Towards Empirical, Quantitative Attribution of Fire-related and other Pollutants as they Affect Production of O$_3$ in California Air

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Abstract

We are able to attribute sources of both radical reactivity and NO that determined chemical production rate of ozone in NASA’s ARCTAS-intensive sampling of California air in June, 2008. We relate formaldehyde, HCHO, and reactive nitrogen oxides, NOx, to a variety of distinct “marker” species that identify origins. We have labeled the sources and markers as (i) Fire emissions (acetonitrile, CH$_3$CN), (ii) Biogenic emissions (isoprene), (iii) Urban/business emissions (CHCl$_3$), (iv) Proximate transport-related (automotive) fuel combustion (refractory CN), (v) probably dairy or livestock emissions (ethanol), (vi) Refining/Port emissions (“residual” toluene), and (vii) an extremely intense but localized source of the coast of Los Angeles. We achieve $R^2$ or explained variance of 83% for HCHO (VOC’s) and 65% for NOx. HCHO and NOx are slowly evolving qualitative measures of potential ozone generation. However, the related but radiation-influenced measures $j_{\text{HCHO}\rightarrow\text{HCO}}$•[HCHO] and [NO] quantitatively but non-linearly relate to instantaneous ozone production in California air, with R-squared of 86–93%, just as in New York City (Chatfield et al., Atmos. Environ., 2010). Making use of this correspondence, we present maps of attribution of the origin for HCHO and NOx for 774 samples from the Port of San Diego to the Northern Sierra foothills, and offshore and interpret these as radical and NO sources for O$_3$ production. We show huge variability in source attributions for VOCs and NOx. Fire-emission contribute greatly to HCHO and peroxy radical concentrations. Extremely fresh emissions show small increases in NOx, but act to reduce NOx from other sources. Comparisons with simulations help to refine our attribution classes and also to check balances of VOC emissions in available inventories.
(Previous Work)

**Technique (i) Measurement Data Sets**

DC-8 data

**An Empirical Approach to Source Apportionment for Smog Production**

This publication attempts to get at origins of smog ozone in California using the VOC measurements made on the NASA DC-8.

Primarily, we seek to quantify “VOC control” of the smog ozone process, and then also the complementary “NOx control.” We seek to do these as a simpler parallel and check to complex three-dimensional photochemical models, but it is an ambitious goal, one that we approach stepwise. First we use a technique quantitatively describing O3 production and VOC (radical) vs NOx control. Because smog chemistry is non-linear, we use nonlinear methods. The technique allows short-term descriptions of O3 production near the sampling time. While this is valuable, it does not tell the whole history of O3 production up to the time of sampling or thereafter. This extends on a method shown in detail in Chatfield et al [Atmospheric Environment, 2010]

For this reason, we move from considering jxHCHO and NO as short-term descriptors to HCHO and NOx as descriptors of potential VOC and nitrogen oxide activity over a longer period, hours to a day or so. (We will expand on this distinction below.) Each of these, HCHO and NOx, have a variety of sources which appear somewhat independent; some are in common such as urban-light-industry sources, some are disjoint, e.g. biogenic VOC emissions. We present these apportionments individually.

One kind of summary is possible for VOC vs NOx control. The concluding analysis brings together the contributions in a “split-pie” graph: the left-hand side of the pie describing VOC sources of HCHO, while the right side describes NOx sources.

**POGO Relationships for California sampling**

Previous work [Chatfield et al., 2010] has shown a way of parameterizing the smog production of ozone that works well over many orders of magnitude, and implicitly encapsulates the long-known “non-linearity of ozone production” [Leighton, 1961, Lin et al., 1987] in a simple form. The form relates the chemical production rate

\[ P_{O3} = c \cdot j_{HCHO} \cdot H + HCO \cdot (HCHO) \cdot \beta \cdot \left[ NO \right]^{\gamma}, \]

where \( \alpha \) and \( \beta \) are estimated by regression and are less than one, typically \( \sim 0.6 \pm 0.9 \). This directly expresses the sub-linear behavior of ozone production with respect to primary emissions. Note that \( \beta \) differs substantially from 1. The regression is a linear regression when logarithms are used, and additionally the pattern of residuals of the log quantities has approximately constant variance. We did find that there were about 10 points out of 800 that were far off the linear trend of the plot, and were inconsistent with an otherwise smooth distribution of prediction error residuals. They failed the Mallows \( C_p \) statistic test (Faraway, 2002) which evaluates both fit to a normal error distribution and “leverage” influencing parameter estimates and were discarded from consideration for the estimate.

