Characterization of the atmospheric chemistry in the southern San Joaquin valley and an initial comparison with atmospheric chemistry in the South Coast air basin

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From the mountain to the valley

At the last Sacramento CALNEX meeting we proposed bringing the BEARPEX team to a site in the Southern SJV.

We are excited that ARB has helped us to make that happen.
BEARPEX Measurements 2007/2009

Unprecedented detail of the chemical composition, vertical gradients and fluxes of gases and aerosol

Mostly NSF sponsored team from CA, CO, PA, WI, OR, WA, and the UK

• Essentials: P, T, winds, NO, NO₂, CO, O₃, CO₂, etc.
• OH, HO₂, OH Lifetime
• 5 methods for NOₓ
• Many organic acids
• Many peroxides
• 5 approaches to VOC (OVOC)
• \( \text{H}_2\text{CO} \)
• glyoxal
• new approaches to aerosol lifetime and composition
Outline

- Hypothesis & target questions
- Some background and example analyses; measurement capabilities
- Opportunities for enhancements
The San Joaquin Valley of California is a region where secondary pollutants ($O_3$ and PM) will respond weakly or not at all to continued anthropogenic VOC controls while $NO_x$ controls will be effective.
Questions to be addressed for SJV

- How well do we understand the sources of NOx and VOC in the SJVAB?
- How well do we understand the coupling of HOx, NOx, O3 and VOC photochemistry under conditions of VOC reactivity typical of the SJVAB?
- What happens to NOx and VOC oxidation products at night? In the nocturnal boundary layer? In the residual layer? How does this chemistry affect NOx, VOC, O3 and aerosol production at night and on the following day?
- What factors affect the time scales for production and removal of 1st, 2nd, 3rd, etc. generation products of VOC and NOx oxidation?
- How do these VOC reactions impact the photochemical production and loss of ozone, OH, NOy species, and aerosols?
Questions to be addressed in collaboration with partners

- Are there significant differences in precursors or ozone formation chemistry between the Central Valley and South Coast Air Basin?

- Will precursor differences between the Central Valley and the South Coast Air Basin lead to different chemical transformation processes and different responses to emissions reductions?

- What is the importance of natural emissions to the ozone formation process? Are there regional differences in the formation rates and efficiency for particulate matter as well?
Tasks—Emissions & $\text{HO}_x/\text{NO}_x/\text{O}_3$ Chemistry

- evaluate how $\text{O}_3$, OH and $\text{HO}_x$ respond to changes in $\text{NO}_x$ at the SJV field site

- assess the sources of OH reactivity in the region comparing total OH loss with the sum of OH losses calculated from observed organics and nitrogen oxides

- compare mechanisms for production and removal of $\text{HO}_x$ that are important to indicator formulations ($\text{HO}_2\text{O}$ and $\text{HNO}_3$), compare these ideas to instantaneous evaluations of ozone production rate models (e.g. Thornton et al. 2002, Spencer et al. 2009) that use $\text{HO}_2\text{NO}_2$, peroxide, organic nitrate and $\text{HNO}_3$ production rates as tests of sensitivity to changes in $\text{NO}_x$ and then assess the chemical regime based on these combined indicators

- evaluate the NOx budget including sources and sinks
Tasks--Biogenics

- evaluate the role of biogenic chemistry in ozone production emphasizing HOx recycling and organic nitrates

- we will calculate the SOA production rate from the observed organics including both a-dicarbonyls and highly oxidized VOC

- Assess the role of biogenic VOC in the sequestration of NO\textsubscript{x} as PAN like molecules and evaluate effect on O\textsubscript{3}. We will compare and contrast our SJVAB observations with those at other CalNex sites and those from BEARPEX-2007 and 2009 in a rural NO\textsubscript{x}-limited forest

- Perform source attribution studies using positive matrix factorization e.g. Lamanna and Goldstein, 1999; Goldstein et al., 2008) for the broad suite of VOC measured, to assess the relative importance of biogenic versus anthropogenic sources, and specific types of anthropogenic sources, affecting air quality in the region.
Background and Example
Analyses: Emissions
Anthropogenic VOC

Emissions

$R_{VOC}$

Steiner et al 2007
Total OH reactivity: Model and summed from VOC and NOx Obs

A) AM

Sacramento

Modeled

9.7

Measured

11.5

Fresno

Modeled

7.0

Measured

17.6

Granite Bay

Modeled

10.6

Measured

10.2

Blodgett

Modeled

9.4

Measured

6.8
VOC emissions from dairies in the California Central Valley and their impact on local and regional ozone - Yang et al.
Acetaldehyde

Armin Wisthaler, Univ Innsbruck
Motor Vehicle VOC Emissions

California EMFAC model predictions for Sacramento in summer 2001
Exhaust vs. Evaporative VOC

Isopentane & methylpentanes are:
- abundant in gasoline (7.5 and 5.8 wt%)
- not very reactive in the atmosphere

- Isopentane greatly enriched in vapor emissions relative to methylpentanes
  - 27 vs. 6.5 wt% in vapor
Granite Bay: 18 July - 15 Sept 2001

