TRENDS AND SOURCES OF PARTICULATE MATTER EMISSIONS FROM GASOLINE AND DIESEL ENGINES

Robert Harley (harley@berkeley.edu)
Department of Civil and Environmental Engineering
University of California, Berkeley

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HEI – Effects of Fuel Composition on PM
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  - US Environmental Protection Agency (STAR Grant RD834553)
  - California Air Resources Board
  - Bay Area Air Quality Management District
# Categories of Vehicle-Related PM

<table>
<thead>
<tr>
<th>PM Constituent</th>
<th>Gasoline Engines</th>
<th>Diesel Engines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Carbon (BC), aka “soot”</td>
<td>Rich-running older engines &amp; cold start. New GDI engines</td>
<td>Diesel fuel pyrolysis (spray combustion, fuel and air not premixed)</td>
</tr>
<tr>
<td>Primary Organic Aerosol (POA) – directly emitted in exhaust</td>
<td><strong>Lubricating oil</strong>&lt;br&gt;Heavy PAH (5-6 rings) in gasoline</td>
<td><strong>Lubricating oil</strong>&lt;br&gt;Heavy HC in diesel fuel</td>
</tr>
<tr>
<td>Secondary Organic Aerosol (SOA) – atmospheric oxidation of emitted gas-phase hydrocarbons</td>
<td>Aromatic HC</td>
<td>Aromatics, heavy HC</td>
</tr>
</tbody>
</table>
Long-Term Emission Trends

- Engine activity based on volume of fuel used
  - On-road (taxable) gasoline & diesel from FHWA
  - Off-road fuel sales from EIA surveys of fuel wholesalers, broken down by end user category

- Emission factors from on-road measurements
  - Highway tunnels, roadside remote sensing
  - Normalize pollutants to CO$_2$ to get emission factors in g/kg units (mass pollutant emitted per mass fuel)
  - Use CO as basis for estimating other LDV emissions
Trends in Gasoline & Fuel Oil Sales
(FHWA and EIA data for California)

McDonald et al. (ES&T 2015)
Heavy-Duty Diesel PM Emissions
(Highway Tunnel Measurements)

McDonald et al. (ES&T 2015)

PM EF (g kg⁻¹ fuel)

Caldecott Tunnel Concentration
(µg m⁻³ truck⁻¹ h⁻¹)

← 0.1 g/hp-hr
(1994-2006 engines)

McDonald et al. (ES&T 2015)
Black Carbon (BC) Emission Trends
(Los Angeles / South Coast Air Basin)

McDonald et al. (ES&T 2015)
Light-Duty Gasoline CO Emissions
(Highway Tunnel & Remote Sensing Measurements)

3.4 g/mile

McDonald et al. (ES&T 2015)
Organic Aerosol Trends
(Los Angeles / South Coast Air Basin)

McDonald et al. (ES&T 2015)
GC-MS Speciation Analysis
What is the Origin of Vehicular OA Emissions?

Use vacuum ultraviolet (VUV) photons for photo-ionization mass spectrometry of organic molecules in fuels, oil & OA.

Advanced Light Source:
A bright, laser-like, tunable source of ultraviolet radiation and X-rays.

Advanced Light Source (ALS) at Lawrence Berkeley National Lab
Past work on speciating primary organic aerosol (POA) has resolved ~5% of total OA mass
- n-alkanes, PAH, hopanes, steranes
- The rest (95%) is unknown “unresolved complex mixture”

This work provides much more complete speciation for diesel fuel, lube oil, and POA emissions
- Directly measure rather than infer composition

Key advance is use of softer (VUV) ionization
- Minimize fragmentation of parent ions in the analysis
Electron Impact (EI) versus Vacuum Ultraviolet (VUV) Ionization

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

EI 70 eV

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

EI 70 eV

VUV 10.5 eV
Given the contributions of C9–11 aromatic species to SOA formation from gasoline and diesel vehicles, it is important that they are better represented in explicit traditional SOA models or the extension of volatility basis set modeling to include the 107 and 108 μg·m⁻³ effective saturation concentration (C°) bins that fall in the VOC range (SI Appendix, Fig. S6) (5, 19, 22). For recent urban studies, we scaled up traditional compound-explicit SOA models (without the volatility basis set) to include the missing 20% to 30% of gasoline SOA and contributions from diesel (assuming 15% diesel fuel use) and calculated a fivefold increase in modeled SOA from vehicular exhaust. Such an inclusion dramatically improves model closure, which has typically underestimated SOA in urban regions by 80% to 90% (19), but additional contributions from other sources of SOA precursors remain critical to model all observed SOA. Further chamber and modeling studies on SOA yields of aromatics with nine or more carbon atoms are important to reduce uncertainties in the SOA-forming potential of gasoline and diesel exhaust emissions and their overall contribution to SOA in urban regions.