We expect to characterize these points in further work, using meteorology as well as the attribution techniques we describe below to understand valid but highly anomalous
observations. (Inadequacy in the averaging-merge of samples and ordinary instrumental/electronic glitches or other possibilities.)

Table T1A

Ozone Chemical Production Rate Based on VOC-Oxidation Rate

Regression in terms of log (production rate) and log predictor quantities

\[
\text{lm(formula} = \text{l.k.HO2.NO.m} - l.j.HCHO.m + l.NO.m, \text{subset} = \text{-LoHiPts, weights = (l.k.HO2.NO.m), x = TRUE})
\]

Coefficients:

| Estimate | Std. Error | t value | Pr(>|t|) |
|----------|------------|---------|----------|
| log10(C) (Intercept) | -2.46722 | 0.08744 | -28.21 | <2e-16 *** |
| log10(j•HCHO) | 0.69706 | 0.01499 | 46.49 | <2e-16 *** |
| log10(NO) | 0.56941 | 0.00809 | 70.38 | <2e-16 *** |

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\[a\] Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 0.3491 on 998 degrees of freedom
Multiple R-squared: 0.9311, Adjusted R-squared: 0.9309
F-statistic: 6738 on 2 and 998 DF, p-value: < 2.2e-16

R-squared for concentrations in non-log units: 0.8519941
Figure 1 A. POGO relationship for California
**Instantaneous Contributions to P(O3) vs Origins of Reactivity**

The description of the chemical production rate of O3 by smog reactions is described by variable closely related to the kinetics of the rate $k[H^\text{O}_2][N\text{O}] + k[RO_2][N\text{O}]$. However, the quantities $j_{\text{HCHO}}$ and $[\text{NO}]$ often vary rapidly due to insolation, albedo, cloudiness, etc, and are poorly matched in timescale to relate O3 production to source emissions, for which we wish to use relatively persistent tracers. For that reason we have chosen related variables for the study of origins: HCHO and NOx = NO + NO2. Both of these variables vary, commonly on timescales of several hours, responding more slowly to emissions and chemical transformation. In a manner of words, HCHO and NOx are more conservative quantities that are released into indicators of chemical activity under the influence of light. The choice of HCHO rather than total VOC mass provides an automatic reactivity weighting for the VOC emphasizing relevance to smog. The following sections describe a partially successful effort to relate HCHO and NOx to more conservative “marker” quantities that describe types of pollution emission.

**VOC and RO2/HO2 production activity**

*Choices of marker compounds for sources of VOC reactivity and NOx.*

**Technique (ii): Identification of Markers**

DC-8 data

The conflagration of large amounts of biomass in wildfires liberates very large quantities of VOC compounds. Our research began by seeking to identify the extent to which the VOC compounds contributed to smog considering their reactivity weighting on their concentrations, but soon found that this question intimately involved the origins of reactivity-weighted VOC and of NOx from all sources. This became particularly important when our initial studies suggested that fires contributed only minutely to the NOx observed.
in California, and indeed that fire tracers suggested diminution of NOx levels, not increase. Overall, do fires decrease ozone production, or do other interactions allow it to promote it?

