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

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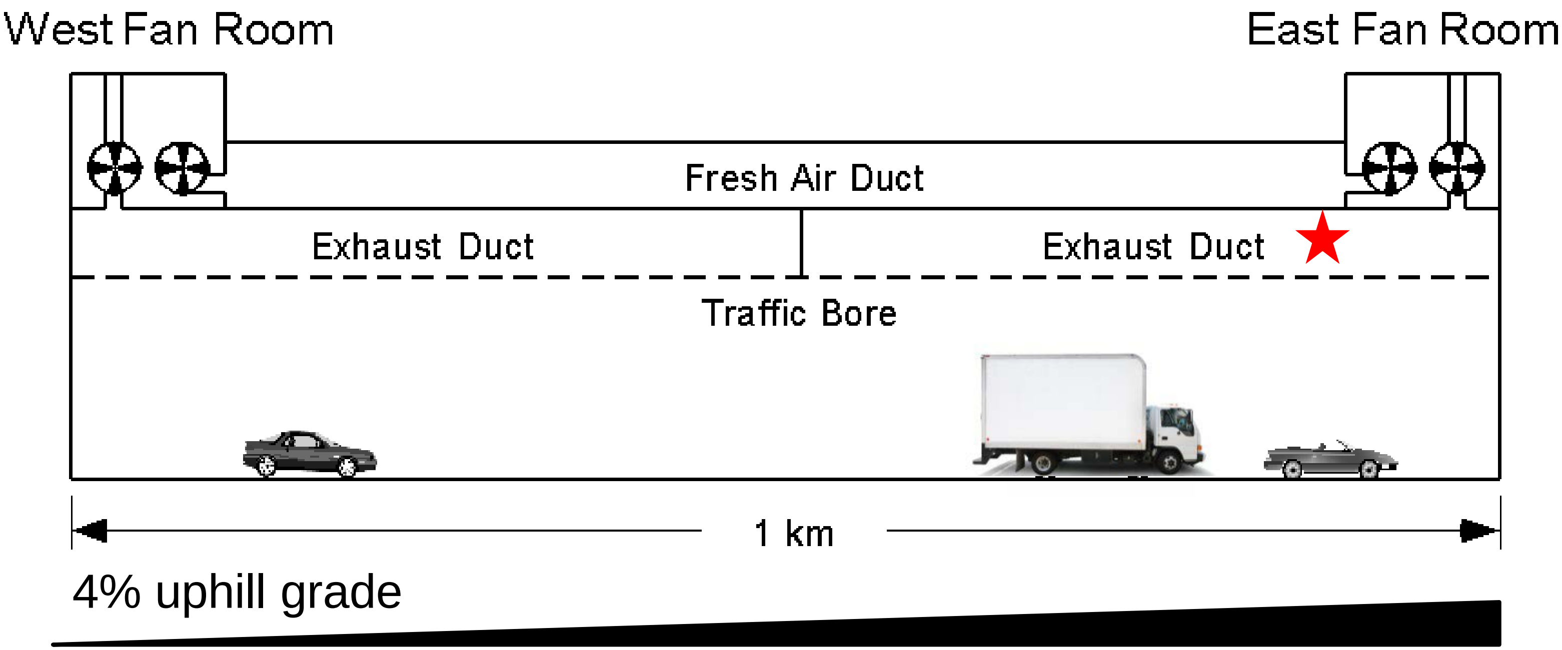
A Highway Tunnel Laboratory

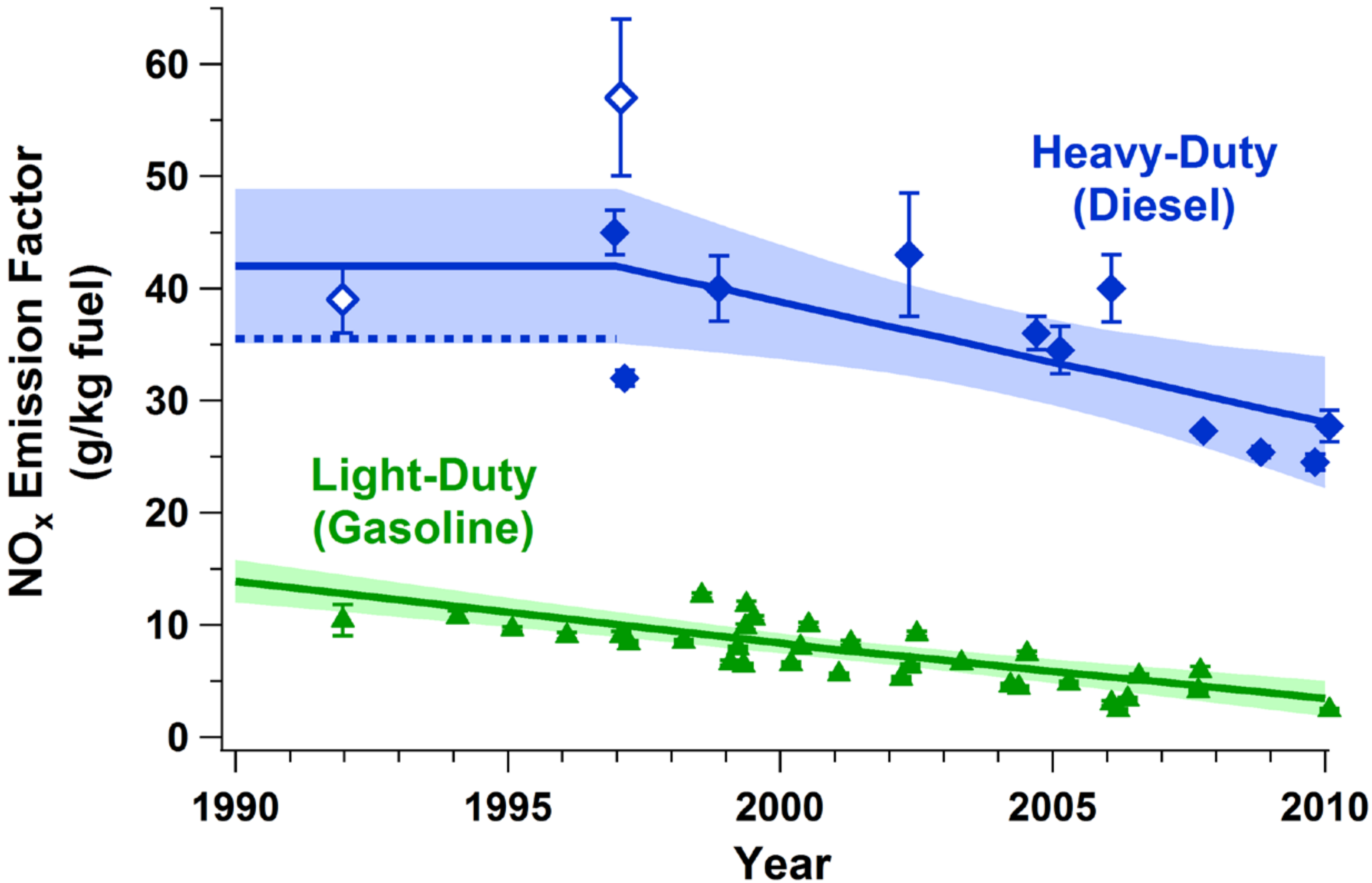
Vehicle emissions measured at Caldecott tunnel in SF Bay area:

