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What do correlations tell us about anthropogenic–biogenic interactions and SOA formation in the Sacramento Plume during CARES?

L. Kleinman¹, C. Kuang¹, A. Sedlacek¹, G. Senum¹, S. Springston¹, J. Wang¹, Q. Zhang², J. Jayne³, J. Fast⁴, J. Hubbe⁴, J. Shilling⁴, and R. Zaveri⁴

¹Brookhaven National Laboratory, Upton, NY, USA

²University of California at Davis, Davis, CA, USA

³Aerodyne Research Inc., Billerica, MA, USA

⁴Pacific Northwest National Laboratory, Richland, WA, USA

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Correspondence to: L. Kleinman (kleinman@bnl.gov)

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Abstract

During the Carbonaceous Aerosols and Radiative Effects Study (CARES) the DOE G-1 aircraft was used to sample aerosol and gas phase compounds in the Sacramento, CA plume and surrounding region. We present data from 66 plume transects obtained during 13 flights in which southwesterly winds transported the plume towards the foothills of the Sierra Nevada Mountains. Plume transport occurred partly over land with high isoprene emission rates. Our objective is to empirically determine whether organic aerosol (OA) can be attributed to anthropogenic or biogenic sources, and to determine whether there is a synergistic effect whereby OA concentrations are enhanced by the simultaneous presence of high concentrations of CO and either isoprene, MVK+MACR (sum of methyl vinyl ketone and methacrolein) or methanol, which are taken as tracers of anthropogenic and biogenic emissions, respectively. Linear and bilinear correlations between OA, CO, and each of three biogenic tracers, "Bio", for individual plume transects indicate that most of the variance in OA over short time and distance scales can be explained by CO. For each transect and species a plume perturbation, (i.e., ΔOA , defined as the difference between 90th and 10th percentiles) was defined and regressions done amongst Δ values in order to probe day to day and location dependent variability. Species that predicted the largest fraction of the variance in ΔOA were ΔO_3 and ΔCO . Background OA was highly correlated with background methanol and poorly correlated with other tracers. Because background OA was $\sim 60\%$ of peak OA in the urban plume, peak OA should be primarily biogenic and therefore non-fossil. Transects were split into subsets according to the percentile rankings of ΔCO and ΔBio , similar to an approach used by Setyan et al. (2012) and Shilling et al. (2013) to determine if anthropogenic-biogenic interactions enhance OA production. As found earlier, ΔOA in the data subset having high ΔCO and high ΔBio was several-fold greater than in other subsets. Part of this difference is consistent with a synergistic interaction between anthropogenic and biogenic precursors and part to an independent linear dependence of ΔOA on precursors. Highest values of ΔO_3 also occur in the high ΔCO –high ΔBio

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many well-studied regions such as the southeastern US and Canadian boreal forest is biogenic (e.g., Guenther et al., 1995; Goldstein et al., 2009; Slowik et al., 2010), (2) large biogenic emission rates and SOA yields are a possible cause for the high fraction of non-fossil carbon found in the summer in many locations (Schichtel et al., 2008; Hodzic et al., 2010), including those that are nominally urban (Weber et al., 2007; Marley et al., 2009), and (3) there are realistic mechanisms whereby biogenic SOA yields depend on the presence of anthropogenic pollutants (Carlton et al., 2010). The later include effects of anthropogenic pollutants on oxidant levels and consequently on biogenic VOC oxidation rates (Kanakidou et al., 2000), increased partitioning of biogenic VOC oxidation products to the aerosol phase because the aerosol volume available for partitioning is increased by an anthropogenic component (Carlton et al., 2010), and effects of sulfate on aerosol phase chemistry (Xu et al., 2015). Explanations of non-fossil carbon based on A-B interactions are constrained by the observation that the difference between modeled and observed OA concentration generally decreases as anthropogenic influence decreases (Tunved et al., 2006; Chen et al., 2009; Hodzic et al., 2010; Slowick et al., 2010).

In multiple studies it has been found that OA, SOA, and/or WSOC (water soluble organic carbon, demonstrated to be a surrogate for SOA) are highly correlated with anthropogenic tracers. High correlations have been observed even at locations where it is suspected that much if not most SOA is biogenic. In a study of the Atlanta region, aircraft flights over the urban core established that WSOC is proportional to CO, while surface observations of aerosol ^{14}C , also in the urban core, established that 70–80% of WSOC was non-fossil and likely biogenic (Weber et al., 2007). While there was a high correlation between WSOC and CO in Atlanta, similar to that observed in the New York City metropolitan region (Sullivan et al., 2006), there was no clear linkage between WSOC and biogenic VOCs. At the Blodgett Forest Research Station, located 25 km downwind from the CARES sampling region, OA was observed to be correlated with CO ($R^2 = 0.79$) but based on ^{14}C filter samples it was determined that the majority of aerosol carbon was non-fossil from biogenic sources (Worton et al., 2011). Although

time span. CH₃OH, has a primary biogenic source and a lifetime of order 10 days (Schade and Goldstein, 2006; Wells et al., 2012) and therefore can provide information on biogenic inputs over a time span comparable to the lifetime of tropospheric aerosols.

In order to understand the roles of anthropogenic and biogenic tracers in describing SOA formation over spatial scales comparable to the Sacramento plume, correlation coefficients between OA and explanatory variables have been determined for each plume transect. For the purpose of determining the sensitivity of OA to conditions that vary over the CARES campaign, we define for each plume transect and species a background concentration and plume perturbation, Δ , and use these quantities in a regression analysis amongst transects. Transects are also split into subsets having the varying combination of low and high values for Δ CO and Δ isoprene, Δ MVK+MACR or Δ CH₃OH. We find that the data subset with high concentrations of both anthropogenic and biogenic tracers has uniquely high values of Δ OA. This result is similar to the A-B enhancement found by Setyan et al. (2012) and Shilling et al. (2013). We consider whether the uniquely high values of Δ OA can be explained by an independent linear dependence of Δ OA on anthropogenic and biogenic tracers, rather than a synergistic effect.

In addition to physically well-grounded A-B mechanisms, OA and its anthropogenic and biogenic precursors are expected to be connected through a common dependence on meteorological conditions such as ventilation, sunlight, and temperature (Goldstein et al., 2009). We find a high correlation between Δ OA and Δ O₃ (Herndon et al., 2008; Wood et al., 2010). Studies of the dependence of O₃ on meteorological factors and on anthropogenic and biogenic precursors have a long history and could yield insights on SOA production.

