012). Long-Term Trends in Nitrogen Oxide Emissions from Motor Vehicles at National, State, and Air Basin Scales. *Journal of Geophysical Research* **117**, D00V18, doi: 10.1029/2012JD018304.

- Worton et al. (2014). Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles. *Environ. Sci. Technol.*, in review.

Measured Tunnel PM Concentrations

(Teflon & Quartz Filters, SP-AMS Data)



Dallmann et al. (ACPD 2014)