### Table 1. Distribution of mass and SOA potential by chemical class for diesel exhaust, gasoline exhaust, and nontailpipe gasoline emissions.

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Weight by carbon, wtC%</th>
<th>Potential SOA formation, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diesel exhaust</strong></td>
<td>68 ± 8</td>
<td>58 ± 28</td>
</tr>
<tr>
<td><strong>Gasoline exhaust</strong></td>
<td>5 ± 44</td>
<td>7 ± 40</td>
</tr>
<tr>
<td><strong>Non-tailpipe gasoline</strong></td>
<td>5 ± 44</td>
<td>7 ± 40</td>
</tr>
<tr>
<td><strong>Total aliphatic</strong></td>
<td>68 ± 8</td>
<td>58 ± 28</td>
</tr>
<tr>
<td><strong>Straight-chain alkanes</strong></td>
<td>7 ± 1</td>
<td>7.7 ± 0.3</td>
</tr>
<tr>
<td><strong>Branched alkanes</strong></td>
<td>23 ± 2</td>
<td>40 ± 16</td>
</tr>
<tr>
<td><strong>Cycloalkanes (single straight alkyl chain)</strong></td>
<td>2.5 ± 0.2</td>
<td>4.3 ± 0.1</td>
</tr>
<tr>
<td><strong>Cycloalkanes [branched/multiple alkyl chain(s)]</strong></td>
<td>18 ± 2</td>
<td>6.2 ± 0.3</td>
</tr>
<tr>
<td><strong>Bicycloalkanes</strong></td>
<td>13 ± 10</td>
<td>0 ± 6.2</td>
</tr>
<tr>
<td><strong>Tricycloalkanes</strong></td>
<td>4.8 ± 0.6</td>
<td>0 ± 4.3</td>
</tr>
<tr>
<td><strong>Single-ring aromatics</strong></td>
<td>19 ± 2</td>
<td>29 ± 12</td>
</tr>
<tr>
<td><strong>Polycyclic aromatic compounds</strong></td>
<td>4 ± 2</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td><strong>Alkenes (straight, branched, cyclic)</strong></td>
<td>0 ± 0.3</td>
<td>7.4 ± 0.3</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td>0 ± 6.9</td>
<td>4.4 ± 0.4</td>
</tr>
</tbody>
</table>

The wt% by total mass for each source can be found in the SI Appendix, Table S2.

**Gentner et al. (PNAS, 2012)**

**GASOLINE HEADSPACE VAPOR SPECIATION**

**LIQUID GASOLINE SPECIATION (CA summer 2010)**

**DIESEL FUEL SPECIATION (CA summer 2010)**

**SI Appendix**

**Fig. 2.** Distribution of mass (A) and SOA formation potential (in μg SOA·μg⁻¹; B) in diesel and gasoline fuel (representative of exhaust) and nontailpipe gasoline emissions. Distributions in A and B are colored by chemical class. Fuel properties (density, carbon fraction) and bulk SOA yields (at an organic particle loading of 10 μg·m⁻³) are superposed on A and B, respectively. Predicted SOA from gasoline exhaust is much lower than diesel and dominated solely by aromatic content, whereas diesel SOA is produced from a mix of aromatic and aliphatic compounds. A distribution of the SOA potential uncertainties is provided in SI Appendix, Fig. S5.
A Highway Tunnel Laboratory

Vehicle emissions measured at Caldecott tunnel in SF Bay area:
Composition of Vehicle OA Emissions
(Caldecott Tunnel 2010; 12-2 and 4-6 PM samples)

Worton et al. (ES&T 2014)
Lubricating Oil Speciation

Worton et al. (ES&T 2014)
More Recent Diesel BC Emission Trends
(Port of Oakland Field Measurements)

California requires modernization of in-use heavy-duty trucks

**Diesel Particle Filters:**
100% DPF by 2018

**Catalytic Converters:**
100% SCR by 2023

**Port drayage trucks:**
100% DPF by 2013
Changes in Truck Age Distribution
(Port of Oakland Drayage Truck Fleet)

Preble et al.
(ES&T in prep)
Changes in Port Truck BC Emissions

Preble et al. (ES&T in prep)
Changes in Port Truck BC Emissions

Preble et al. (ES&T in prep)
Concluding Remarks

- **Durable** (long-lived) and **robust** (work well under all conditions) emission controls should be top priority
  - Finding & **fixing** high-emitting vehicles is hard in practice

- Primary OA emissions dominated by lubricating oil
  - Little POA benefit from changes to fuel composition

- Fuel changes can help to reduce BC and SOA
  - Trying to address atypical situations (e.g., high-emitting vehicles) using across the board fuel changes is **not** an efficient strategy
References