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



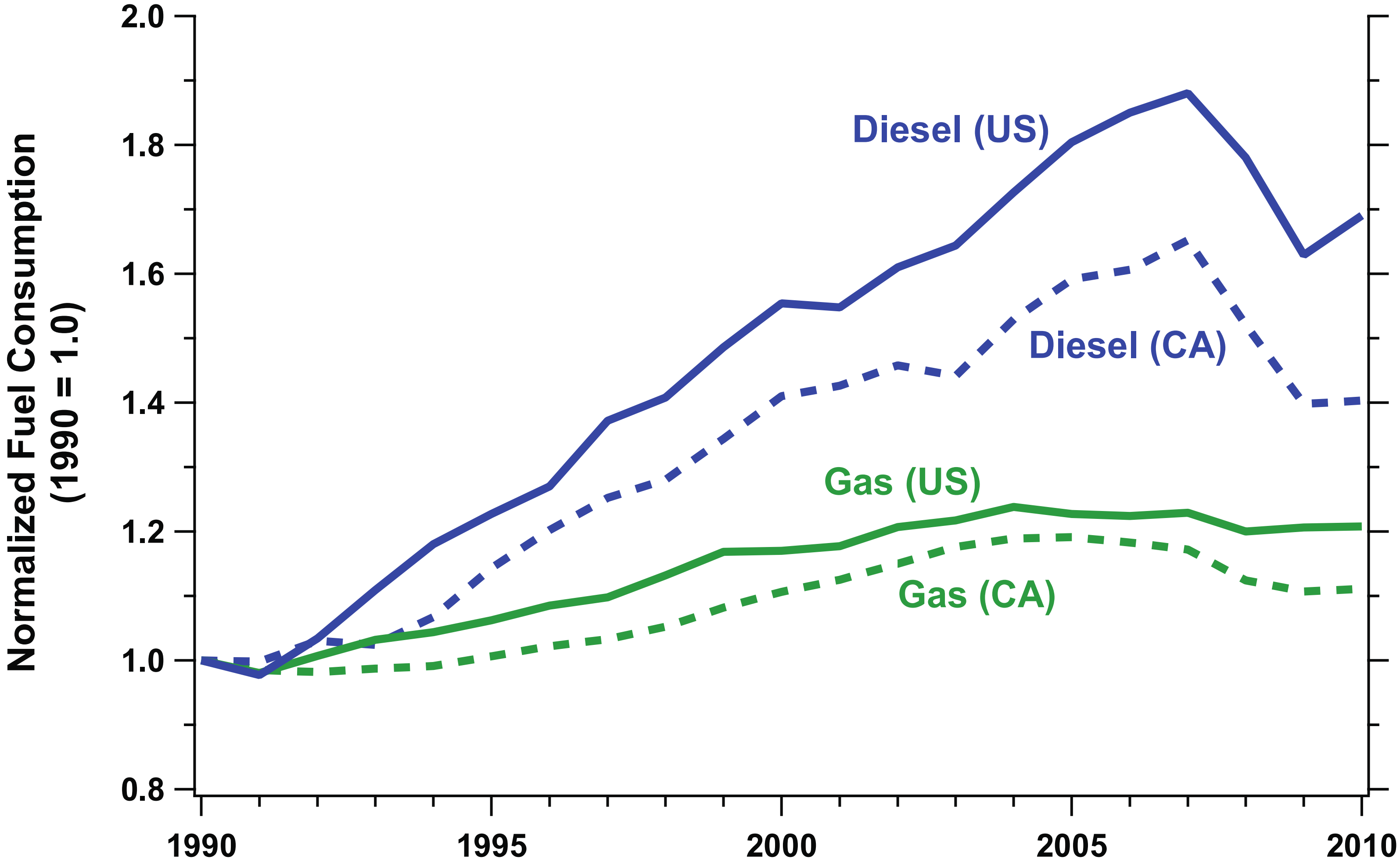
Pollutant	Tunnel Measurement Method
CO_2	Infrared absorption
Nitric Oxide (NO)	Chemiluminescense
NO_2, CO HCHO, C_2H_4	Tunable infrared laser spectroscopy
PM mass & composition	Aerosol mass spectrometer
Black Carbon (BC)	Aethalometer
Light absorption & scattering (532 nm)	Photoacoustic spectrometer and 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



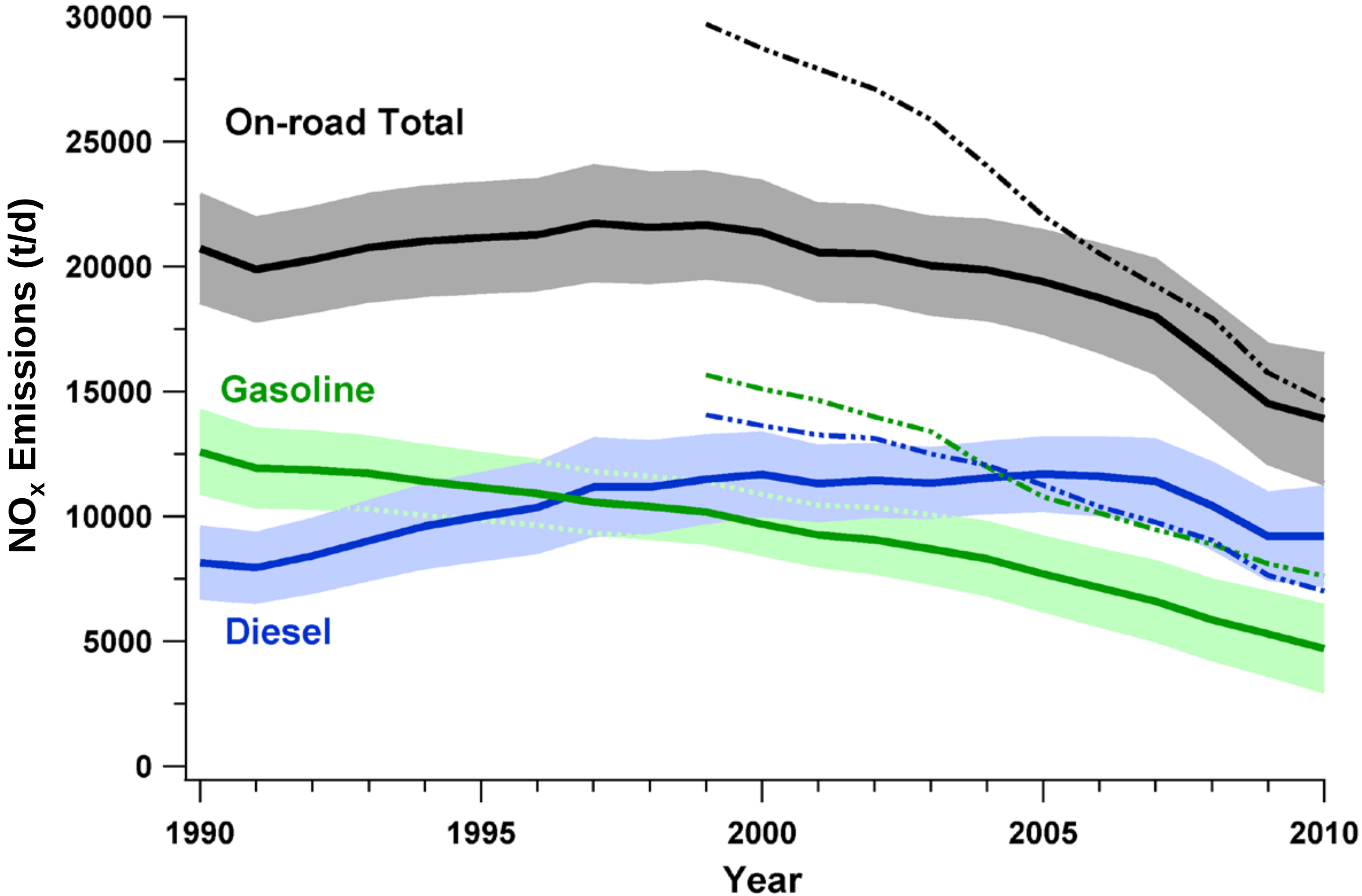
McDonald et al. (JGR 2012)

Fuel Sales Trends, 1990-2010



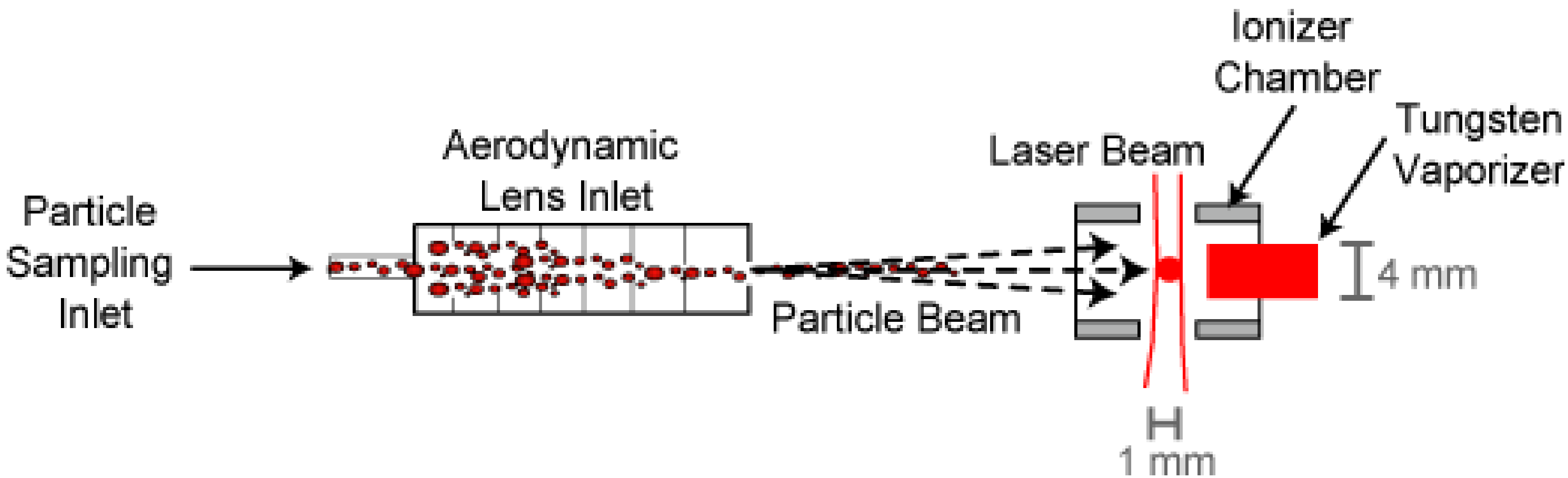
McDonald et al. (JGR 2012)