Although there is a high anthropogenic, high biogenic, subset that stands out as having high concentrations of Δ OA, most of the spatial variability of OA within a transect and Δ OA amongst transect can be explained by CO or Δ CO, respectively. These observations suggest a primarily anthropogenic origin for OA produced in the Sacramento plume. In contrast, the variability of background OA is much better explained

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by background CH₃OH, which suggests a biogenic origin. As background OA is more abundant than OA formed in the Sacramento plume, the plume OA, though correlating best with CO, is expected to have a ¹⁴C signature of non-fossil, biogenic carbon. The plume composition would then resemble that observed in Atlanta (Weber et al., 2007) and that observed in the afternoon outflow from Los Angeles (Zotter et al., 2014).

2 Experimental

Data for the CARES field campaign including the G-1 data used in this study can be accessed from DOE's ARM Climate Research archive at <http://www.archive.arm.gov>. AMS and PTR-MS data were recorded at the instruments cycle time of 13 and 4 s, respectively. Most other measurements were collected at 1 Hz. Data used in this study was interpolated or averaged to a 10 s time base. Units for aerosol concentration are μg m⁻³ at 1013 mb and 23 °C. Trace gas abundances are expressed as mixing ratios in units of ppbv. When referring to aerosol and gas phase species collectively, the term concentration is used.

2.1 Instruments

The primary chemical measurements used in the regression analysis are (1) organic aerosol, designated hereinafter as OA, (2) CO, a surrogate for anthropogenic precursors of OA, (3) isoprene, MVK+MACR, and CH₃OH, surrogates for biogenic OA precursors, and (4) O₃, a product of OH driven photochemistry. These species were measured using an Aerodyne HR-ToF-AMS, a VUV resonance fluorescence detector built at BNL, an Ionicon PTR-MS (Lindinger et al., 1998), and a TEI49 O₃ detector, respectively. An overview of instrumentation used in CARES is given in Zaveri et al. (2012).

Operational principals of the AMS are described by Canagaratna et al. (2007) and references therein. It's use on the G-1 during CARES is described by Shilling et al. (2013). In brief, the AMS on the G-1 operated in V-mode, with the duty cycle devoted

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transect is at the western edge of a 20–25 km band of oak woodlands. Still further to the northeast there is a shift in vegetation, so that at the Blodgett Forest research station, 75 km from Sacramento, monoterpenes are the dominate source of SOA (Dreyfus et al., 2002).

2.3 Plumes

On many flights the Sacramento plume was crossed multiple times at the same location. If these crossings were consecutive, at the same altitude, and within the boundary layer, they were grouped together for the purpose of calculating concentrations and for regression analysis. If plume crossings were separated in time or were at different altitudes they constituted separate data entries. Henceforth, the term “plume crossing” will refer to individual crossings whilst the term “transect” collapses consecutive crossings (that meet criteria given above) into a single entity. As listed in Table 2, there were a total of 83 plume crossings that made up 66 plume transects. The number of 10 s data points in a single plume crossing is about 60. For each transect, frequency distributions for aerosol and trace gas concentration were determined. Background concentrations are operationally defined by the 10th percentile. Perturbations above background were calculated as the difference between the 90th and 10th percentile of concentration and are denoted by the symbol Δ .

3 Data analysis

In our analysis of the G-1 data set we consider variations in OA observed along a plume transect and a larger scale variability that includes the effects of day to day changes in meteorology. Variations in OA are correlated with anthropogenic and biogenic explanatory variables, which are surrogates for the actual compounds that form SOA.

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for SOA formation. As the atmospheric lifetime of isoprene with respect to OH oxidation is of order 1 h (at $\text{OH} = 3 \times 10^6 \text{ molec cm}^{-3}$), its presence in the atmosphere reflects local conditions rather than the longer time span over which SOA production is thought to occur. Because reaction of MVK+MACR with OH is ~ 3 to 4 times slower than isoprene, atmospheric residence times are closer to the timescale for transport of the Sacramento plume within our sampling region. Transport times from the Sacramento urban center to T1 have been calculated to be 2 to 8 h from WRF-Chem simulations (Fast et al., 2012). However, under high NO_x conditions such as found in the photochemically active regions of an anthropogenic plume, the formation of OA from isoprene emissions proceeds primarily from second and higher generation oxidation products rather than directly from MVK+MACR (Ng et al., 2006; Carlton et al., 2009). While there might not be a direct link between concurrently measured isoprene or MVK+MACR and SOA, the occurrence of high mixing ratios of isoprene and its oxidation products can indicate a potential for future SOA production or be a general indicator that meteorological conditions such as temperature, sunlight, ventilation, and wind direction are favorable for the occurrence and accumulation of biogenic VOCs. Methanol, in contrast, addresses source attribution for biogenic aerosol in much the same way as CO is used as a tracer of anthropogenic SOA precursors. The atmospheric lifetime of methanol is ~ 10 days and while not an SOA precursor, it is co-emitted with biogenic VOCs that are. Under conditions prevailing in the experimental area it is expected that the source of methanol is almost entirely biogenic (Wells et al., 2012). Emission rates for CH_3OH , especially the biogenic component from new leaf production, have a pronounced seasonal variability peaking in the spring and early summer (Schade and Goldstein, 2006; Wells et al., 2012), nearly coincident with the CARES field campaign. In other regions and at other times, a greater fraction of CH_3OH may derive from maritime sources, forest fires, or peroxy radical combination reactions, which could compromise the utility of CH_3OH as a tracer of biogenic aerosol precursors.

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3.2 Regression analysis

A series of single variable and multi-variable regressions were performed using time series measurements for each of 66 transects. M1 to M5 designate the models used. Standardized variables, indicated with a subscript S , have zero mean and unit standard deviation. The term “Bio” designates a tracer of biogenic emission, which in this study is isoprene, MVK+MACR, or CH_3OH . Models M1–M4 are based on CO and Bio as explanatory variables. M4 uses a bilinear combination of CO and Bio and M3 measures multi-collinearity, the extent to which the two explanatory variables, CO and Bio, are correlated. M5 is a linear relation between OA and O_3 .

