Observations of NO$_2$, total peroxynitrates, total alkyl nitrates, and HNO$_3$ on the Western Slopes of the Sierra:

Implications for Transport of Nitrates to Lake Tahoe

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Visibility in Lake Tahoe

The depth at which a white disk can be seen from the surface changes from year to year but generally has become shallower over the decades.

Jassby, et al. TRG UC Davis
• Low natural nutrient concentrations

• Water has a 650 year residence time in the lake

• Visibility decline is due both to algae and mineral particulate

• Nitrogen was the limiting nutrient in 60’s, now phosphorous is
How much of the N that gets to the basin is from west of the basin?

What is a general framework for understanding transport and chemistry within and surrounding the Sacramento plume?

Note: Focus of this talk is on long-term mean—not on extreme events.
Possible transport paths from the West into the Tahoe basin

- Advection upslope within the boundary layer
- Vertical Mixing above the boundary layer
- Horizontal transport above the boundary layer
- Recirculation within upslope/downslope boundary layer flows
- Downward mixing within the basin
Photochemistry

\[ \text{NO} \rightarrow \text{NO}_2 \rightarrow \text{RO}_2 \rightarrow \text{RO}_2\text{NO}_2 (\Sigma \text{PNs}) \]

\[ \text{NO}_2 \rightarrow \text{OH} \rightarrow \text{HNO}_3 \]

\[ \text{RO}_2 \rightarrow \text{RONO}_2 (\Sigma \text{ANs}) \]

\[ \text{NO}_x \rightarrow \text{NO}_y \]
• How far does ‘Sacramento plume’ travel?

• How much dilution and oxidation occurs as the plume moves downwind?

• What do observations of NO$_{yi}$ show?

• Summary and Implications
East-West Net Air Flow at UC-BFRS 2001

Weekly Net Air Flow (km)

from the East

Julian Day of 2001

from the West
• How far does ‘Sacramento plume’ travel?

• How much dilution and oxidation occurs as the plume moves downwind?

• What do observations of $\text{NO}_y$ show?

• Summary and implications?
Long-lived hydrocarbons define the fraction of the Sacramento Plume that reaches the foothills.

Acetylene at Blodgett Forest

Dillon, Lammana, Schade, Goldstein and Cohen, JGR 107 2002.
n-Pentane (ppt) at Blodgett Forest - July 1997
Key results

• The Sacramento plume can be accurately described with a model representing advection into the foothills, dilution into the regional background and oxidation.

• The lifetime (e-folding time) with respect to dilution is 4 hours.

• An OH concentration of order $1-1.4 \times 10^7$ molecules/cm$^3$ describes the oxidation that occurs during plume transport.
Pure transport contribution to NO$_y$ (an upper limit)
Implications for $\text{NO}_y$

- We have a good first order model of the amount of $\text{NO}_y$ that could be arriving from the west to the foothills of the Sierra (and perhaps as far east as Tahoe).

- The lifetime (e-folding time) with respect to dilution is 4 hours.

- Oxidation converts most of the $\text{NO}_2$ present in Sacramento and its suburbs to $\text{HNO}_3$, PANs and $\text{RONO}_2$ on the same time scale.
• How far does ‘Sacramento plume’ travel?

• How much dilution and oxidation occurs as the plume moves downwind?

• What do observations of NO\textsubscript{yi} show?

• Summary and Implications?
**NO\textsubscript{x} measurements with catalyst**

- The catalyst always converts NO\textsubscript{2} and some other stuff to NO.

- Typically accurate at the source and in urban areas during the night. Factors of two or more are not unusual at midday in urban areas (for example overestimates of NO\textsubscript{x} e.g. 2ppb vs. 1ppb at noon are typical results from field comparisons).

- Usually assume an overestimate of daytime NO\textsubscript{x} but an underestimate of daytime NO\textsubscript{y}. 
LIF NO$_2$

Pulsed Dye laser
Anal. Chem. 72, 528 2000

- Direct and specific
- accurate: ±5%, 1s
- sensitive: 6ppt/min, S/N=2
- detection limit 1ppt

Since 2000
- sensitivity <1ppt/min
- ~7 days unattended
LIF detection of NO₂

Analytical Chemistry, 72, 528, 2000
NO$_2$ Instrument Comparison (SOS 99)
Diode laser (Patti Cleary)
Applied Optics 41(33), 6950, 2002

- 638nm laser and a ss-jet
- sensitivity of 75ppt/min
- 130lbs
- weeks without an operator
$\Sigma$PNs, $\Sigma$ANs, & HNO$_3$ + heat $\rightarrow$ RO$_x$ + NO$_2$

**Thermal Dissociation-LIF**

$\Sigma$PNs, $\Sigma$ANs, & HNO$_3$ + heat $\rightarrow$ RO$_x$ + NO$_2$
HONO$_2$ and C$_2$H$_5$ONO$_2$
September 28, 2000, 9:30 PM

Graph showing the relationship between temperature (°C) and NO₂ detected (ppb). The graph indicates a significant increase in NO₂ as temperature increases. Key labels include [NO₂], [ΣPANs], and [Nitric Acid].
Inlet and Dissociation Heaters