National On-Road NO_x Emission Trends



McDonald et al. (JGR 2012)

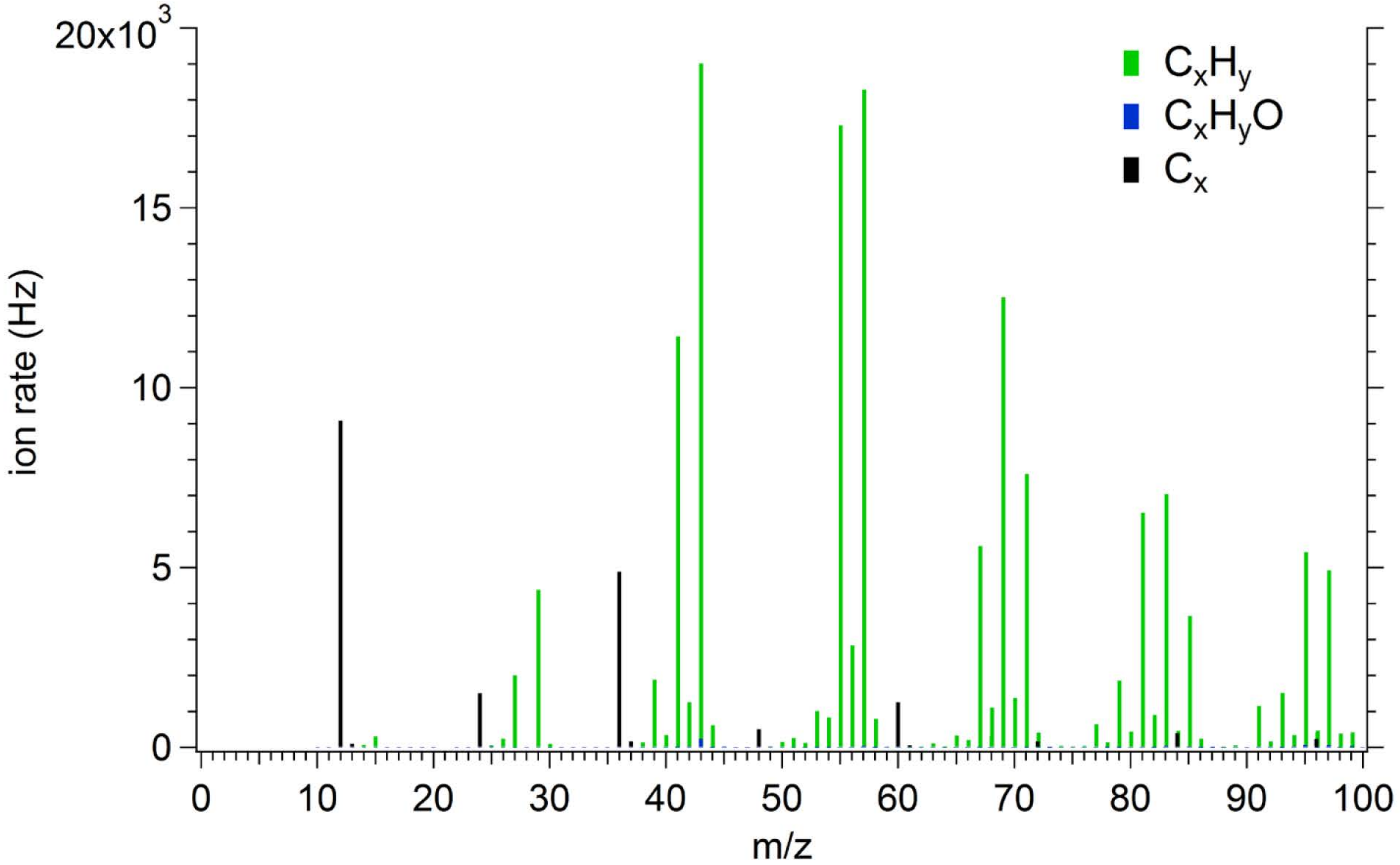
Aerosol Mass Spectrometer (SP-AMS)



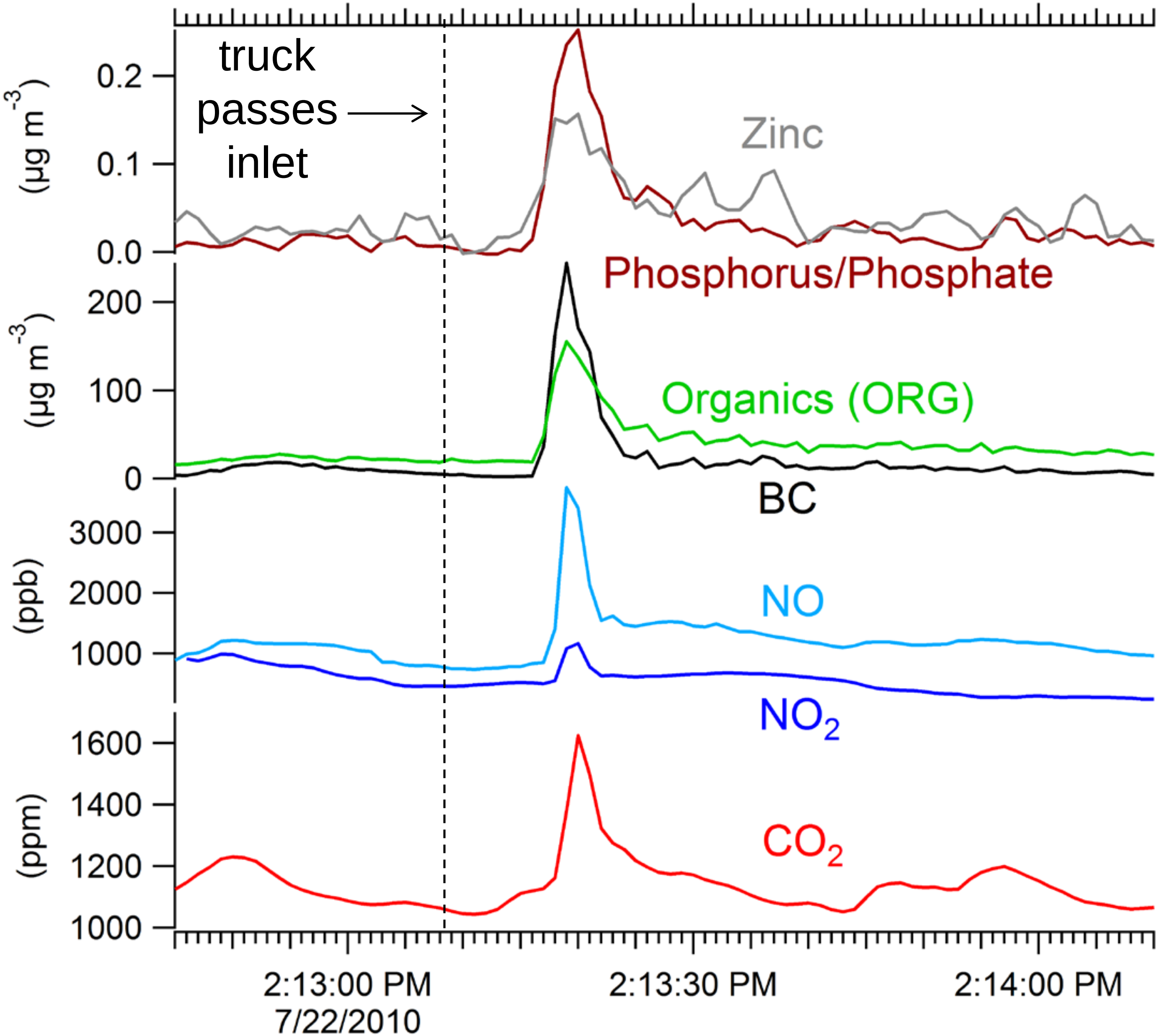
- Heated tungsten vaporizer combined with laser to vaporize organic *and* refractory aerosol (e.g., soot)
- Both vaporizers on at all times
- Operate in fast MS mode to capture individual truck plumes