The same models were used to compare backgrounds and concentration perturbations (e.g. ΔOA , ΔCO , etc.) amongst transects. M1 to M5 are defined by:

$$\begin{aligned} \text{M1} & \quad \text{OA} = a_1 + B_1 \text{CO} \\ \text{M2-Bio} & \quad \text{OA} = a_2 + B_2 \text{Bio} \\ \text{M3-Bio} & \quad \text{CO} = a_3 + B_3 \text{Bio} \\ \text{M4-Bio} & \quad \text{OA} = a_4 + B_4 \text{CO} + B_4 \text{Bio} \\ \text{M4}_S\text{-Bio} & \quad \text{OA}_S = \beta_4 \text{CO}_S + \beta_4 \text{Bio}_S \\ \text{M5} & \quad \text{OA} = a_5 + B_5 \text{O}_3 \end{aligned}$$

where the a 's are intercepts and the B 's and β 's are regression slopes. In order to improve legibility MVK+MACR will be shortened to MVK when used as a subscript. Quadratic models with terms such as CO_S times Bio_S were also considered, but did not yield insights or appreciable increases in performance.

For the standardized model, M4_S , a comparison of $\beta_4 \text{CO}_S$ with $\beta_4 \text{Bio}_S$ gives the relative effect on OA_S of changing CO_S and Bio_S by the same multiple of their respective standard deviations. Standardization does not affect the value of R^2 nor does it change the signs of the coefficients of the explanatory variables. Standardized coefficients can

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structures with fewer degrees of freedom than data points, the usual ways of determining statistical significance such as *t* or *f* tests do not apply (Thiébaux and Zwiers, 1984; Trenberth, 1984).

4 Results

Tables 3 and 4 summarize chemical measurements from the G-1, providing backgrounds and plume perturbations for OA, CO, isoprene, MVK+MACR, CH₃OH, and O₃ averaged over transects according to location. Background concentrations of the long-lived constituents, OA, CO, and CH₃OH are to first order about the same on all 5 legs. The short lived species isoprene and MVK+MACR, increase by approximately an order of magnitude from east to west, following changes in emissions. Ozone is an intermediate case. Calling the 10th percentile of concentration “background” comes closest to matching the traditional definition for species with long atmospheric residence time. Even so, backgrounds for OA, CO, and CH₃OH have significant variability which we will take advantage of for source attribution of OA.

From T0 eastward, ΔCO is elevated relative to upwind values. Biogenic mixing ratios have their major increase east of the City-Edge transect. Effects of dilution are apparent in the decrease of ΔCO and ΔOA at the Foothills transect, albeit based on only 5 transects from 3 flights.

4.1 Correlations for the spatial variability within individual transects

Figure 2 shows values of R^2 obtained from models M1–M4. Regressions are done for each transect, then R^2 is averaged over transects at each location. Results are presented in three panels corresponding to the biogenic tracer used; isoprene, MVK+MACR, or CH₃OH. Each panel has a common blue trace representing R^2 from model M1, OA vs. CO. Adding a biogenic tracer to M1 gives the bilinear model, M4, with an R^2 shown by the black trace. The additional variance in OA explained by M4

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4.2 Regression analysis of plume perturbations

Correlations have also been calculated amongst plume perturbation concentrations, defined for each transect as the 90th percentile minus the 10th percentile, and denoted here by the symbol Δ . While correlations on individual transects are only sensitive to cross-plume spatial variations, the correlations between Δ quantities test how well plume perturbations in OA follow perturbations in CO, MVK+MACR, isoprene, CH₃OH, and O₃ as these compounds vary in concentration according to position (i.e., T0 to Foothills) and according to day to day variations in meteorological conditions. Table 7 summarizes values of R^2 for linear regressions of all pairings of Δ OA, Δ CO, Δ MVK+MACR, Δ isoprene, Δ CH₃OH, and Δ O₃. Also included are regression slopes and R^2 for the standardized bilinear models. Adding the explanatory variable Δ isoprene, Δ MVK+MACR, or Δ CH₃OH to Δ OA vs. Δ CO increases the explained variance from 69 to 76, 72 or 76 %, respectively. For independent transects, increases in R^2 are significant with a p value of 0.02 or better.

The inter-plume correlation analysis was repeated using background (10th percentile) values in place of Δ 's. Figure 7 shows scatter plots for background OA vs. background CO, MVK+MACR, isoprene, and O₃, paired with the corresponding scatter plots for Δ variables. Plots of Δ variables correspond to the first column of data in Table 7. Color coding identifies points according to transect location. Background OA is poorly correlated with other background species, with the exception of OA vs. CH₃OH ($R^2 = 0.82$). In that case there is a similar relation and goodness of fit for transects at all locations. The poor correlation between background OA and CO is surprising in view of model results that show the Bay Area to be an important source region (Fast et al., 2012). Amongst the Δ variables, Δ OA has the highest correlation with Δ O₃ ($R^2 = 0.88$). Similar to the within-transect spatial correlations, the variance of OA is better described by the anthropogenic tracer, CO ($R^2 = 0.69$), than by a biogenic tracer.

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The spatial correlation between CO and, for example, MVK+MACR on individual transects is highly variable (Figs. 3b and S2). On average it is somewhat greater than the correlation between OA and MVK+MACR. It is not clear what processes causes a sometimes high but variable correlation between anthropogenic and biogenic VOCs. A possible explanation is that it is an accident of geography whereby under certain wind directions the plumes from urban and forested areas line up, while under other wind directions the overlap is lessened or eliminated. Faster oxidation of isoprene in the high NO_x anthropogenic Sacramento plume could be a contributing factor. Perhaps related is the observation by Dreyfus et al. (2002) of the co-advection of anthropogenic and biogenic compounds from the direction of Sacramento to the Blodgett Forest Research Station .

In Method 2, plume perturbations (Δ 's) are defined on each downwind transect and for each species of interest. Correlation coefficients calculated amongst transects quantify the extent to which linear and bilinear combinations of Δ tracers (CO, isoprene, MVK+MACR, CH_3OH , and O_3) can explain the variations of ΔOA that occur as chemical and meteorological conditions vary from flight to flight and with transect location. As with Method 1, we find that CO is more successful in explaining the variability of OA, in comparison to biogenic tracers. This can be seen from the scatter diagrams in Fig. 7 and from the standardized coefficients for the bilinear model M4_S in Table 7.