Our methodology sought an intermediate path between naming isolated, simple source-attribution compounds (e.g., CH3CN above background levels indicates degree of fire influence) and a mathematics-dominated approaches such as positive matrix factorization or “partial least squares.” We began with marker species with clear attributions (CH3CN implies fire, isoprene implies arboreal emissions, ...). When linear regressions with these species left residuals requiring attribution, new variables were added, respecting both statistics (essentially, correlation) and physical meaning. We progressed until the variance explained by the linear regression was high and attribution became less clear. This method addresses the difficulties of valuable tracers responding to more distinct sources in distinct circumstances (e.g. forest fires or very local automotive combustion, ... see below) and it remains closer to explanation by identifiable physical processes. There follows a summary of desirable properties for marker-based linear regressions for attribution; not all are completely attainable while retaining high explanation value in a regression.

**Desired Property 1.** Positive contribution. The choice of acetonitrile as a fire marker has been discussed. Similarly, the tracer CHCl3, chloroform or trichloromethane, is logical and commonly used (Singh et al., and referenced work), and is thought to represent urban sources associated with light industry and offices. Methyl chloroform, CH3CCl3, 1,1,1-trichloroethane, has even more distinct origins, but in our analysis, there was no noticeable in correlations of using either one, and CHCl3 had a lower background concentration.

This feature brings up another desirable feature for a marker-based attribution. If there is a “background concentration,” a nearly constant lower value observed in all but exceptional cases (e.g., air strongly affected by stratospheric processing), this should be removed.

**Desired Property 2** is that when markers are used for attribution, that effect-concentrations of zero should correspond to marker-values of 0. In making attributions, ([CHCl3] − 6.5 ppt) has essentially this property. Similarly, ([CH3CN] − 45 ppt) has this property for fire emission effects. Background concentrations are easily seen in normal q-q plots (Stat Ref), and small errors in estimation have small effects, since the range of marker concentrations is commonly a factor of 50 or more. The implementation of both of these properties must be approximated for one of our tracers.

**Desired Property 3** is that the tracers do not simply repeat the chemical origin of either HCHO or NOx; e.g., NOy or HNO3 is not chosen to highlight origins of NOx.

**Desired Property 4** is that the markers repeat information on sources as little as possible, and seem to have source information that is plausibly somewhat different from other markers. “Urban emissions” and “automotive combustion” will tend to have similar sources, but it is still expected that different VOC origins be associated with light industry, with automotive sources, and with large refining or shipping operations. We indicate that it is possible to approach this property using linear regressions to remove a strong effect (e.g., forest fires or urban emissions) when a marker variable can be identified with several sources.

Using these criteria, we made a progressive assignment of marker compounds, seeking in a stepwise manner to add markers that correlated strongly with the residuals not accounted for by previous linear regression runs.
### Table T-2A
Markers Chosen for Source Attribution

<table>
<thead>
<tr>
<th>Marker</th>
<th>VOC Activity</th>
<th>NOx Source</th>
<th>Suggested major influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3CN</td>
<td>√</td>
<td>(✓)</td>
<td>Fire sources (all sorts, especially forest fires)</td>
</tr>
<tr>
<td>CHCl3</td>
<td>√</td>
<td>✓</td>
<td>Urban sources; light industry and businesses</td>
</tr>
<tr>
<td>Isoprene</td>
<td>√</td>
<td></td>
<td>Biogenic emissions, mostly from trees</td>
</tr>
<tr>
<td>Refractory CN</td>
<td>✓</td>
<td>✓</td>
<td>Automotive fuel burning emissions (?)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>✓</td>
<td></td>
<td>Source concentrated in Sacramento Valley, also San Joaquin. Possible biogenic, dairy-related or other livestock feeding. Implies excess CH4</td>
</tr>
<tr>
<td>i-Butane</td>
<td>✓</td>
<td></td>
<td>Fuel emissions not necessarily related to SO2</td>
</tr>
<tr>
<td>Toluene Residual</td>
<td>✓</td>
<td>✓</td>
<td>Toluene not explainable by CH3CN or CHCl3 or SO2. Possible heavier industry and shipping</td>
</tr>
</tbody>
</table>

Having presented these variables, we will describe our process of identification.