Onasch et al. (AS&T 2012)

Sample AMS Data – Diesel Truck Plume



Capturing Individual Truck Exhaust Plumes

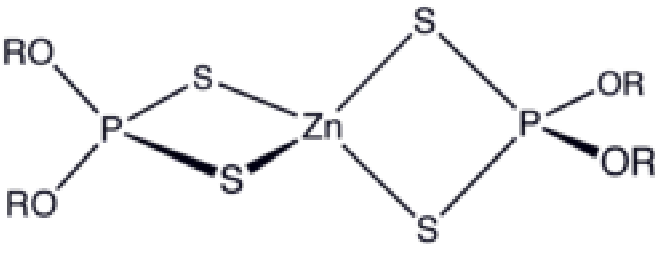


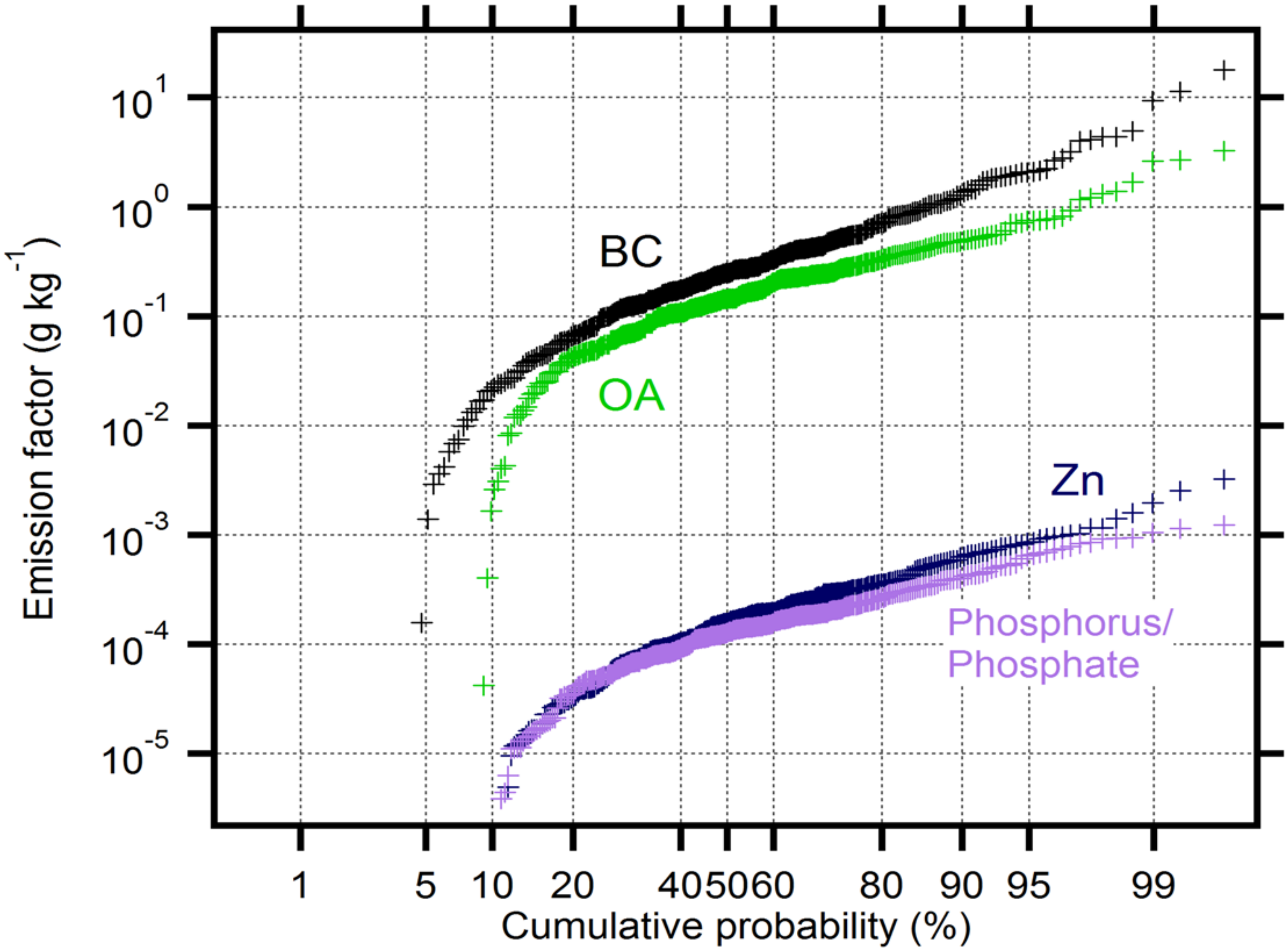
Chemical speciation of exhaust particles, including trace elements