A notable feature of the correlations amongst transects is that ΔO_3 explains 88 % of the variance in ΔOA . A display of Fig. 7j on a log log scale (not shown) indicates that the $\Delta\text{OA}-\Delta\text{O}_3$ relation stays approximately constant at low concentrations. Figure 7j also shows that the same relation holds at each of the 4 downwind transect locations. The high $\Delta\text{OA}-\Delta\text{O}_3$ correlation is evidence that most OA above background originates from secondary chemistry. This assignment is in agreement with findings from many locations that SOA is correlated with other oxidized species and in agreement with the analysis of CARES observations by Setyan et al. (2012) and Shilling et al. (2013). A mechanistic reason for a relation between OA and O_3 was proposed by Herndon et al. (2008) based on a chemical mechanism in which $\text{OH} + \text{VOC}$ was the rate limiting

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Figure 7 shows that the variance in background OA is uniquely captured by background CH_3OH , with an explained variance of 82 % compared to 23 to 27 % for background CO, isoprene, or MVK+MACR. The excellent fit between background OA and background CH_3OH and the poor fit with CO is what would be expected if background SOA is primarily biogenic.

In Method 3, concentrations in the form of Δ values are used to define plume-transect subsets which have low or high mixing ratios of CO and either isoprene, MVK+MACR, or CH_3OH . Of the 4 combinations of low and high values of ΔCO and ΔBio , only the subset with a high mixing ratio of both anthropogenic and biogenic tracers has high average ΔOA . However, according to Method 1, most transects have a correlation between OA and biogenic tracers that is low and/or spurious, such that the addition of a biogenic to an OA vs. CO model, produces only a modest improvement in explaining the variance of OA during a plume transect. In Method 2, there is a poor correlation between ΔOA and $\Delta\text{isoprene}$ or $\Delta\text{MVK+MACR}$. The correlation between ΔOA and $\Delta\text{CH}_3\text{OH}$ is somewhat higher but still lower than that between ΔOA and ΔCO . We recognize the deficiencies in using short lived biogenic tracers, yet in Method 3 these same biogenic tracers as well as the long-lived CH_3OH can split the data set into subsets with and without high ΔOA .

The association between simultaneous high mixing ratios of anthropogenic and biogenic tracers and high ΔOA is heavily reliant on data from two flights on 28 June as this was the only day in which ΔOA exceeded $6 \mu\text{g m}^{-3}$. What was unusual about this day? According to Fast et al. (2012), from 22 June till the end of the field campaign on 28 June, winds at 700 hPa were light and variable. After 25 June there was a steady increase in maximum day time temperature. 27 and 28 June had the warmest temperatures, approaching 40°C at T0 on 28 June. Ozone also reached its highest value of 90 ppb at T0. Wind speeds at the G-1 altitude were $\sim 2 \text{ m s}^{-1}$. A detailed description of chemical conditions on 28 June is given by Shilling et al. (2013). In brief, during these two flights isoprene reached 13 ppb, O_3 approached 120 ppb, CO was in excess

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Thus, the highest SOA concentrations are likely to occur coincident with elevated mixing ratios of both anthropogenic and biogenic tracers. Although several possible A-B mechanisms are enabled, the demonstration of an A-B effect requires a synergism such that SOA increases more than it would by independent increases in anthropogenic and biogenic precursors.

By its very nature conclusions based on correlations are inferential. It would be highly desirable to test our results against a high resolution chemical transport model.

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Table 2. Number of plume crossings and transects.

Location	Number	
	Plume crossings	Transects
Upwind	11	10
T0	25	22
City-Edge	15	12
T1	26	17
Foothills	6	5

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Table 3. Backgrounds averaged over transects at 5 locations.

Transect	Background*					
	OA	CO	Isoprene	MVK+MACR	CH ₃ OH	O ₃
Upwind	3.9	127	0.29	0.18	4.7	35
T0	4.1	132	0.30	0.13	4.6	41
City-Edge	4.8	133	0.26	0.11	4.4	53
T1	5.3	134	1.1	0.97	5.5	50
Foothills	4.2	133	1.9	1.5	5.1	57

* Background = lowest 10th percentile. Units are ppbv, except for Organic Aerosol (OA) which is $\mu\text{g m}^{-3}$.

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Table 4. Plume perturbations, Δ 's, averaged over transects at 5 locations.

Transect	Δ^*					
	OA	CO	Isoprene	MVK+MACR	CH ₃ OH	O ₃
Upwind	3.0	23	0.32	0.26	3.1	13
T0	3.2	42	0.38	0.38	1.9	12
City-Edge	3.7	39	0.55	0.51	1.2	15
T1	3.9	31	2.0	1.2	2.2	15
Foothills	1.3	13	1.0	0.75	1.3	6.4

* Δ = 90th percentile – 10th percentile. Units are ppbv, except for Organic Aerosol (OA) which is $\mu\text{g m}^{-3}$.

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Table 5. Coefficients of determination for models M1–M5 with Bio = isoprene, MVK+MACR, or CH₃OH, applied to within-transect data. Average determined for 56 transects.

Model ^a	Variables		average R^2
	Y	X(s)	
M1	OA	CO	0.68
M2-isoprene	OA	isoprene	0.16
M3-isoprene	CO	isoprene	0.18
M4-isoprene ^b	OA	CO, isoprene	0.71
M2-MVK+MACR	OA	MVK+MACR	0.40
M3-MVK+MACR	CO	MVK+MACR	0.47
M4-MVK+MACR ^c	OA	CO, MVK+MACR	0.73
M2-CH ₃ OH	OA	CH ₃ OH	0.42
M3-CH ₃ OH	CO	CH ₃ OH	0.32
M4-CH ₃ OH ^d	OA	CO, CH ₃ OH	0.77
M5	OA	O ₃	0.57

^a Within a set of regressions, M1 to M4, missing values of either OA, CO, or biogenic tracer were treated by removing all three data (listwise deletion).

^b Average of standardized regression slopes for model M4-isoprene_S,

$\beta_{4\text{CO}} = 0.80$, $\beta_{4\text{ISOPRENE}} = -0.01$.

