Enhanced SOA formation from mixtures of biogenic and anthropogenic emissions during the CARES campaign.

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Anthropogenically Enhanced SOA Formation

- SOA has correlates with anthropogenic tracers such as CO.
- $^{14}$C studies indicate most (40-80%) of the aerosol carbon is modern.
- Observed SOA levels cannot be explained by known chemistry.
- Implies an enhancement of biogenic SOA by anthropogenic emissions.
- Affects aerosol loading and therefore aerosol direct and indirect effects.

Carlen et al., ES&T, 2010, 44, 3376-3380
CARES Overview

- NW flow pattern transports the Sacramento plume into the valley and away from the biogenic sources in the foothills.

- SW flow pattern transports the plume into the foothills.

- Different meteorology allows us to investigate anthropogenic/biogenic interactions.

- G-1 flow 22 research flights to sample the plume

J.D. Fast et al., 2011
Overview of AMS particle measurements

- Fine particle mass is dominated by organics regardless of the meteorology.
- NW flow pattern generally produced low organic loadings.
- Extended periods of SW flow lead to elevated organic loadings.
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Case 1: SW flow pattern on June 28th: interaction of anthropogenics and biogenics.

- Sacramento plume transported to T1 in early afternoon.
- Bay area plume predominantly transported to the south.

For more information see J.D. Fast et al., ACP, 2012.
G-1 observations of urban plume evolution on June 28th.

- Urban plume transported to the foothills in the afternoon.
June 28th OA Formation in Mixed Plume

- Increase in organic mass correlates with loss of isoprene and its oxidation products.
- During the morning flight, organic mass increased 4 μg/m³ in 1.5 hours.
- Organic loading is reduced in afternoon relative to morning due to dilution.
  - Correcting for dilution suggests organic mass increased 6 μg/m³ over 6 hours (additional 2 μg/m³ from morning).
Plot of Organic loading vs CO supports additional OA productions in the afternoon.

- Morning is complicated due to simultaneous production and emissions
- Higher afternoon slope indicates OA production.
Case 2: Airmass impacted primarily by biogenic emissions on June 28th

- Urban plume remains in southern foothills.

Morning

Afternoon
June 28th: OA formation in Biogenic Airmass

- Though OA levels are significant, no net OA production was observed.

- Large concentrations of isoprene and its oxidation products are present.

- Significant ozone (60 - 80 ppbv) is present.
  - Sufficient OH should be available to oxidize VOCs.
OA vs CO in biogenic airmass on June 28th

- $\Delta OA/\Delta CO$ is zero, but there is little dynamic range in the measurement.
- OA and CO are near the background for the day.
Case 3: Airmass impacted primarily by anthropogenic emissions: June 12th

Sacramento plume transported to the south through regions with little biogenic emissions.

Morning

Afternoon

m/z 69 + 71
OA production in anthropogenically dominated airmass

- Airmasses influenced primarily by anthropogenic emissions showed lower OA production.
Summary of OA vs. CO plots as a function of meteorology

- SW flow pattern (biogenic/anthropogenic mix) produced more OA than NW flow pattern (anthropogenic).

![Graph showing the comparison of Organic Loading (μg/m³) vs. CO (ppbv) for different flow patterns.](image)
Summary of OA vs. CO plots as a function of meteorology

More OA is produced when anthropogenic and biogenic emissions mix.
Tracer binning of organic loading

- Tracer species percentiles are calculated and organic loading is binned based on levels of biogenic (m/z 69 + 71) and anthropogenic (CO) tracers.
  - Upper and lower quartiles define high and low, respectively.
- OA loading largest when both anthropogenic and biogenic tracers are elevated.
Conclusions

- Highest organic loadings were observed when both biogenic and anthropogenic tracers were elevated.

- Production of OA was enhanced by an unknown mechanism when biogenic and anthropogenic emissions mixed.

- Controlled laboratory studies will be key in determining the mechanism for the enhancement.

- Models must account for this process to constrain aerosol forcing and aerosol-cloud interactions.
  - Anthropogenic and biogenic emissions are in close proximity over wide regions of the world.
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- **ACRF operations team:** B. Schmid, J. Hubbe, C. Kluzek, J. Comstock, J. Tomlinson.
Chemical composition of the plume

Comparison to literature spectra suggest organics are dominated by OOA (SOA).
No correlation between $\Delta OA/\Delta CO$ and aging of airmass on the timescale of the $NO_x$ clock.
Intense plume dominated by organics is observed SE of city in morning.

Evidence of fast growth ~ 5 μg/m³ mass added in 1.5 hr.
Plume transported to the NE toward T1 in agreement with WRF predictions.

Plume evolution can be investigated.
June 28th Morning PTRMS

- Significant MVK/MACR and isoprene in plume
- Benzene/Toluene clock suggests plume age is 9 hours.
June 28th Afternoon PTR-MS

Concentration (ppbv)

- 33 (methanol)
- 59 (acetone)
- 61 (acetic acid)
- 107 (xylene)
- 93 (toluene)
- 79 (benzene)
- 69 (isoprene +?)
- 71 (MVK + MACR)
- 87 (MBO)

Local Time

3:30 PM 4:00 PM 4:30 PM 5:00 PM 5:30 PM
Our observations of the plume temporal evolution are consistent with chamber observations of SOA formation from isoprene.

- O:C and H:C ratios and evolution are consistent.
- Yields are not consistent.
Plot of Organic loading vs CO supports additional OA productions in the afternoon.

- Higher afternoon slope, suggests OA production.
- Slope of morning points flattens as m/z 69, 71 deplete and CO emissions continue.