Independent measurements of NO and NO_2

Peak in CO_2 denotes capture of exhaust plume

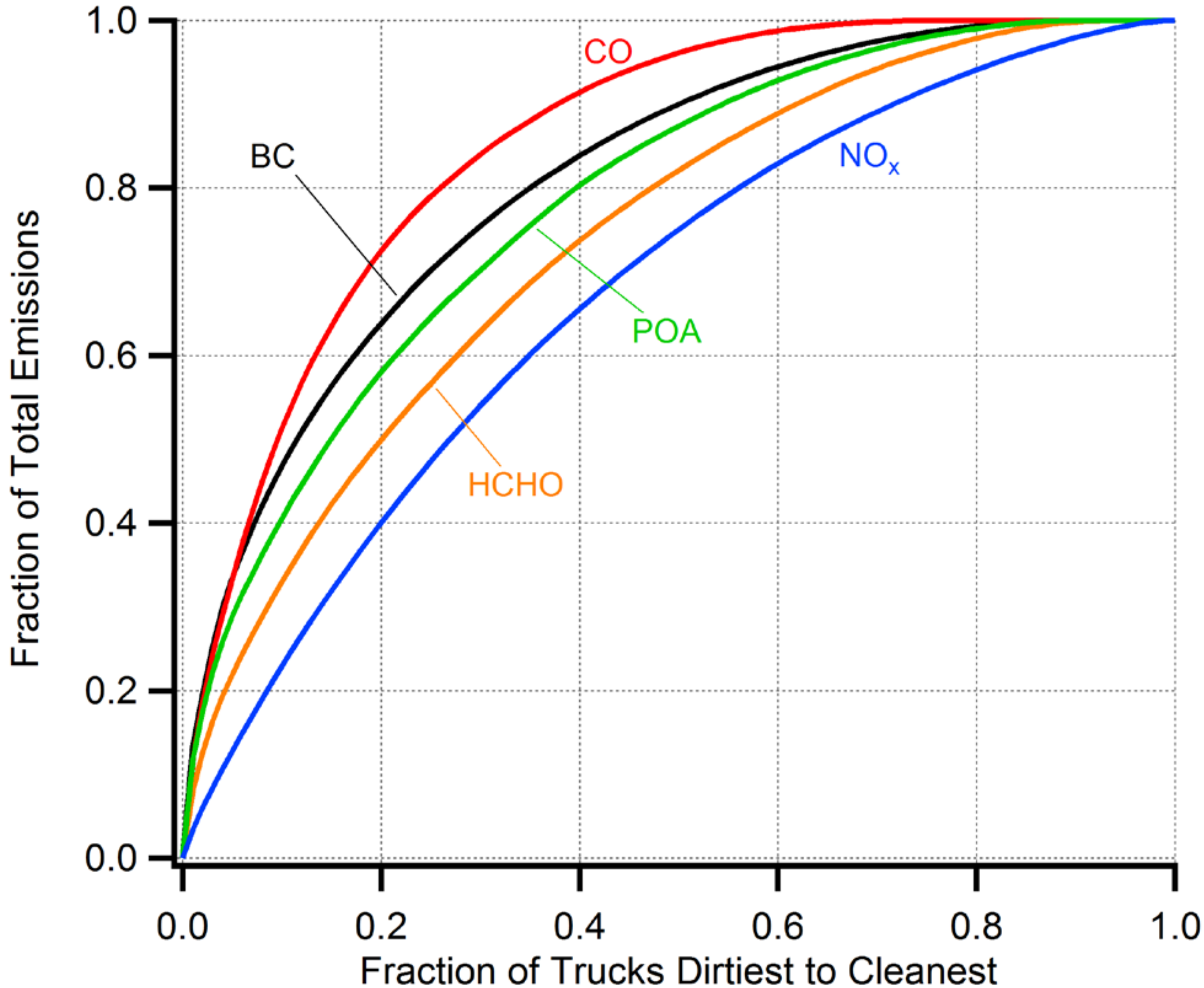
HDDT Emission Factor Distributions





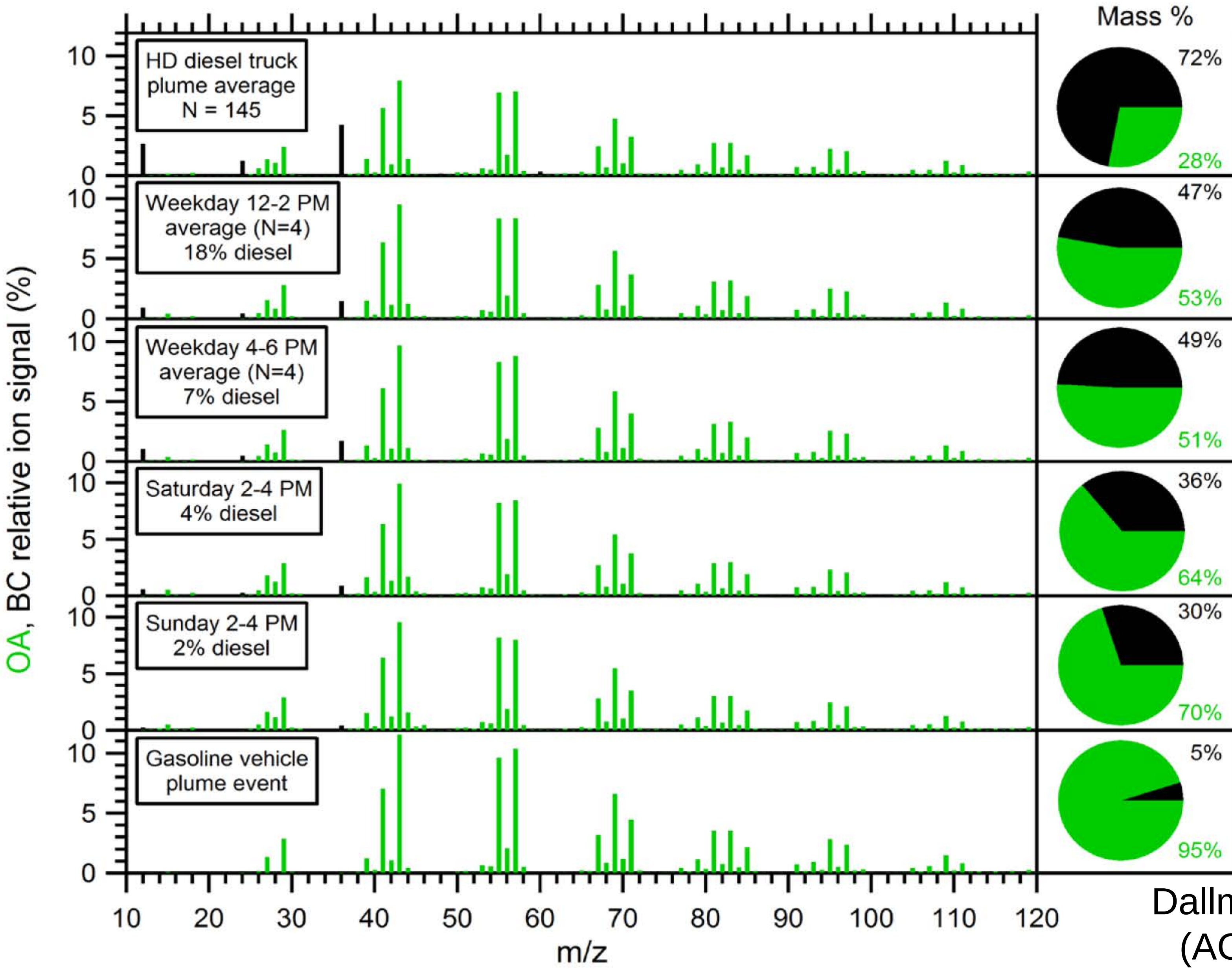
Dallmann et al. (ACP 2014)

Cumulative Contributions to Total Emissions from Heavy-Duty Diesel Trucks



Dallmann et al. (ES&T 2012)

OA mass spectra similar for Gasoline and Diesel

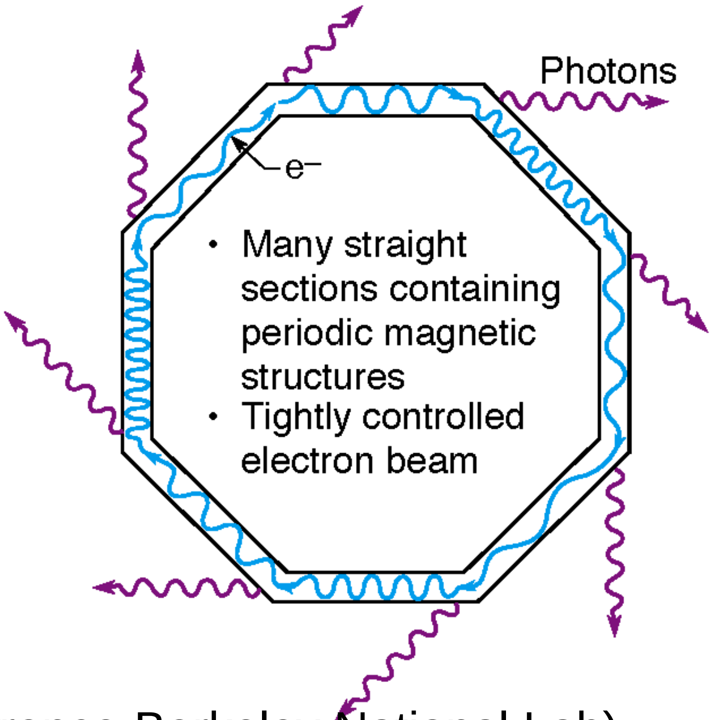


Dallmann et al. (ACP 2014)

GC-MS Analysis of Organic Compounds

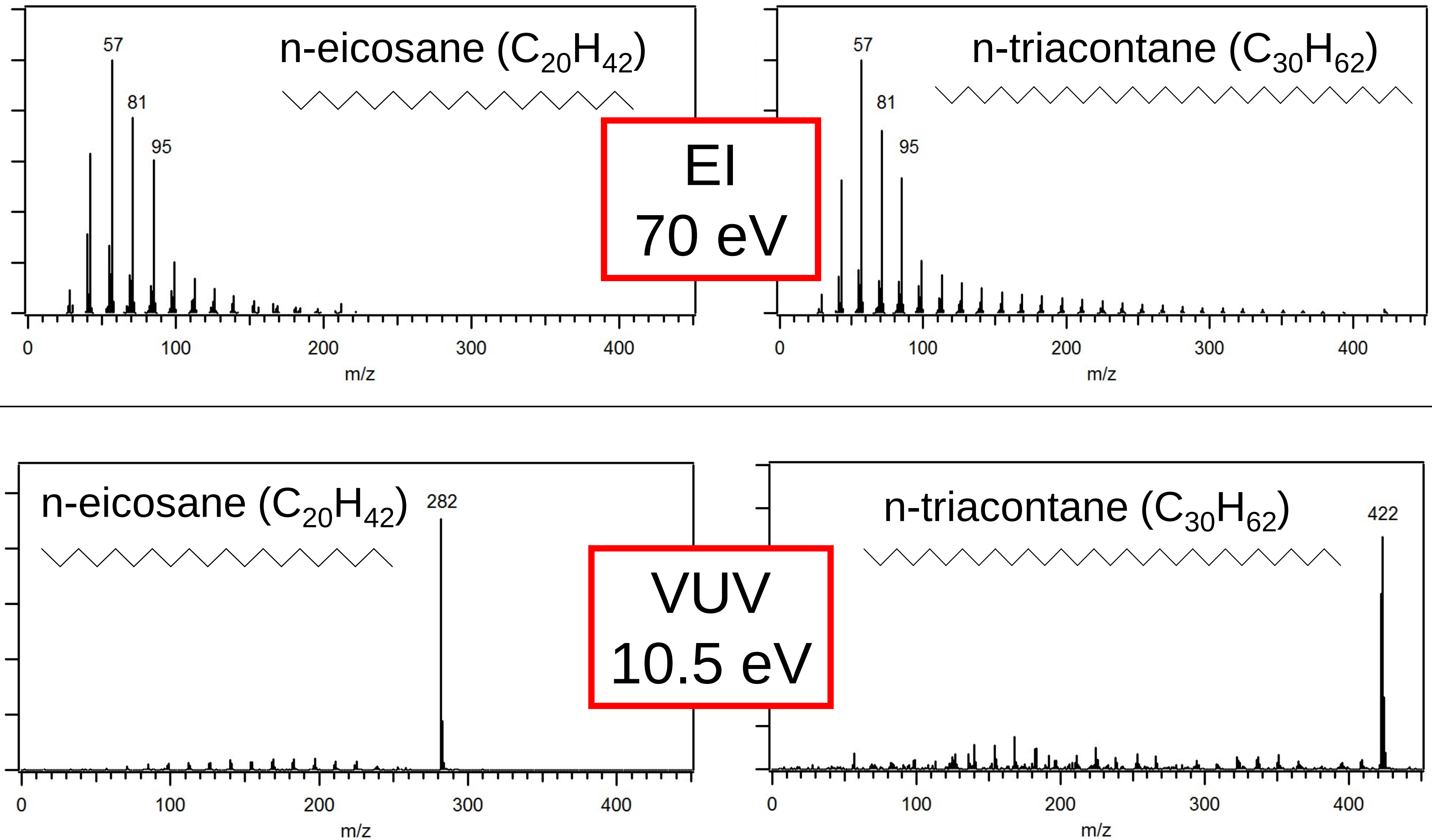
Previous GC-MS analyses of vehicular OA emissions typically identify only a small fraction (~5%) of total mass.