^c Average of standardized regression slopes for model M4-MVK+MACR_S,

$\beta_{4\text{CO}} = 0.74$, $\beta_{4\text{MVK}} = 0.06$.

^d Average of standardized regression slopes for model M4-CH₃OH_S,

$\beta_{4\text{CO}} = 0.67$, $\beta_{4\text{CH3OH}} = 0.29$.

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Table 6. Coefficients of determination for models M1–M4 and standardized regression slopes for model M4_S for three transects.

Model	Variables		608b*	608b*	628b*
	Y	X(s)	City-Edge	T1	T1
M1, R^2	OA	CO	0.94	0.74	0.99
M2, R^2	OA	MVK+MACR	0.89	0.89	0.01
M3, R^2	CO	MVK+MACR	0.89	0.69	0.00
M4, R^2	OA	CO, MVK+MACR	0.95	0.91	0.99
M4 _S , $\beta_{4\text{CO}}$	OA _S	CO _S , MVK+MACR _S	0.70	0.24	0.99
M4 _S , $\beta_{4\text{MVK}}$	OA _S	CO _S , MVK+MACR _S	0.29	0.75	0.07

* See Figs. 4–6.

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Table 7. Coefficients of determination between plume Δ^a values for OA, CO, isoprene, MVK+MACR, CH_3OH , and O_3 based on data set of 56 transects.

Dependent variable	Explanatory variable ^a					
	ΔOA	ΔCO	$\Delta\text{Isoprene}$	$\Delta\text{MVK+MACR}$	$\Delta\text{CH}_3\text{OH}$	ΔO_3
ΔOA^b	1	–	–	–	–	–
ΔCO	0.69	1	–	–	–	–
$\Delta\text{Isoprene}$	0.11	0.01	1	–	–	–
$\Delta\text{MVK+MACR}$	0.15	0.06	0.57	1	–	–
$\Delta\text{CH}_3\text{OH}$	0.55	0.43	0.13	0.25	1	–
ΔO_3	0.88	0.61	0.08	0.08	0.35	1

^a Δ defined for each transect as the 90th percentile of concentration – 10th percentile;

^b bilinear regression with standardized variables $\Delta\text{OA}_S = \beta_{4 \Delta \text{CO}} \Delta\text{CO}_S + \beta_{4 \Delta \text{ISOPRENE}} \Delta\text{Isoprene}_S$:

$\beta_{4 \Delta \text{CO}} = 0.80$, $\beta_{4 \Delta \text{ISOPRENE}} = 0.26$, $R^2 = 0.76$.

$\Delta\text{OA}_S = \beta_{4 \Delta \text{CO}} \Delta\text{CO}_S + \beta_{4 \Delta \text{MVK}} \Delta\text{MVK+MACR}_S$: $\beta_{4 \Delta \text{CO}} = 0.78$, $\beta_{4 \Delta \text{MVK}} = 0.19$, $R^2 = 0.72$.

$\Delta\text{OA}_S = \beta_{4 \Delta \text{CO}} \Delta\text{CO}_S + \beta_{4 \Delta \text{CH}_3\text{OH}} \Delta\text{CH}_3\text{OH}_S$: $\beta_{4 \Delta \text{CO}} = 0.60$, $\beta_{4 \Delta \text{CH}_3\text{OH}} = 0.35$, $R^2 = 0.76$.

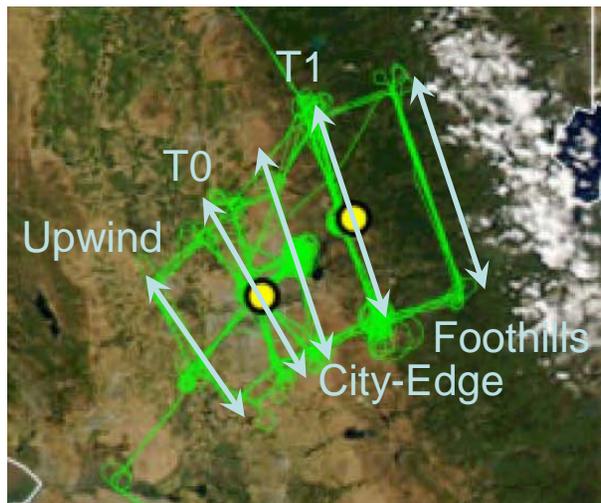


Figure 1. Map of sampling region, showing composite ground track for SW flights. Five transects more or less perpendicular to the boundary layer wind direction are indicated. Adapted from Zaveri et al. (2012).

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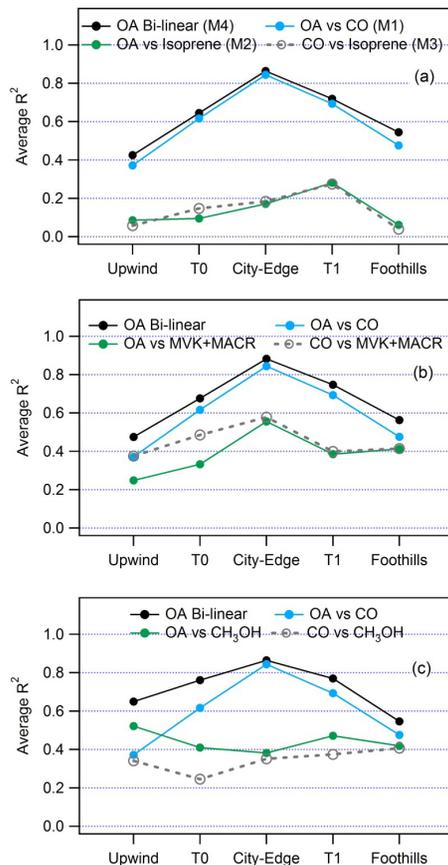


Figure 2. Average coefficient of determination (R^2) for bilinear or linear least squares regressions using data from five locations for plume transects shown in Fig. 1. Explanatory variables are **(a)** CO and isoprene, **(b)** CO and MVK+MACR, and **(c)** CO and CH_3OH . Panel **(a)** gives regression model in parenthesis.