Both formaldehyde and the reactive nitrogen oxides have many sources. We sought marker compounds; we found that several of these markers also suggested multiple sources; for example CH3CN is a clear indicator of combustion, almost always wood combustion as in forest fires. Our examination of correlation plots repeatedly pointed out the usefulness of a variable reported as “Hot CN,” i.e. counts in a simple condensation nucleus (CN) counter for the number of particles that have survived passage through a chamber heating them to 400 C. Since all CN measurements including “Hot CN” are dominated by very fine particles which aggregate on to accumulation mode aerosol within hours (Zembla or Anderson, 20xx), they indicate recent emission. Hot CN indicate recent combustion activity. Fresh fire emissions increase Hot CN greatly, but only in a relatively small number of cases. Consequently, it is reasonable to describe a “Refractory CN residual” which removes the wood-fire effect but is positive:

\[
\text{Hot-CN residual} = \max (1, \text{Hot-CN} - (\text{Hot-CN predicted by linear regression on CH3CN, CH3CN > 400 ppt}))
\]
Similarly, toluene and ethanol had dependences on fire emissions (CH3CN) and urban emissions (CH3Cl), noted in the highest 10%, or more, concentration-levels of these markers. When these were removed by linear regression, substantial variation remained in the residuals. These residuals had considerable explanatory power for HCHO or NOx. The compound iso-butane also had many sources that could be removed by linear regression, leaving a residual. There were a very few situations in which NOx was extremely high, above 15 ppb, but i-butane was the only species with significant correlation. These were geographically very restricted (Western Los Angeles, offshore, and port regions, some nearby areas). We seek the sources of these high values, but meanwhile i-butane serves to

**Notes on specific choices.** The choice of CHCl3 for general urban emissions has frequently been made; Singh et al. [20xx] prefer the very related methylated tracer, CH3CCl3. We found little difference in explanatory power, and found the higher background concentration of CHCl3 easy to remove by employing probability distribution functions (q-q plots). “Refractory CN” is an aerosol measurement, not a standard sample and a measurement that relates in a complex way to a specific chemical composition. However, it is technically quite simple to measure and gives high-response measurements. As such, it is an attractive add-on to future surface stations oriented towards air pollution research that are aimed at aiding analysis of pollutant origins. Since “Refractory CN” is produced strongly by forest fires, “Desired Property 4” suggested that we construct a residual measure that removed the forest fire signal. Similarly, graphical analysis showed that i-butane was a marker for extremely localized, very high NOx values. (Possible reasons are discussed below.) The i-butane information could be made specific by removing emissions from fires (using CH3CN) and urban influences (using CH3Cl); the highest values of these showed clear linear features which made this correction relatively easy. (Graphs are provided in the Supplementary Material.)

(An alternative choice of SO2 served fairly well as the refractory CN. In 2008 these were a stronger tracer than now, according to the experience of California ARB, SO2 is currently a less clear indicator of there automotive/trucking emissions in recent years (A. Kaduwela, RC Vancurren, personal communication, 2012). SO2 is also more difficult to measure at levels useful for research.)

Another common automotive emission associated with urban areas is i-butane. This proved to be a better marker for NOx sources; it added less explanation power for HCHO. A residual “excess Butane” was calculated that removed the effects of both forest fires (CH3CN) and urban fixed sources (CHCl3).

The last choice, the toluene residual, was somewhat more problematic. Toluene was a remarkable species in that had several significant sources. This was verified by scatter plots of toluene against other marker species like CH3CN or CHCl3; there appeared separate correlation lines. However, there was also toluene that was independent of these markers. A residual was calculated which subtracted out the linear regression relationship with CH3CN and CHCl3. This residual seemed to maximize in areas where the DC-8 flew near refining complexes and possibly port regions. Maps describing the prevalence of HCHO, NOx, and our suggested marker species are given in the supplementary material.