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

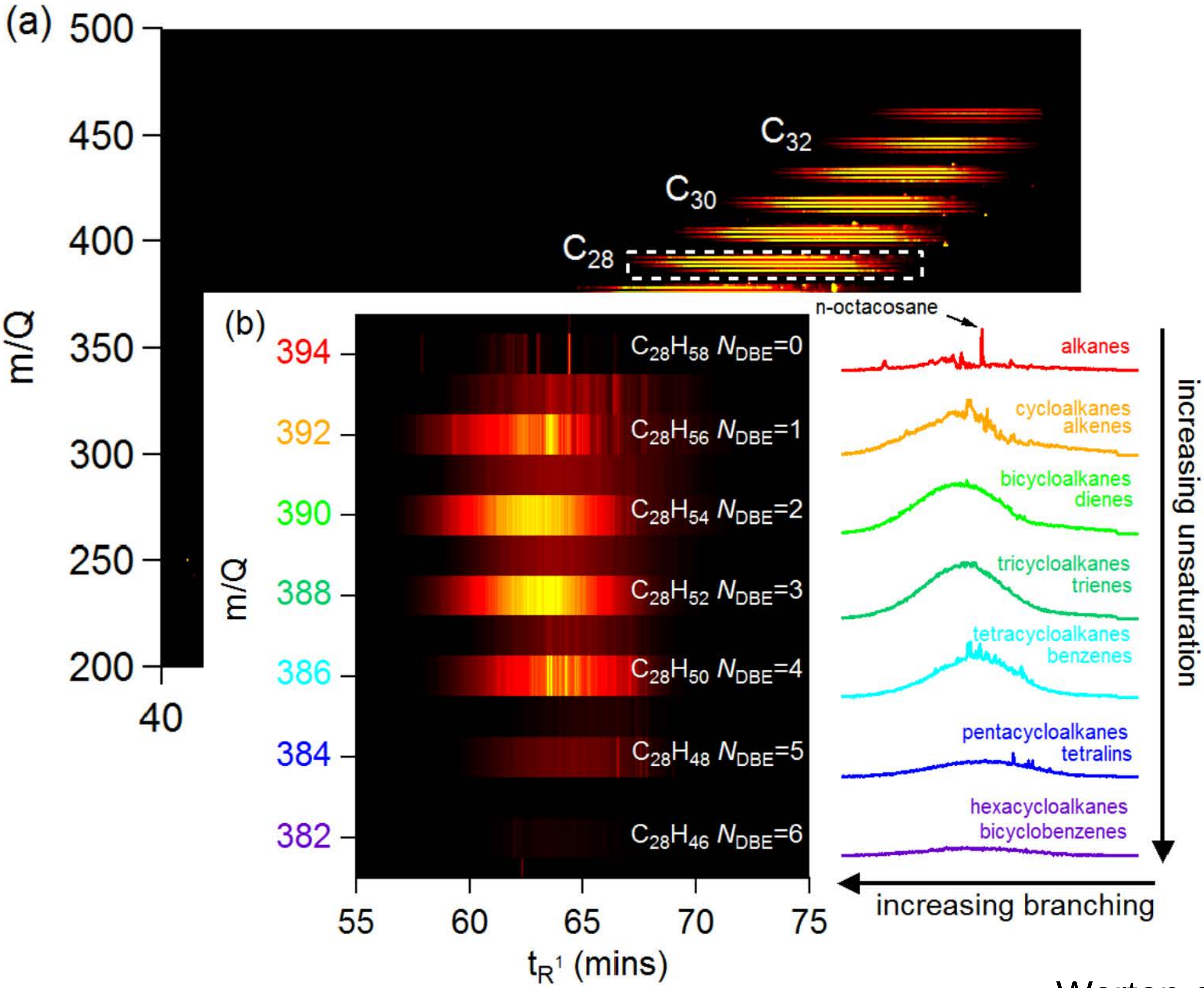


Contacts: Allen Goldstein (UCB) & Kevin Wilson (Lawrence Berkeley National Lab)