*Ambient Pressure*

*Zeroing*

*Calibration gas*

*Pinholes*

*2-4 Torr*
[\text{\Sigma PANs + NO}_2]
TD-LIF

Accuracy 15%

Sensitivity ~10 ppt

Used at
UC-Blodgett Forest, CA
Granite Bay, CA
Big Hill, CA
Houston, TX and
from the NCAR C-130 (0-7km ASL 35°-85°N Latitude)
Daytime NO\textsubscript{x} (ppb) in the Sacramento Area

Month of the Year

Elk Grove

Folsom

T Street
Concentrations
and Fluxes of:
HNO$_3$, $\Sigma$ANs,
$\Sigma$PNs, NO$_2$,
VOCs, OVOCs,
CO$_2$, water,
ozone, and heat

Other Measurements:
NO, NO$_y$, CO, temperature,
radiation, Aerosol Properties,
winds, sap velocity, leaf physiology,
soil T, soil H$_2$O, ...
Big Hill Observations from Tower atop trailer
Jennifer Murphy and Paul Wooldridge

Observations at Big Hill

Preliminary
Summertime plume
Pure transport contribution to NO$_y$ (an upper limit)
Blodgett has bigger T swings, smaller H$_2$O swings, slower winds.
More NO$_2$ at Blodgett suggests less processed, younger air. HNO$_3$ at Big Hill doesn’t disappear at night.
NO$_y$ at UC Blodgett Forest

August 2001

7 8 9 10 11 12 13 14 15
NO\textsubscript{yi} at UC Blodgett Forest

\[ \Sigma \text{PNS} \]

\[ \Sigma \text{ANs} \]

\[ \Sigma \text{NO}_3 \]

\[ \Sigma \text{NO}_y \]

December 2001
$\text{NO}_{yi}$ at Big Hill

Aug 24-30, 2003
NO\textsubscript{yi} at Big Hill

![Graph showing the concentration of various nitrogen compounds over a period from December 2-8, 2003.](image)
The two sites sample similar air during the day.

Reactive nitrogen at Big Hill is more oxidized and diluted.
Day

\[ k_{\text{OH} + \text{NO}_2} [\text{OH}][\text{NO}_2] \cong k_{\text{deposition}} [\text{HNO}_3] \text{ or } k_{\text{OH} + \text{NO}_2} \frac{[\text{OH}]}{k_{\text{deposition}}} \cong \frac{[\text{HNO}_3]}{[\text{NO}_2]} \]

Expect \([\text{HNO}_3]/[\text{NO}_2]\) to follow \(\text{OH}\) since \(k\)'s are roughly constant and fast.

Night

Chemistry of \(\text{NO}_3\) and deposition approaches zero.
Blodgett Forest deposition of $\text{HNO}_3$
$\text{HNO}_3/\text{NO}_2$ slightly higher at Big Hill than Blodgett, implying deposition is less efficient or OH concentration is higher.

The two sites cannot be perfectly modeled using a single transport path with one effective deposition velocity.
ΣANs and ΣPNs

• Day

Measurements show concentrations follow OH in urban source regions but are decoupled downwind. Implies deposition of ΣANs is rapid (<4 hours) and thermal decomposition of ΣPNs is rapid (<4 hours).

• Night

Chemistry of NO₃ and deposition approaches zero.
ΣANs  ppb

- **BLOGDETT FOREST**
- **GRANITE BAY**
- **HOUSTON**

**Hour of Day**
The observed variance of $O_3$ mixing ratios at Blodgett and Big Hill.
The observed variance of NO$_2$ and $\Sigma$PN mixing ratios at Blodgett and Big Hill
The observed variance of NO$_2$ and $\Sigma$PN mixing ratios at Blodgett and Big Hill
• The variance of the $\text{NO}_{yi}$ chemicals is proportional to the local $\text{NO}_2$ concentration.

• Extreme events are even less important at Big Hill than at Blodgett.
Correlations of water and NO$_y$ at Big Hill (July ‘03) suggest mixing of air from the valley with the free troposphere
It may be possible to use these correlations and observations of water mixing ratio at other sites down wind of Big Hill to estimate potential transport fluxes.
• How far does ‘Sacramento plume’ travel in one day?

• How much dilution and oxidation occurs as the plume moves downwind?

• What do observations of $\text{NO}_y$ show?

• Summary and Implications?
Conclusions

- Transport from the west is an extremely small contribution to the \( \text{NO}_y \) in the air at Lake Tahoe on the daily time scale—factors that contribute to a large regional background that accumulates over multiple days of \( \text{NO}_y \) may contribute. The source of this background is not understood.

- During the day \( \text{HNO}_3 \) has a lifetime of about 3 hours and its mixing ratio is controlled by OH, \( \text{NO}_2 \) and deposition rates. Since OH is strongly buffered, local (within 3 hrs transport time) sources of \( \text{NO}_x \) and are the major atmospheric variable affecting \( \text{HNO}_3 \) dry deposition fluxes.

- We don’t yet have a complete story explaining \( \sum \text{PNs} \) and \( \sum \text{ANs} \), but to the extent that they do deposit rapidly they are unlikely to be a source for N-transported into the basin.

- There is a wealth of high time resolution annual and multi-year data to assess chemistry and transport of nitrogen oxides along the western slopes of the Sierra.
Cohen Group

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