# Nocturnal nitrogen oxide chemistry on board R/V *Brown*


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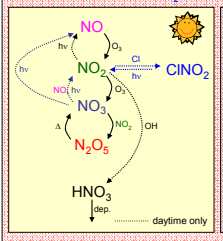
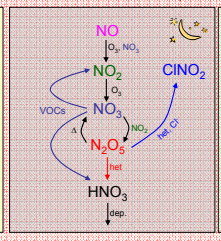
## Introduction

- Nitrogen oxides ($NO_x$ = NO + $NO_2$) catalyze photochemical $O_3$ production.
- At night, $NO_x$ is removed *via* reactions of the nitrate radical ($NO_3$) and dinitrogen pentoxide ($N_2O_5$).
- $NO_3$ is an important oxidant of certain VOCs (e.g., alkenes and aldehydes).
- During the day, $NO_3$ (and $N_2O_5$) is removed by reaction with NO and photolysis.
- Prior to this work, $ClNO_2$ had not been observed in the atmosphere.



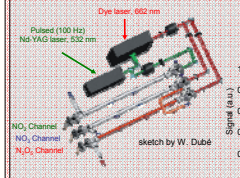

Measurements on R/V *Brown*:

- NO and $NO_2$ by $O_3$-chemi-luminescence.[1]
- $NO_2$, $NO_3$ and $N_2O_5$ by cavity ring-down.[2-3]
- $ClNO_2$ by $I^-$-CIMS (new).[4]
- $HNO_3$ by mist chamber.[5]
- $NO_y$ (= sum) by $O_3$-chemi-luminescence.[1]

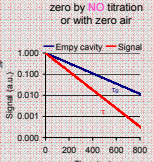
- Aerosol size distribution and composition.[6]
- VOCs by GC-MS.[7]

## Cavity Ring-Down Spectrometer[2-3]

- stated uncertainties for TexAQS-GoMACCS: $NO_3^-$: ±(25%+1pptv); $NO_2^-$: ±(10%+0.5 ppbv); $N_2O_5$: ±(25%+10%*$NO_2$+1pptv)




zero by NO titration or with zero air

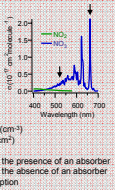



**Concentration:**

$$\alpha = N\sigma = \frac{R_L}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

**Sensitivity:**

$$\alpha_{min} \approx 5\times10^{-11}\ cm^{-1}$$



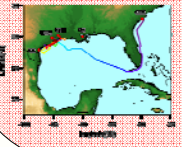

| | |
|---|---|
| $\alpha$ | absorption ($cm^{-1}$) |
| N | molecular number density ($cm^{-3}$) |
| $\sigma$ | absorption cross section ($cm^2$) |
| c | speed of light ($cm\ s^{-1}$) |
| $\tau$ | ring-down time constant in the presence of an absorber |
| $\tau_0$ | ring-down time constant in the absence of an absorber |
| $\alpha_{min}$ | minimum detectable absorption |
| $\sigma(\tau_0)$ | standard deviation in $\tau_0$ |
| $R_L$ | ratio of the absorption path over which the absorber is present with respect to the total cavity length |

convert $N_2O_5$ to $NO_2$ in heated channel
increase in $[NO_2] = [N_2O_5]$

## TexAQS-GoMACCS 2006

http://www.esrl.noaa.gov/2006

Texas Air Quality Study – Gulf of Mexico Atmospheric Composition and Climate Study, July 27– Sept. 11, 2006



NOAA vessel *Ronald H. Brown* (R/V *Brown*)

In the Houston ship channel (HSC)

## $NO_3$ and $N_2O_5$ chemistry

- $NO_3$ and $N_2O_5$ were generally short-lived in the marine boundary layer along the Texas coast, i.e. not reservoir species.
- Reactions of $NO_3$ and $N_2O_5$ lead to $NO_x$, $O_3$, and VOC loss.
- Production: $P(NO_3) = k_8[NO_2][O_3]$, $k_8 = 3\times10^{-17}\ cm^3\ molecule^{-1}$.
- Reactive losses are affected by
  - temperature (high T shifts equilibrium and losses towards $NO_3$).
  - emission of VOCs (towards which $NO_3$ is reactive).
  - emission of $NO_x$ (shifts equilibrium and losses towards $N_2O_5$).
  - aerosol surface area (enhances $N_2O_5$ losses)

First-order loss rate coefficients:

$k(NO_3) = k_3 + k_4K_{eq}[NO_2]$

$k(N_2O_5) = k_5 + k_4/(K_{eq}[NO_2])$

$K_{eq}[NO_2] = \frac{[N_2O_5]}{[NO_3]}$

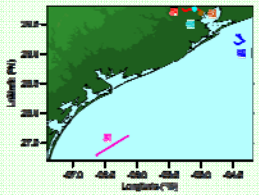
$k_x$ = sum of all $NO_3$ loss rate coefficients

$k_x \approx k_{NO}[NO] + \sum_{VOC}(k_{VOC,i}[VOC_i])$ (at night).