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

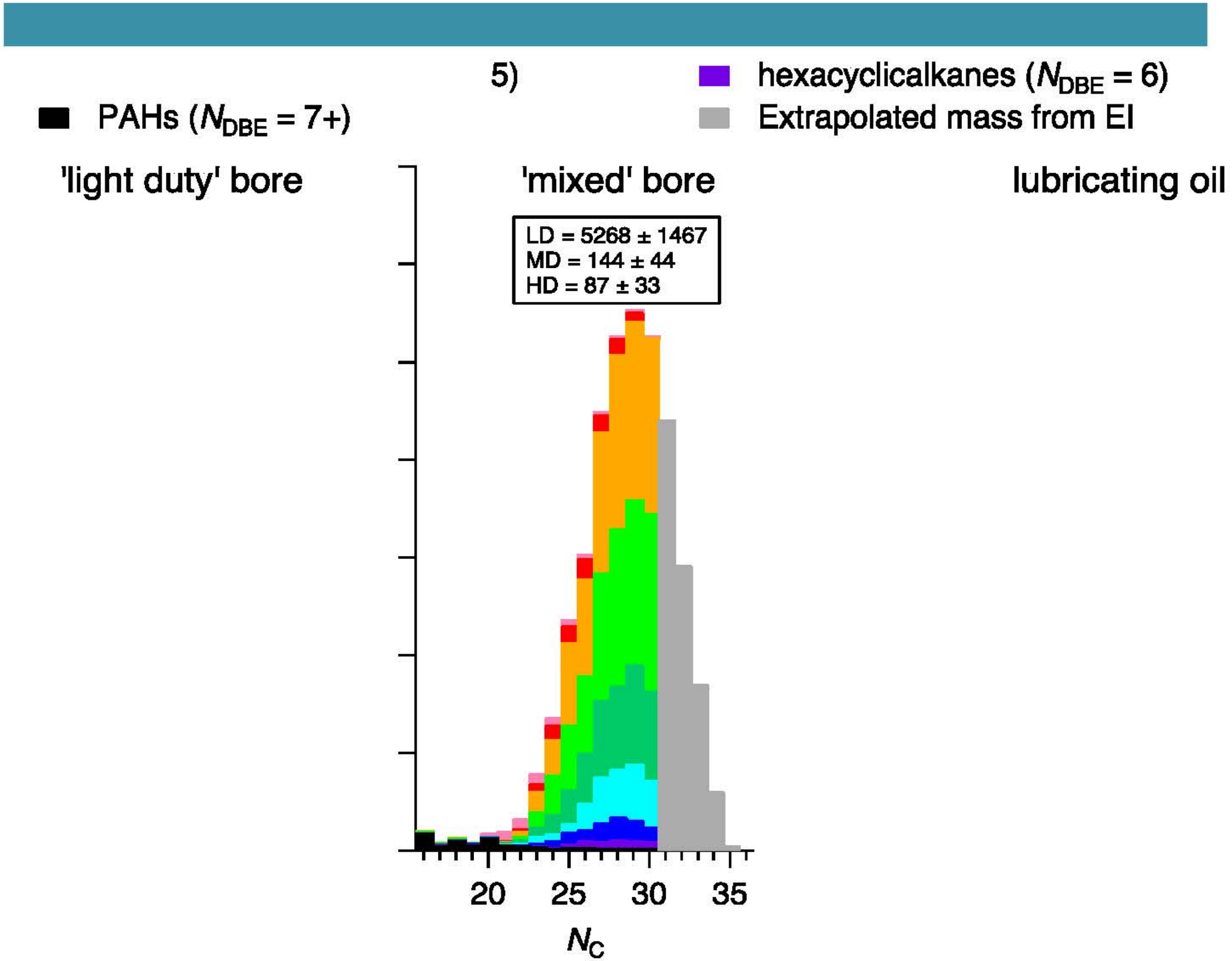


Sample GC-MS Results for Tunnel OA



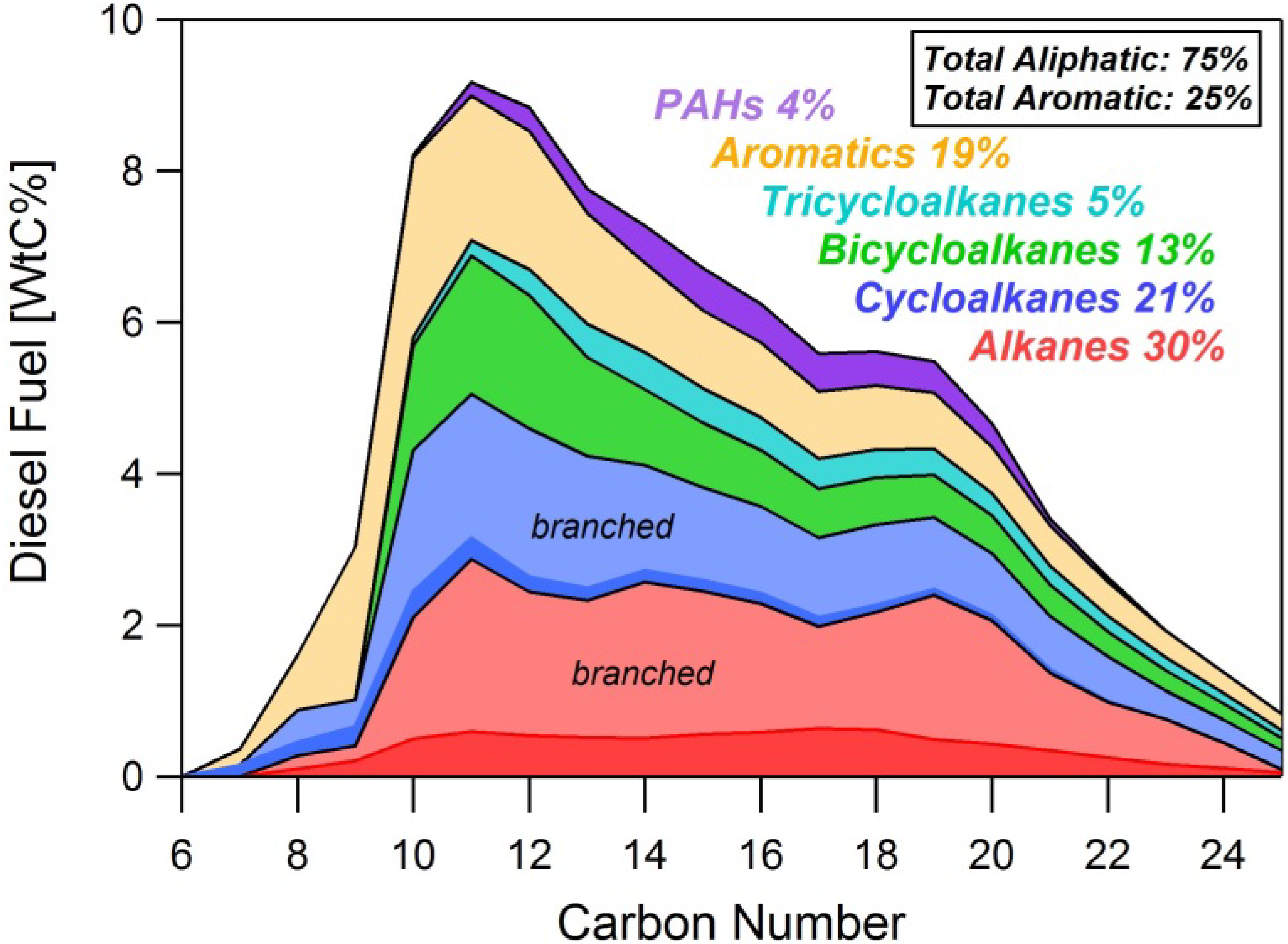
Worton et al. (ES&T 2014)

Chemical Composition of Tunnel OA



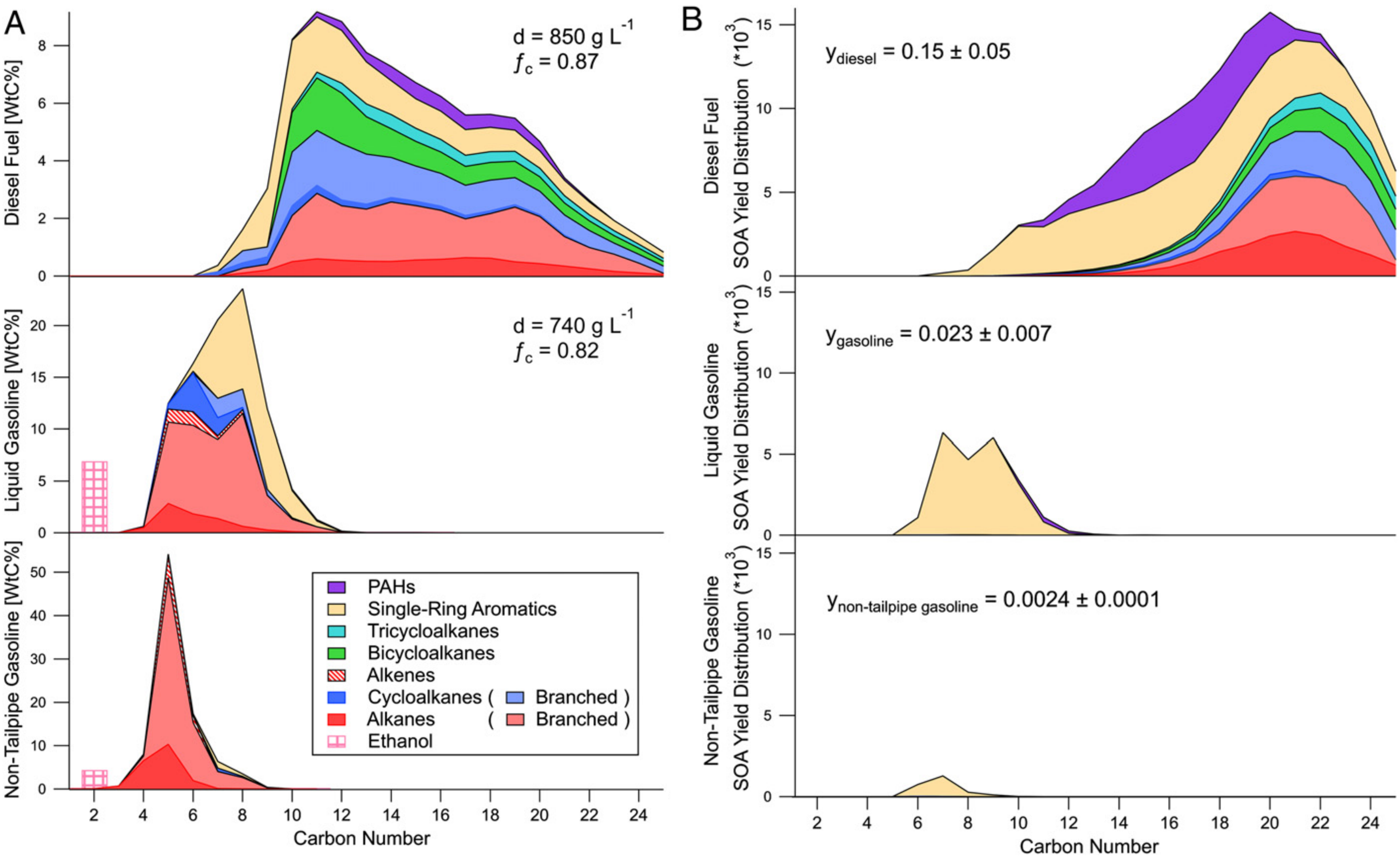
Worton et al. (ES&T 2014)

Diesel Fuel Speciation
(Gentner et al. PNAS 2012)