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Simply removing the correlation of our marker species does not guarantee that the species will perform well with respect to Desired Property 2: the desirability linear (not affine)
response, with zero marker contributing zero effect on HCHO or NOx. For strong effects, this could be guaranteed by extrapolating down to zero from the maximum effects, i.e., situations where fire emissions or urban (CHCl3) emissions dominated, as seen by graphical analysis, noting a strong linear trend at high values. For other variables, e.g. ethanol, there was not a clear high-marker trend. For these cases, we made use of standard analysis techniques for linear regressions, “added variable” (or “partial regression”) and also “partial residual” techniques (Faraway, 2002). Flat or decreasing response in the partial residuals shown in “added variable” for all marker values near zero could be noted up to a breakpoint. The R routine “termplot” made such transitions obvious, revealing changes in the pattern of increase near zero effect. A transition towards linear increase identified a background value that should be subtracted from the marker variable in order to insure linear response near zero. Except for CH3CN and CHCl3, with very clear backgrounds, response near 0 often proved complex. When larger baseline effects were removed, the intercept in the complete regression approached zero (possibly a desirable effect), but explained variance declined (bad). Clearly, the process required decisions by the scientist. It is important to note that such minor errors of identification had minor ramifications, since significant responses to the marker variable occurred only at values 10 times (or more) than the identified breakpoint. This approach reaffirmed the identifications of a background level for CH3CN and CHCl3, but did not suggest background values be subtracted for other variables.

**Results: Reactivity-Weighted VOC Sources for Ozone Production**

Our analysis of formaldehyde highlighted the important sources of VOC as they were weighted by their reactivity and the flow of organic oxidation. For time periods beyond a few hours, independent of current photolysis drivers, this is an apportionment of HCHO. The results of a simple multiple regression using the tracers we described is shown in Table T3-A, and it gives us considerable confidence in our understanding of sources. Influences swept into the “Intercept” term could be due to either other VOC sources or HCHO that has “lost traceability” due to random errors in sampling or the disappearance to low values of the marker compounds.

### Table T3-A

**Organic Reactivity as Described by Markers that Explain HCHO via Linear Regression**

|                | Estimate | Std. Error | t value | Pr(>|t|) |
|----------------|----------|------------|---------|---------|
| (Intercept)    | 390.76391| 84.45389   | 4.627   | 4.36e-06*** |
| ab.CH3CN       | 9.20908  | 0.18437    | 49.948  | < 2e-16 *** |
| ab.CHCl3       | 84.05451 | 8.52739    | 9.857   | < 2e-16 *** |
| Refr.CN.xFire.resid | 0.23695 | 0.02393    | 9.900   | < 2e-16 *** |
| Isoprene       | 0.54565  | 0.06533    | 8.352   | 3.12e-16 *** |
| Ethanol        | 0.80795  | 0.05979    | 13.513  | < 2e-16 *** |
| Toluene.resid.pos | 2.93300 | 0.54554    | 5.376   | 1.01e-07 *** |

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### Table T4-A

Organic Reactivity as Described by Markers that Explain NOx via Linear Regression

#### No Fire Tracer

**Linear Model:**

\[
\text{NOx} = a_1 \cdot (\text{CHCl}_3 - XX) + a_2 \cdot (\text{CNR}_{\text{refract}}) + a_3 \cdot (\text{i. Butane}_x) + a_4 \cdot (\text{TolueneResid}) + \text{Intercept}
\]

**Residuals:**

<table>
<thead>
<tr>
<th>Min</th>
<th>1Q</th>
<th>Median</th>
<th>3Q</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>-8819</td>
<td>-938</td>
<td>-8</td>
<td>574</td>
<td>31731</td>
</tr>
</tbody>
</table>

**Coefficients:**

|        | Estimate | Std. Error | t value | Pr(>|t|) |
|--------|----------|------------|---------|----------|
| (Intercept) | -1.155e+03 | 1.705e+02 | -6.775 | 2.46e-11 *** |
| ab.CHCl3 | 1.534e+02 | 1.788e+01 | 8.581  | < 2e-16 *** |
| ab.i.Butane.xs | 6.276e+00 | 4.743e+01 | 13.233 | < 2e-16 *** |
| Toluene.resid.pos | 9.375e+00 | 1.174e+00 | 7.986  | 5.10e-15 *** |

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**Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1**

