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

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Acknowledgments

- UC Berkeley: Tim Dallmann, Arthur Chan, 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:

West Fan Room

Fresh Air Duct

Exhaust Duct

Traffic Bore

East Fan Room

4% uphill grade

1 km
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<th>Pollutant</th>
<th>Tunnel Measurement Method</th>
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<td>$\text{CO}_2$</td>
<td>Infrared absorption</td>
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<td>Nitric Oxide (NO)</td>
<td>Chemiluminescence</td>
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<td>$\text{NO}_2$, CO, HCHO, C$_2$H$_4$</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>
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<td>Light extinction (630 nm)</td>
<td>Cavity attenuation phase-shift</td>
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</table>
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 \textit{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

![Sample AMS Data](image)
Capturing Individual Truck Exhaust Plumes

- Chemical speciation of exhaust particles, including trace elements
- Independent measurements of NO and NO₂
- Peak in CO₂ denotes capture of exhaust plume

Graph showing the concentration of various pollutants over time.
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

n-eicosane (C_{20}H_{42})

EI
70 eV

n-triacontane (C_{30}H_{62})

VUV
10.5 eV
Sample GC-MS Results for Tunnel OA

Worton et al. (ES&T 2014)
Chemical Composition of Tunnel OA

- PAHs ($N_{DBE} = 7+$)
- hexacyclic alkanes ($N_{DBE} = 6$)
- Extrapolated mass from EI

'light duty' bore

'mixed' bore

lubricating oil

Worton et al. (ES&T 2014)
Diesel Fuel Speciation
(Gentner et al. PNAS 2012)

![Graph showing the speciation of diesel fuel.](image)

- **Total Aliphatic:** 75%
- **Total Aromatic:** 25%
- PAHs: 4%
- Aromatics: 19%
- Tricycloalkanes: 5%
- Bicycloalkanes: 13%
- Cycloalkanes: 21%
- Alkanes: 30%

**Carbon Number**

**Diesel Fuel [WtC%]**
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

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 losses 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\textsubscript{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


Publications