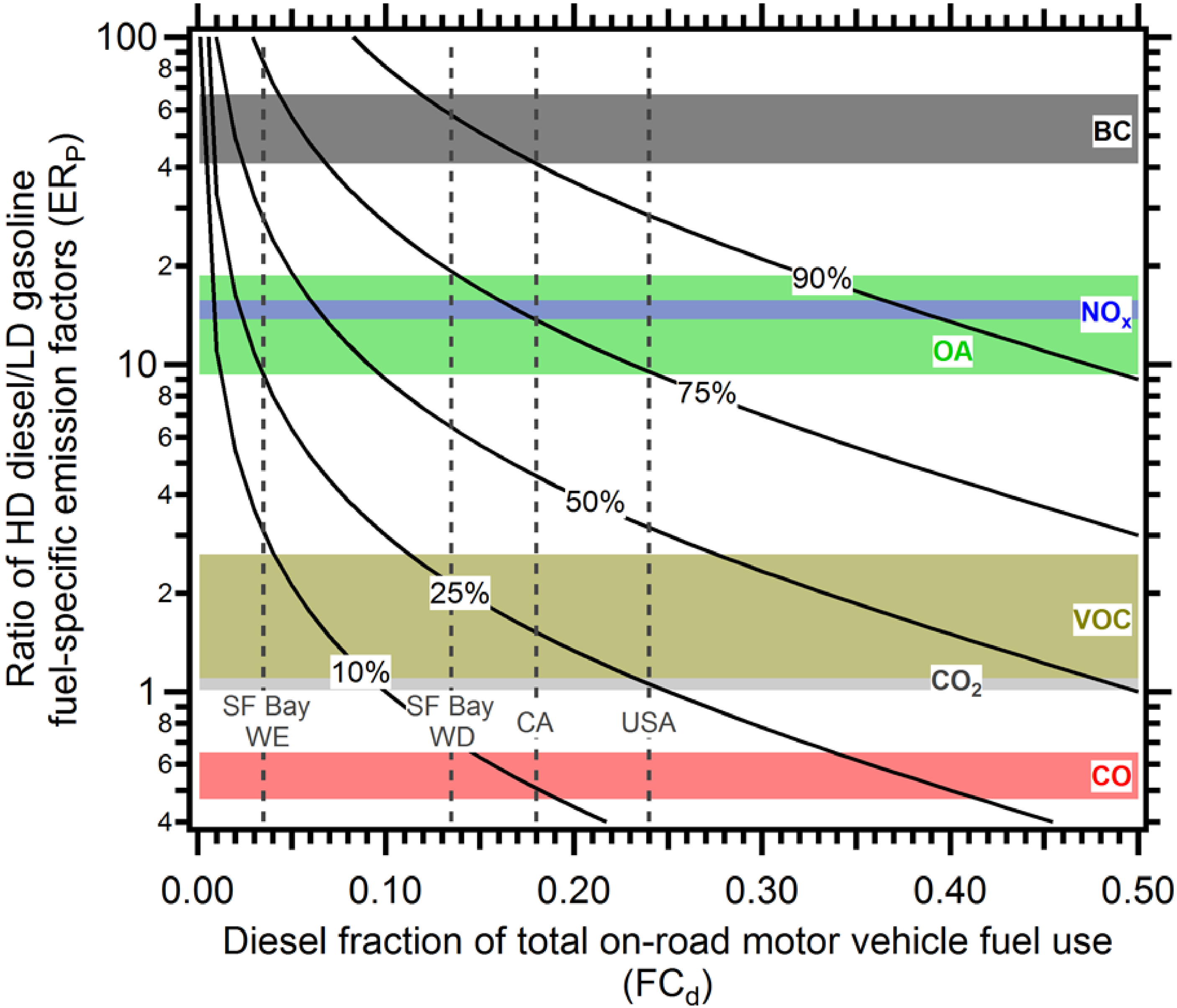
Gasoline and Diesel and SOA Yields

(Gentner et al. PNAS 2012)



Diesel Contribution to On-Road Emissions

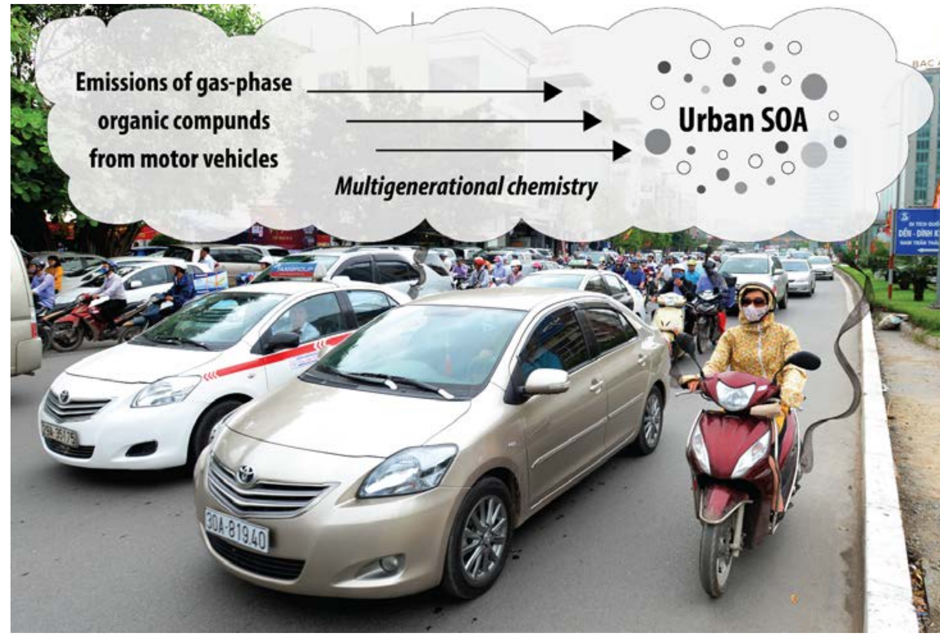
Stabilized Running Emissions – as of 2010



Dallmann et al. (ES&T 2013)

A review of urban secondary organic aerosol formation from gasoline and diesel motor vehicle emissions

Summarizes evidence, research needs, and discrepancies between top-down and bottom-up SOA estimation methods



Analyzes key inconsistencies between molecular-level understanding and regional observations

Discusses the effect of emission controls (e.g. exhaust aftertreatment technologies, fuel formulation) on SOA precursor emissions

ES&T, 2017, Drew R. Gentner, Shantanu H. Jathar, Timothy D. Gordon, Roya Bahreini, Douglas A. Day, Imad El Haddad, Patrick L. Hayes, Simone M. Pieber, Stephen M. Platt, Joost de Gouw, Allen H. Goldstein, Robert A. Harley, Jose L. Jimenez, André S. H. Prévôt, Allen L. Robinson

Key takeaways: Urban secondary organic aerosol formation from gasoline and diesel vehicle emissions

- Both gasoline and diesel vehicles are responsible for some urban SOA.
- The SOA yield of diesel exhaust in chamber studies is consistent with the SOA yield predicted from fuel components.
- SOA yields for older gasoline vehicles (pre-LEV, before 1994) are also consistent, but newer (LEV1+2) have greater observed SOA yields despite lower VOC (and IVOC) emission factors (w/ unidentified precursors).
- SOA from diesel vehicles is due to mix of aromatic AND aliphatic precursors. All explainable gasoline SOA is from aromatics.
- Aftertreatment of diesel exhaust: Diesel particulate filters (DPFs) with oxidation catalysts reduce SOA precursor emissions.
- There is no weekday/weekend variation in SOA in greater Los Angeles, so diesel trucks are determined to not be dominant contributors.

Future research priorities

Emissions

- Real-world emissions: Realistic vehicle operating modes/cycles, and the lifetime efficacy of exhaust aftertreatment technologies
- Characterize the unspeciated ~30% of LEV-1/2 gasoline emissions
- Magnitude and composition of VOC emissions and SOA yields from emerging LEV-3 vehicles (starting 2017)
- Emerging fuels and fuel reformulation

Chemistry & Modeling

- SOA yield studies on: precursor wall loses and understudied SOA precursors
- Multigenerational SOA formation after initial stages of oxidation
- Auto-oxidation of unsaturated, non-aromatic hydrocarbons
- Past and future changes in urban chemistry (incl. indirect effects of motor vehicle emissions on SOA formation chemistry)
- Modeling motor vehicle SOA with a better representation of the complex organic mixtures in vehicle emissions
  - Need comprehensive emissions data on VOCs, IVOCs, and SVOCs (diesel VOCs need to be included)

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

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.* **14**, 7585-7599.

- 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.* **48**, 3698-3706.

- Gentner et al. (2017). Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions. *Environ. Sci. Technol.* **51**, 1074-1093