**Residual standard error:** 2510 on 769 degrees of freedom

**Multiple R-squared:** 0.6522,
**Adjusted R-squared:** 0.6504

**F-statistic:** 360.4 on 4 and 769 DF,  **p-value:** < 2.2e-16

#### With "Imposed" Fire Emissions

**Linear Model:**

\[
(\text{NOx} - 4.999 \cdot \text{CH}_3\text{CN}) = a_1 \cdot (\text{CHCl}_3 - XX) + a_2 \cdot (\text{CNR}_{\text{refract}}) + a_3 \cdot (\text{i. Butane}_x) + a_4 \cdot (\text{TolueneResid}) + \text{Intercept}
\]

**Residuals:**

<table>
<thead>
<tr>
<th>Min</th>
<th>1Q</th>
<th>Median</th>
<th>3Q</th>
<th>Max</th>
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<tbody>
<tr>
<td>-8962</td>
<td>-941</td>
<td>-8</td>
<td>588</td>
<td>31729</td>
</tr>
</tbody>
</table>

**Coefficients:**

|        | Estimate | Std. Error | t value | Pr(>|t|) |
|--------|----------|------------|---------|----------|
| (Intercept) | -1.195e+03 | 1.714e+02 | -6.975 | 6.61e-12 *** |
| ab.CHCl3 | 1.500e+02 | 1.797e+01 | 8.345  | 3.29e-16 *** |
| Refr.CN.xFire.resid | 6.362e-01 | 4.573e-02 | 14.503 | < 2e-16 *** |
| ab.i.Butane.xs | 6.349e+00 | 4.768e+01 | 13.314 | < 2e-16 *** |
| Toluene.resid.pos | 9.197e+00 | 1.180e+00 | 7.791  | 2.15e-14 *** |

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**Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1**

**Residual standard error:** 2523 on 769 degrees of freedom

**Multiple R-squared:** 0.6509,
**Adjusted R-squared:** 0.649

**F-statistic:** 358.4 on 4 and 769 DF,  **p-value:** < 2.2e-16
This suggested decomposition of sources based on markers was unexpectedly clear. Rather than a single “urban pollution” source with all compounds mixed, the low correlations between the marker compounds and the high explanatory power of each of the variables suggested that the analysis of air pollution may be analyzed by sector in observations and models; allowing controls by sector of emissions to be more confidently evaluated. The results of this attribution will be discussed below in a larger context.

**NOx Sources for Ozone Production**

We then attempted to describe the nitrogen side of ozone production using similar tracers. This endeavor appeared more difficult due to the short lifetime of NOx in the boundary layer. Only four of the markers gave clear positive contributions, and those are described in Table T4A. The role of fire, marked by CH3CN, was peculiar. Linear regression suggested that CH3CN had a significant influence on NOx, but the effect was negative. Even when it the CH3CN effect was limited, insisting that only CH3CN concentrations above 1000 ppt were to be used to gauge fire influence (predictor max(CH3CN–1000, 0)), estimates were negative. Apparently although California fires emit some NOx, that NOx along with any preexisting NOx is very rapidly tied up, presumably into organic nitrates like PAN and perhaps HNO3. The fact that the named predictors only explain about 60% of the total NOx might be interpreted as suggesting other NOx sources. We venture that it is as likely that since NOx is so quickly removed, links with longer lasting markers are tenuous.

**Relative Roles of Various Sources and VOC/NOx Limitation**

We used maps with a special symbolic marker system to display the wealth of information.

