Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass

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Introduction: Secondary Organic Aerosol (SOA) can be formed from volatile and intermediate-volatility organic compounds (VOCs, IVOCs) in gasoline and diesel exhaust as well as biogenic hydrocarbons. SOA is a large fraction of ambient submicron aerosol mass and may contribute to regional air quality and climate change. However, its sources and formation pathways are not well understood.

**Question: What sources dominate urban SOA formation?**

- Vehicular emissions different on weekends
- Use weekday-weekend measurements from NOAA-P3 aircraft in the LA Basin, during CalNex-2010
- Estimate diesel and gasoline contribution to SOA

**OA in LA Basin**

- Increase in photochemical processing = decrease in Toluene/Benzene
- Significant increase in ΔOA/ΔCO with photochemical processing
- Significant SOA production with photochemical processing
- Similar diurnal profile between photochemically produced gas phase species like acetaldehyde and fossil fraction of total carbon (TC fossil)
- SOA dominated by sources of fossil carbon (i.e., vehicular emissions) in LA Basin

**Vehicular Emissions**

- Diesel fuel used ~15% of total fuel used in CA

<table>
<thead>
<tr>
<th></th>
<th>NOx</th>
<th>CO</th>
<th>Reactive Gases</th>
<th>Black Carbon (BC)</th>
<th>POA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>Low</td>
<td>High</td>
<td>VOCs?</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Diesel</td>
<td>High</td>
<td>Low</td>
<td>IVOCs?</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
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- Diesel emissions lower on weekends compared to weekdays (e.g., Marr et al., Atmos. Environ., 2002; Harley et al., EST, 2005; Murphy, ACP, 2008; Pollack et al., JGR, 2012)
  - Higher O3 and lower BC on weekends

**Weekday (WD) vs. Weekend (WE) Observations**

- WD and WE ΔOA/ΔCO higher than estimated primary enhancement ratios (ΔPOA/ΔCO, de Gouw et al., JGR, 2008) (A-B)
  - SOA produced on both WD and WE
  - WE ΔOA/ΔCO higher than WD by 57%
  - OA production per CO higher on WE

**Question: How different WE-WD emissions are?**

- WE and WD CO similar (Pollack et al., JGR, 2012)
  - Similar gasoline emissions on WE and WD
  - WE ΔNOx/ΔCO lower by 63% compared to WD (C)
  - WE ΔBC/ΔCO lower by 47% compared to WD (D)
    - Diesel emissions lower by 54% on WE
    - Diesel emissions contribute to 87% and 76% of BC on WD and WE, respectively
  - WE ΔBenzene/ΔCO similar to WD (E)
    - Similar emissions of light aromatics on WE and WD
  - WE ΔToluene/ΔBenzene lower than WD (F)
    - ~2-3 times faster photochemistry on WE

**Question: How to separate role of photochemistry from emission differences?**

- Consider SOA production on WE and WD in air masses with similar Toluene/Benzene ratios

**Estimating SOA from Diesel Emissions**

- ΔOA/ΔCO increases by ~1.5 with increase in photochemical processing
- Similar ΔOA/ΔCO on WD and WE in similarly processed plumes
- ΔSOA/ΔCO = ΔOA/ΔCO- ΔPOA/ΔCO

- ΔSOA/ΔCO (WE) = 0.72 ± 0.39
  - Average diesel contribution to SOA is zero within the uncertainties
  - Upper limit contribution from diesel emissions to SOA is 20%

**Question: What are the implications?**

- Valuable to identify species in gasoline responsible for SOA formation
- SOA from gasoline ~4 Tg/yr globally (within a day of processing); ~16% of global biogenic SOA
- Reducing gasoline emissions may significantly reduce SOA production, locally and globally