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

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- UC Berkeley: Tim Dallmann, Drew Gentner, Arthur Chan, Allen Goldstein, Gabriel Isaacman, Steven DeMartini, Brian McDonald, and Dave Worton.

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A Highway Tunnel Laboratory

Vehicle emissions measured at Caldecott tunnel in SF Bay area:

![Diagram of a highway tunnel laboratory](image-url)
<table>
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<th>Pollutant</th>
<th>Tunnel Measurement Method</th>
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<td><strong>CO₂</strong></td>
<td>Infrared absorption</td>
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<td>Nitric Oxide (NO)</td>
<td>Chemiluminescence</td>
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<td>NO₂, CO HCHO, C₂H₄</td>
<td>Tunable infrared laser spectroscopy</td>
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<td>PM mass &amp; composition</td>
<td>Aerosol mass spectrometer</td>
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<td>Black Carbon (BC)</td>
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<td>Light absorption &amp; scattering (532 nm)</td>
<td>Photoacoustic spectrometer and reciprocal nephelometer</td>
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<td>Light absorption (630 nm)</td>
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<td>Light extinction (630 nm)</td>
<td>Cavity attenuation phase-shift</td>
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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

Peak in CO₂ denotes capture of exhaust plume

Chemical speciation of exhaust particles, including trace elements

Independent measurements of NO and NO₂
HDDT Emission Factor Distributions

![Graph showing emission factor distributions for different elements: BC, OA, Zn, and Phosphorus/Phosphate. The graph plots cumulative probability against emission factor on a logarithmic scale.](image)

(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

n-eicosane ($\text{C}_{20}\text{H}_{42}$)

- EI 70 eV

n-triacontane ($\text{C}_{30}\text{H}_{62}$)

- VUV 10.5 eV
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)

![Chemical Composition Diagram](image-url)

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 NOx
  - 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


Publications


Measured Tunnel PM Concentrations
(Teflon & Quartz Filters, SP-AMS Data)

Dallmann et al.
(ACPD 2014)