[Graph showing mixing ratio (ppb) over the day of the year.]
Vapor Contribution vs. $T$

Granite Bay

Weekdays only; 3-4 PM

Headspace Vapor Contribution

$T$ (Celsius)

$R^2 = 0.66$

Rubin et al., JGR 2006
\( \sim 8\% / \text{yr decrease in } \text{NO}_x \)

weekdays and weekends
San Francisco
5%/yr decrease
San Joaquin Valley: Decrease not detectable
Caldecott Tunnel study of NOx emission factors

WE
Day of Week Profiles: OMI & CARB

Surface & Satellite NO₂ Day of Week Profiles

Background and Example Analyses: Chemistry
Catalytic Cycles

HO_x Cycle

NO_x Cycle

\[ \text{RH, O}_2 \xrightarrow{\text{OH}} \text{RO}_2 \xrightarrow{\text{NO}} \xrightarrow{\text{O}_2} \text{R'O} \xrightarrow{\text{HO}_2} \xrightarrow{h_v} \text{NO}_2 \xrightarrow{\text{O}} \text{O}_3 \]
Photochemical Ozone Production
\(\text{NO}_x\), VOC Reactivity, \(\text{HO}_x\) production

\begin{align*}
\text{P}(\text{O}_3) \text{ (ppb/h)} & \\
\text{Noon} & \\
\text{3PM} & \\
\text{Base Case} & \\
2^*\text{VOC} & \\
2^*\text{VOC, P(\text{HO}_x)/2} & \\
\end{align*}
NO\textsubscript{x} and OH

[Diagram: [OH] as a function of NO\textsubscript{2}]

- Steady-State [OH] (molecules cm\textsuperscript{-3})
- NO\textsubscript{2} (ppb)

- [OH] peaks at around 10\textsuperscript{6} molecules cm\textsuperscript{-3} for NO\textsubscript{2} concentrations between 10\textsuperscript{-1} and 10\textsuperscript{1} ppb.

- The graph shows the relationship between NO\textsubscript{x} and OH concentrations, indicating the chemical dynamics involved in photochemical smog formation.
Do we understand OH/HO$_2$/RO$_2$ chemistry?

The answer is no at high NO$_x$ and at high isoprene levels.

That means all models have incorrect ozone production rates under these conditions.
Thornton et al. 2002

\[ \text{OH} + \text{NO}_2 \text{ sole } \text{HO}_x \text{ sink} \]

\[ \text{HO}_2 + \text{RO}_2 \text{ sole } \text{HO}_x \text{ sink} \]

Estimate \( \sim 50\% \) of \( \text{RO}_2 \) derived from isoprene.

\[ \frac{P_{\text{HO}_x}}{L_{\text{HO}_x}} \]

\[ \text{HO}_2 + \text{RO}_2 / L_{\text{HO}_x} \]
Implication: RO₂ + HO₂ not understood

In 2002 we suggested that the products of RO₂ + HO₂ are mostly (90%) chain carriers not chain terminators, for example

\[ \text{ROOH} + h\nu \rightarrow \text{RO} + \text{OH} \]

\[ \text{RO}_2 + \text{HO}_2 \rightarrow \text{RO} + \text{OH} + \text{O}_2 \]

Result at least partly confirmed in the lab and by 4 different groups measuring OH/HO₂ and RO₂.

At high isoprene OH + isoprene has the effect of increasing the HOₓ source by much more than the effect of the H₂CO produced.
RO\textsubscript{2} + HO\textsubscript{2} \rightarrow \text{RO} + \text{OH} + \text{O}\textsubscript{2}

Hasson, Tyndall and Orlando J. Phys. Chem. A 108 5979, 2004
also Jenkin et al. 2007 and Dillon and Crowley 2008

For oxygenated RO\textsubscript{2} radicals + HO\textsubscript{2} (~30-50\% OH yields)

Consistent with direct measurements of OH by Penn State (Brune). Mainz (Lelieveld) groups and more recently Juelich and NCAR.

OH much larger than predicted when isoprene is high.

Some analyses suggest isoprene oxidation products amplify HO\textsubscript{x} increasing it by more than the reaction above would indicate.
**HO\textsubscript{x} Chemistry during ARB-ARCTAS**

Brune et al.
Implication: $\text{O}_3$ production is faster than in our models at high $\text{NO}_x$ and at high isoprene.
Do we understand $\text{NO}_x/\text{NO}_y$ chemistry?

Isoprene and aromatics are important puzzles to examine.
RONO$_2$ significant, often ignored

RONO$_2$ is often limited due to NO$_x$ availability, and NO$_x$ can become saturated. The graph shows the relationship between NO$_x$ (ppb) and PO$_3$, PHNO$_3$, and PANs (ppb/hr).
Wu et al, 2007

A ~10% change in global $\text{O}_3$ when isoprene branching ratio was changed from 4.4% to 12%.
RONO$_2$ formation (especially from isoprene and other biogenics) is one of the key uncertainties in current and future AQ.

Models with high RONO$_2$ production remove NO$_x$ faster than they increase O$_3$ when isoprene emissions grow.