![Figure 3A](image_url)

Figure 3A. (Left) A situation in which all sources contributed to smog ozone production over California. Colors give the attribution of the HCHO and NOx as shown; similar colors are used to mark similar effects to each species, e.g., light blue air of urbanized origin for air contributing to NOx, dark darker blue for contributing to HCHO and reactive VOCs. Sectors indicate the regression coefficient for NOx (or VOC) CHCl3 multiplied by the locally observed concentration of CHCl3. This area, near Santa Barbara, is one which is relatively VOC dominated, i.e., NOx-sensitive. (Right) Samples from a region near Roseville and Auburn, northwest of Sacramento, which showed a variety of influences. The aircraft samples along the track running SE to NW was strongly influenced by fire. The track running from SW to NNE shows the rapidly increasing role of isoprene as the aircraft flew into a progressively forested area.
available from the six different flights made by the DC-8 up and down the length of California in several forays. (See maps in Jacob et al., 2010 and supplementary material.) The coding takes the form of colored wedges in a “split-pie” graph, with the left hand semicircle describing HCHO origins, and the right hand side describing NOx origins. The radius of the left and right are proportional to log of HCHO or NOx referred to their maximum values. This is a strictly relative approximation to “VOC excess” (NOx control) or “NOx excess” (VOC control). The colors used for the two sides have some relation to the marker; e.g., orange colors denote Local fuel combustion, “Hot” CN, on each side. Blue colors describe urban emissions, and a similar violet color toluene-related emissions.

(The following maps of various areas have notes about major features. The text will describe the markers in the context of all of the map plots. Overlapping symbols are common; adjacent split-pies usually supply the obscured information.)
Figure 2A. Origin attributions for HCHO and NOx (reactivity-weighted VOC and NO) for the San Francisco Bay Area, California Delta, and the Northern San Joaquin Valley. Contours of elevation in gray. Valley cities of Sacramento, Stockton, Modesto, and Fresno are shown as black circles. Notable features regarding VOC’s are the importance of fire emissions seen in the transect up the western San Joaquin (red), the significance of isoprene over the upland regions with tree emissions (dark green), and the ethanol-marked emissions over varied agricultural regions. Nitrogen oxides are seen to trace mainly to cities and localized combustion emissions, with localized significant contributions from toluene-related emissions, mostly in industrial.
Figure 3A. Origin attributions for HCHO and NOx (reactivity-weighted VOC and NO) for interior Northern California. Notable features of reactive VOC origins are the intermittent but overwhelming effect of fire emissions (red) (emitted the same day according to winds and fire records), the restriction of strong isoprene contributions to the wooded higher elevation regions. For NOx, the frequently strong toluene-related emissions around Sacramento gave simultaneous high VOC-NOx values conducive to strong ozone production.
Figure 4A. Origin attributions for HCHO and NOx (reactivity-weighted VOC and NO) for San Joaquin Valley and offshore samples. Most offshore samples are notably affected by fire emissions for HCHO, but NOx levels are low; even when there are effects from the Valley, NOx levels have been reduced, perhaps by transformation to organic nitrates. Cities of Stockton, Modesto, Fresno, Visalia, and Bakersfield are shown by black circles. A mixture of urban (medium blue) and local emissions (light orange) are commonly seen as contributing to NOx. Near Bakersfield, there are more toluene-associated NOx sources. VOC activity (HCHO) is associated with livestock/agriculture (light green) and local sources (Residual CN) when fire emissions do not affect the area. Offshore concentrations appear to be reaction-diminished onshore emissions except when fire emissions are dominant.
Figure 5A. Origin attributions for HCHO and NOx (reactivity-weighted VOC and NO) for urban Southern California and offshore. Urban emissions (light blue) dominate NOx emissions as expected; however many samples have very high NOx associated with i-butane but few other hydrocarbon compounds; this contribution is seen only in Western Los Angeles, offshore, and along the Mexican border and San Diego, not in other parts of California.

Figure 6A: Attributions for Southern California region, including border area and offshore. Description is like coastal urban Southern California. Most samples over ocean were influenced by winds from the shore, sometimes showing high fire influence. Samples along the border showed high i-butane influence unique to Southern California.
Comparison with Simulations and Thoughts for Further Analysis

Conclusions

References

Faraway, Julian, 2002: Practical Regression and Anova in R, internet text
http://www.maths.bath.ac.uk/~jjf23/book/,


(http://www.sciencedirect.com/science/article/pii/S1352231006004067)

Keywords: Ozone control; Precursor limitations; Photochemical transport model; CCOS; OBM