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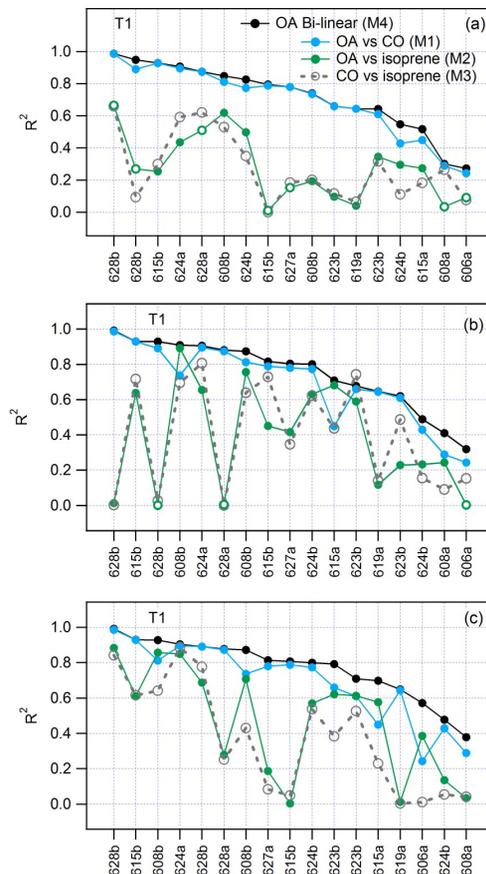


Figure 3. Coefficient of determination (R^2) for transects on Leg T1, using CO as an anthropogenic tracer and **(a)** isoprene, **(b)** MVK+MACR, and **(c)** CH_3OH as a biogenic tracer. Results rank ordered according to R^2 of bilinear model, M4-Bio. Open green circles indicates transects in which OA is anti-correlated with Bio. Legend in panel **(a)** identifies regression models.

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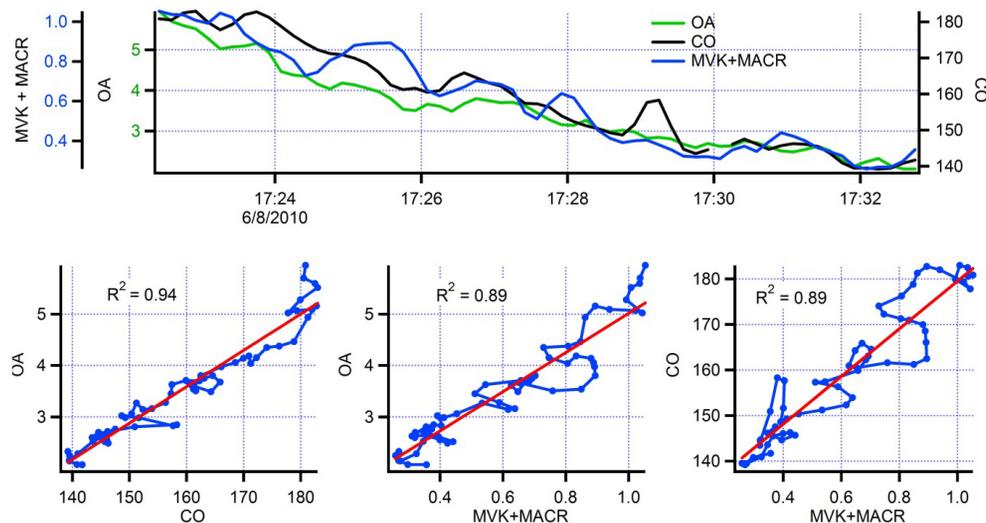


Figure 4. 608b City-Edge transect. Top graph, time series of OA, CO, and MVK+MACR. OA in $\mu\text{g m}^{-3}$, CO and MVK+MACR in ppbv. Time is Pacific Standard Time. Bottom plots, correspond from left to right to Models M1, M2, and M3 Listwise deletion used for correlations but not used for graphs. Data points on scatter plots connected to give a sense of time continuity. Red lines are least squares fit to data.

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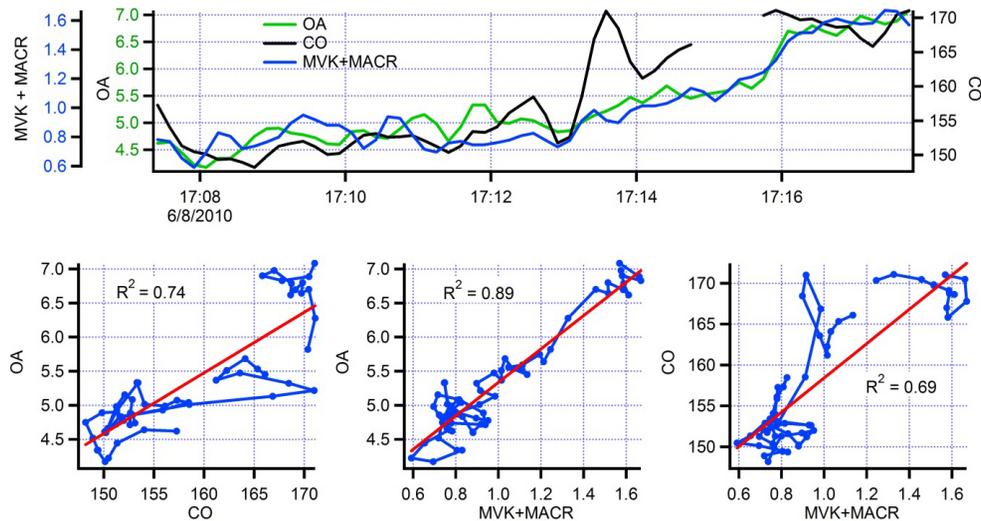


Figure 5. 608b T1 transect. Same format as Fig. 4.