RONO$_2$ are observed to be 15-25% of the NO$_x$ sink. What happens to that N upon oxidation of the initial RONO$_2$? The spectrum of models make every imaginable choice.
Measurements
Assumptions/Ideas that guide site our experimental strategy

1. VOC reactivity, NO\textsubscript{x} chain termination rates, and T are the key parameters.
2. Local measurements of key species, their reaction products and precursors contain information about emissions and chemistry.
3. Biogenic VOC cannot be controlled—thus a crucial design parameter for control strategies is the fraction of VOC reactivity that we can control.
4. The same processes occur everyday at rates that depend on temperature, RH and available sunlight—thus day-to-day variability is one of the most important tests of our understanding.
5. NO\textsubscript{x} reductions on weekends are one of the only “controlled” experiments we have available.
Strategy--SJV

Measure biogenic and anthropogenic organic molecules, including their reaction products.

Measure $\text{NO}_x$ and its reaction products.

Measure $\text{HO}_x$ and related reaction products

Examine as many closure relationships as possible to establish that detailed mechanisms of emissions, ozone and aerosol formation are correct.

Observe for long enough to capture statistics of day of week effects

Use these detailed evaluations to estimate how reality is different from predictions using a current generation AQ model.
The current SJV team

Allen Goldstein: VOC, CO, O₃, meteorological state variables

Ronald Cohen: NO, NO₂, Σperoxynitrates, ΣRONO₂, HNO₃

William H. Brune: OH, HO₂ ΣOH reactivity, potential aerosol mass

Joel Thornton: PAN, PPN, MPAN, RO₂NO₂ ...

Frank Keutsch: H₂CO, HCOHCO, Σα-dicarboxyls

Paul Wennberg: HOOH, CH₃OOH, HNO₃, HO₂NO₂, HCN, other peroxides and several non-traditional isoprene oxidation products
MPAN/PAN and PPN/PAN vs. T

Air Temperature (°C)

- PPN/PAN
- MPAN/PAN
Day of Week Effect

![Graph showing Day of Week Effect with MPAN/PAN and PPN/PAN data points and error bars.]
Ozone vs. MPAN/PAN and PPN/PAN

O$_3$ (ppb)

MPAN or PPN relative to PAN
Caltech

HNO₃

H₂O₂

HCN
Caltech
**\( \alpha \)-dicarbonyls and Formaldehyde: Central OVOCs for Ozone and SOA Production**

- Formaldehyde proven tracer of VOC oxidation chemistry
- \( \alpha \)-dicarbonyls are higher generation oxidation products of biogenic VOCs \(^1\), thus allow new insights into VOC oxidation chemistry
- Glyoxal contributes to SOA (>15% of SOA proposed for Mexico City \(^2\))

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The Madison Laser-Induced Phosphorescence Instrument: Direct, Highly Specific and Sensitive Measurement of $\alpha$-dicarbonyls

- Precision ($1\sigma$) 2 pptv/min in the field (more than order of magnitude better than other instrumentation)
- Highly specific (no inlet effects detected, no interference from NO$_x$, O$_3$, H$_2$O, VOCs or OVOCs)
- First LIP instrument for atmospheric measurements
- Custom Ti:Sapphire laser (440-441 nm; $\Delta\nu=0.04$ cm$^{-1}$; 80 mW)
- Tuning fast (25 ms) and piezo controlled
- Wavemeter for wavelength tracking
- White Cell multipass configuration
- Digital gating and photon counting PMT

High glyoxal mixing ratios observed
Overall good correlation with isoprene and MBO
Days 268-271 show higher glyoxal/[isoprene,MBO]
Analysis of VOC Oxidation: Biogenic vs. Anthropogenic Precursors of Glyoxal from BEARPEX 2007

- Change of biogenic and anthropogenic precursors for different T-regimes show that biogenics are main glyoxal precursor
- During third period glyoxal precursors are under investigation
Formaldehyde Measurements PROPHET 2008

- Field test of the formaldehyde LIF instrument was successful
- Prototype laser tested in Madison with ambient measurement
- The upgraded instrument will allow fast highly sensitive measurements including the first formaldehyde flux measurements via eddy correlation
Riverside Summer

TAG-defined Organic Aerosol Sources

AMS Total Organic Aerosol = 10.0 - 20.8 µg m⁻³
2010 Vision for AQ

- In 2010 satellites will be major contributors to our understanding of AQ, with daily coverage for PM, NO₂, H₂CO and CO.

- In 2010 the comparatively low cost of modeling will lead to a new opportunity to use and emphasis one statistics within long term data sets.

- In 2010 the capabilities for detailed chemical tests of aerosol and O₃ (and other chemicals) models will bring our attention to establishing the precursors are right first, so we can show the end products we model are correct for the right reasons.
Strategy--Partners

Integrate our measurements with a wide range of partners during CalNex

Integrate with Satellite based observations of NO$_2$, aerosol and land-cover

Integrate our measurements with a broad perspective based on observations collected in previous CA experiments by the same teams.

BEARPEX, ARB-ARCTAS, INTEX-B, ITCT 2002

Work together to bring new resources and additional measurements to CALNEX overall and to this site.
Thank you