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

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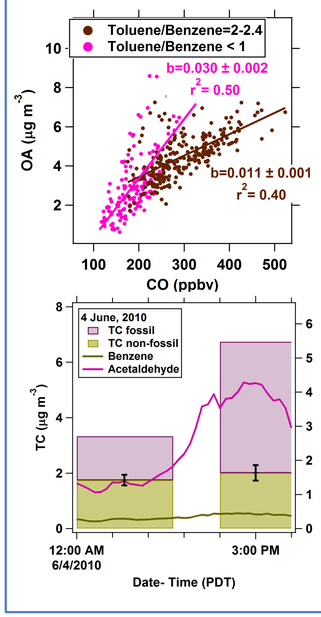
Introduction: Secondary Organic Aerosol (SOA) can be formed from volatile and intermediate-volatility organic compounds (VOCs, IVOCs) in gasoline and diesel exhaust as well as biogenic hydrocarbons. SOA is a large fraction of ambient submicron aerosol mass and may contribute to regional air quality and 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

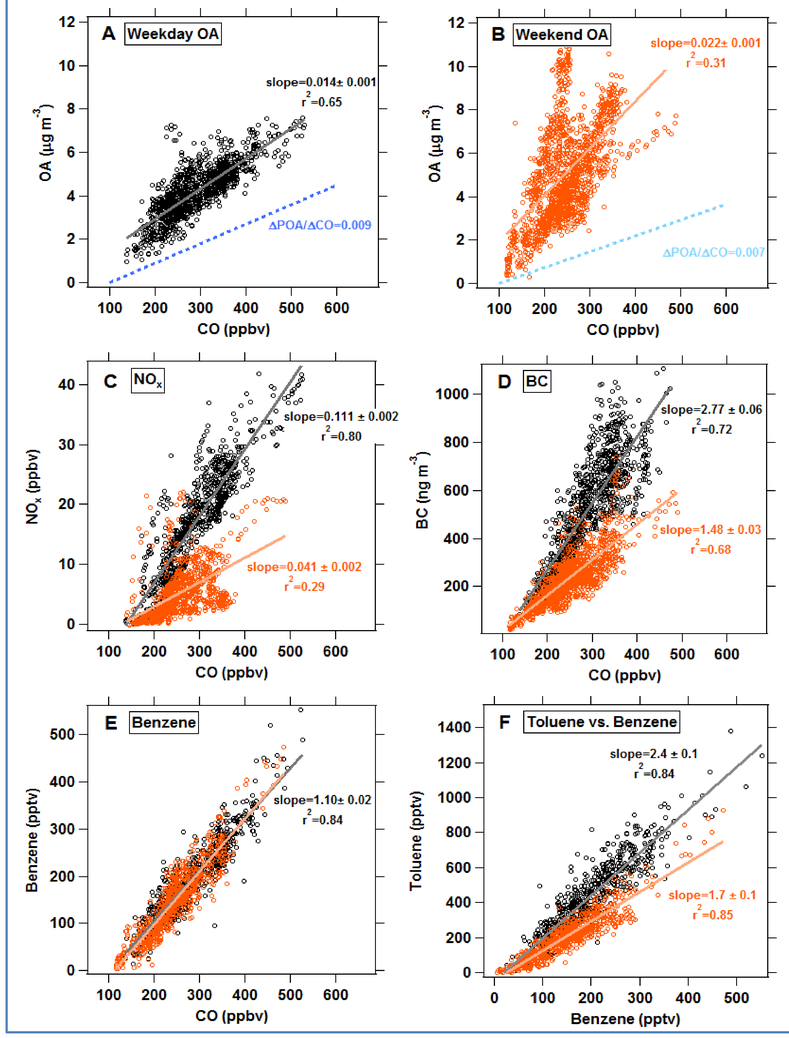
Vehicular Emissions

- ❑ Diesel fuel used ~15% of total fuel used in CA (http://www.boe.ca.gov/sptaxprog/spftrpts.htm)

	NO_x	CO	Reactive Gases	Black Carbon (BC)	POA
Gasoline	Low	High	VOCs?	Low	Low
Diesel	High	Low	IVOCs?	High	High

- ❑ 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 O_3 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 e t 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

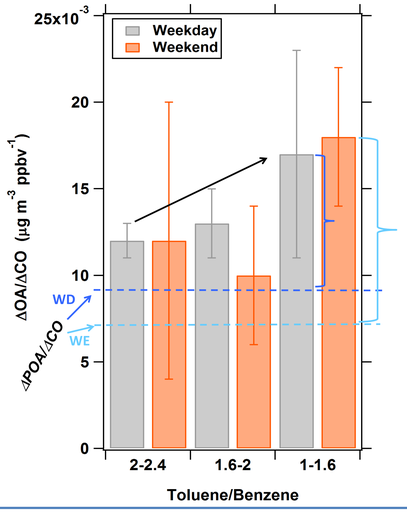
Question: How different WE-WD emissions are?

- ❑ WE and WD CO similar (*Pollack et al., JGR, 2012*)
  - ❑ Similar gasoline emissions on WE and WD
- ❑ WE $\Delta NO_x/\Delta CO$ 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
- ❑ $\frac{(\Delta SOA/\Delta CO)_{WD}}{(\Delta SOA/\Delta CO)_{WE}} = 0.72 \pm 0.39$
  - ❑ 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