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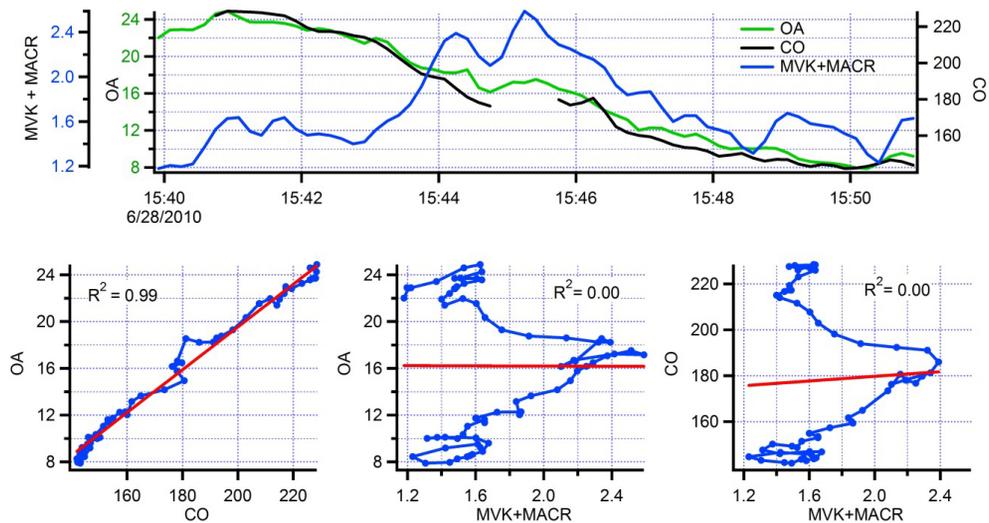


Figure 6. 628b T1 transect. Same format as Fig. 4.

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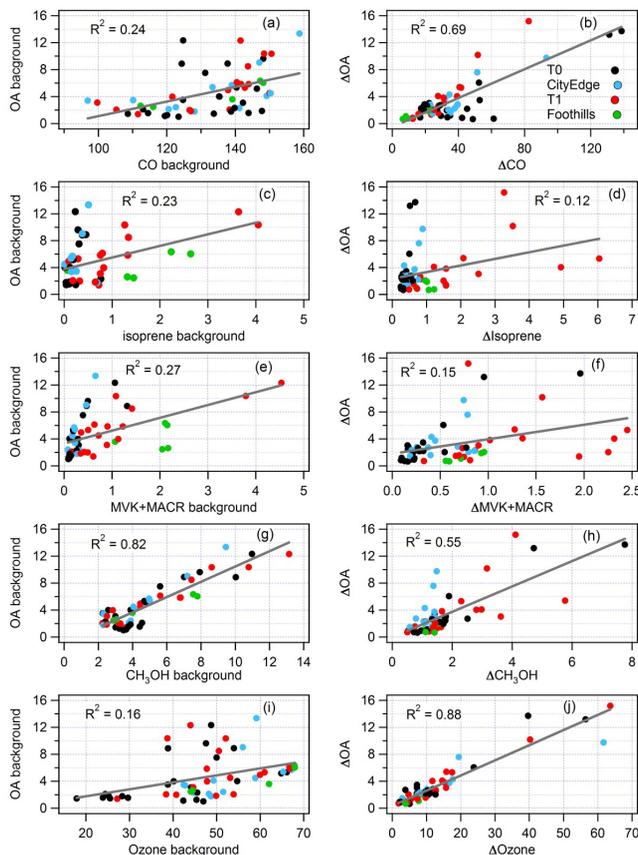


Figure 7. OA as a function of CO, isoprene, MVK+MACR, CH₃OH, and O₃ for 56 transects. Background concentrations in panels on left hand side, Δ Concentrations on the right hand side. Color legend in panel (b) identifies data according to location. Gray lines are linear least squares fits with R^2 given in each panel.

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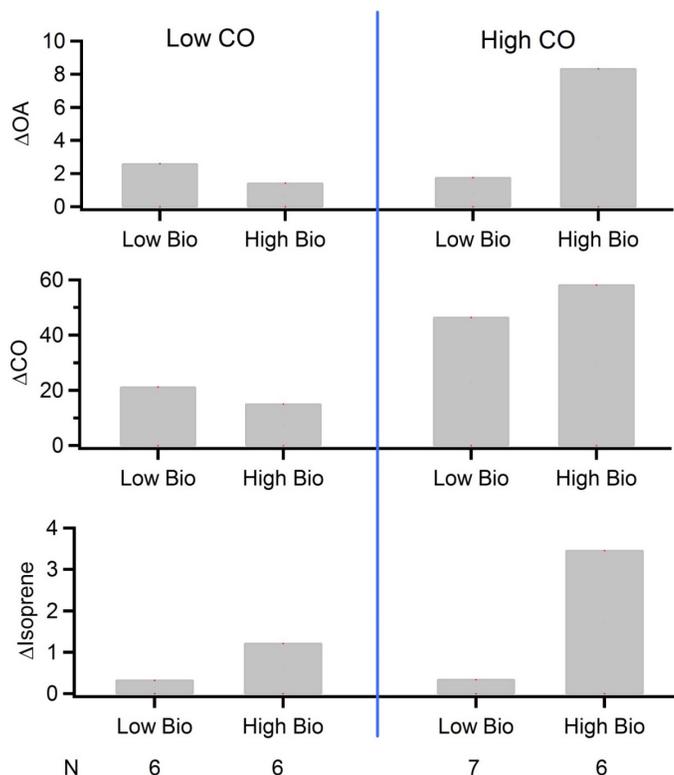


Figure 8. Values of ΔOA , ΔCO , and $\Delta\text{Isoprene}$ for 4 subsets of transects. Pairs of bars labelled Low CO and High CO have ΔCO values that are below the 33rd percentile and above the 67th percentile, respectively. Bars labelled Low Bio and High Bio have $\Delta\text{Isoprene}$ values that are below the 33rd percentile and above the 67th percentile, respectively. Number of transects in each subset given at bottom. ΔCO Ratio and ΔBio Ratio give effects of precursor mixing ratio on an A-B interaction relative to the expectation that ΔOA is a bilinear function of ΔCO , and ΔBio : ΔCO Ratio = $(\Delta\text{CO}: \text{high CO, high Bio}) / (\Delta\text{CO}: \text{high CO, low Bio})$. ΔBio Ratio = $(\Delta\text{Bio}: \text{high CO, high Bio}) / (\Delta\text{Bio}: \text{high CO, low Bio})$.

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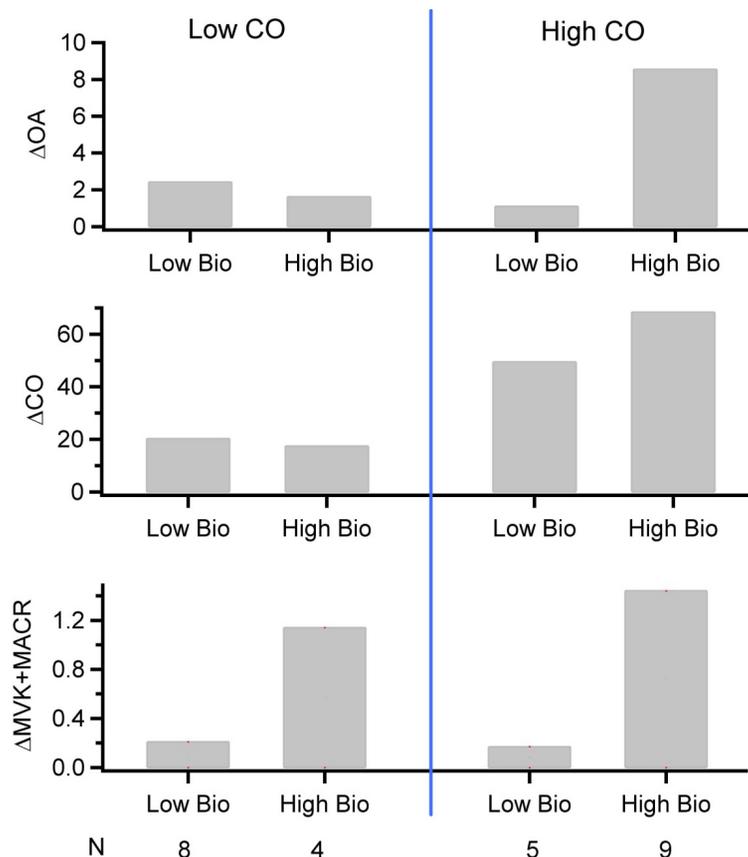


Figure 9. Bar graphs for subsets defined on the basis of ΔCO and $\Delta\text{MVK}+\text{MACR}$. Same format as Fig. 8.

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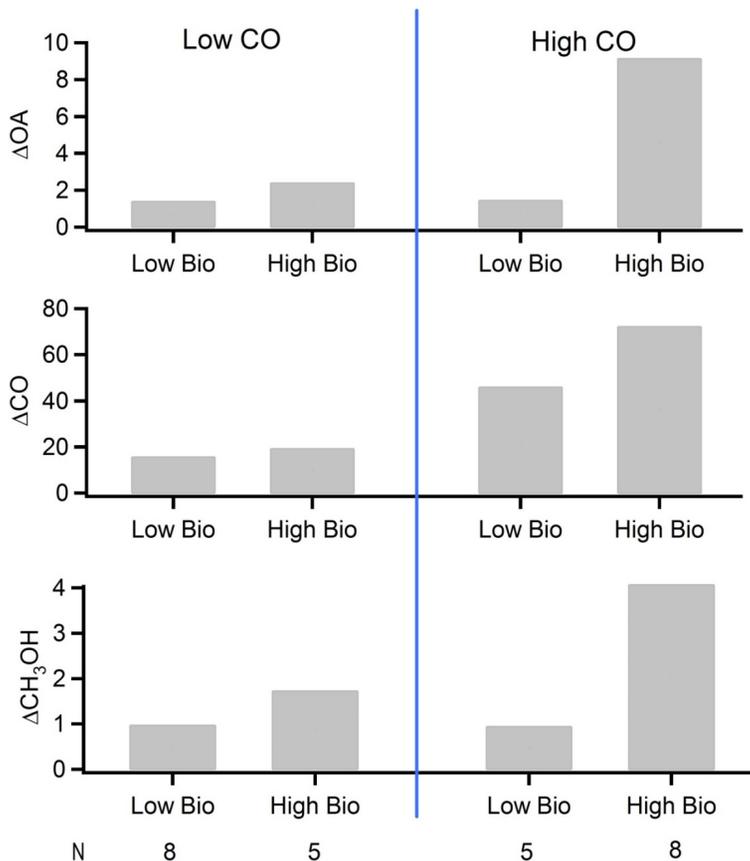


Figure 10. Bar graphs for subsets defined on the basis of ΔCO and $\Delta\text{CH}_3\text{OH}$. Same format as Fig. 8.

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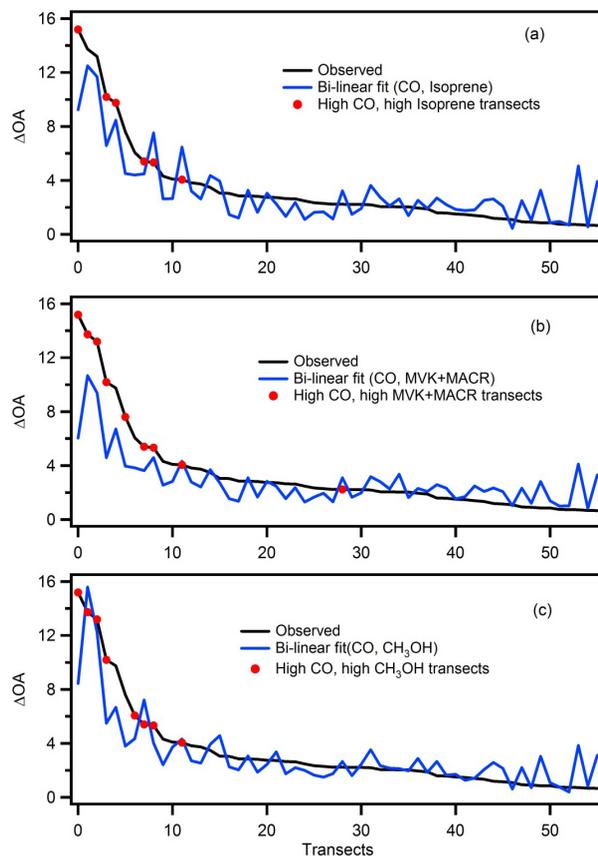


Figure 11. Observed ΔOA presented in descending order. Blue trace is ΔOA from bilinear model using ΔCO and **(a)** Isoprene, **(b)** $\Delta\text{MVK}+\text{MACR}$, and **(c)** $\Delta\text{CH}_3\text{OH}$ as explanatory variables. Regressions did not use transects from the high ΔCO , high ΔBio subsets, indicated by red symbols.

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