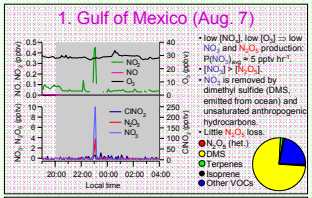
$k_y$ = het. loss rate coefficient of $N_2O_5$

$k_y \approx ¼ * c * S_{aerosol} * \gamma$ (use $\gamma = 0.03$)

## Case studies



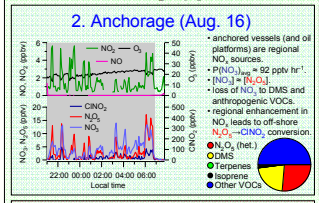

### 1. Gulf of Mexico (Aug. 7)



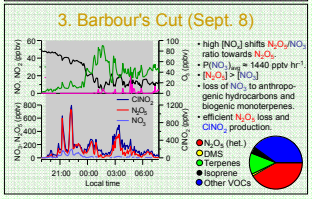

- low $[NO_x]$, low $[O_3]$ ⇒ low $NO_3$ and $N_2O_5$ production: $P(NO_3)_{avg} \approx 5$ pptv $hr^{-1}$.
- $[NO_3] > [N_2O_5]$.
- $NO_3$ is removed by dimethyl sulfide (DMS, emitted from ocean) and unsaturated anthropogenic hydrocarbons.
- Little $N_2O_5$ loss.




### 2. Anchorage (Aug. 16)



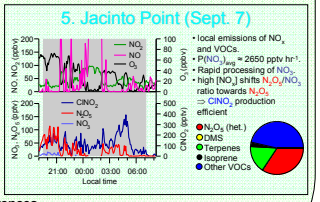

- anchored vessels (and oil platforms) are regional $NO_x$ sources.
- $P(NO_3)_{avg} \approx 92$ ppbv $hr^{-1}$.
- $[NO_3] \approx [N_2O_5]$.
- loss of $NO_x$ to DMS and anthropogenic VOCs.
- regional enhancement in $NO_x$ leads to off-shore $N_2O_5 \rightarrow ClNO_2$ conversion.



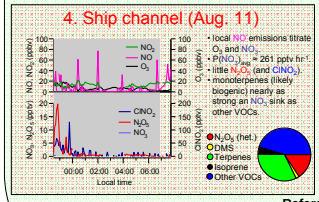

### 3. Barbour's Cut (Sept. 8)




- high $[NO_x]$ shifts $N_2O_5/NO_3$ ratio towards $N_2O_5$.
- $P(NO_3)_{avg} \approx 1440$ ppbv $hr^{-1}$.
- $[N_2O_5] > [NO_3]$
- loss of $NO_3$ to anthropo-genic hydrocarbons and biogenic monoterpenes.
- efficient $N_2O_5$ loss and $ClNO_2$ production.




### 4. Ship channel (Aug. 11)




- local NO emissions titrate $O_3$ and $NO_3$.
- $P(NO_3)_{avg} \approx 261$ ppbv $hr^{-1}$.
- little $N_2O_5$ (and $ClNO_2$).
- monoterpenes (likely biogenic) nearly as strong an $NO_3$ sink as other VOCs.




### 5. Jacinto Point (Sept. 7)




- local emissions of $NO_x$ and VOCs.
- $P(NO_3)_{avg} \approx 2650$ ppbv $hr^{-1}$.
- Rapid processing of $NO_x$.
- high $[NO_x]$ shifts $N_2O_5/NO_3$ ratio towards $N_2O_5$ ⇒ $ClNO_2$ production efficient




### References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## Heterogeneous uptake of $N_2O_5$

### Generation of $ClNO_2$

On most aerosol, uptake of $N_2O_5$ leads to $HNO_3$ production and, ultimately, to $NO_x$ and $O_x$ loss:

$$N_2O_5(g) \rightleftharpoons N_2O_5(aq) \rightleftharpoons NO_2^+NO_3^-(aq) \xrightarrow{H_2O} 2HNO_3(aq) \longrightarrow 2HNO_3(g)$$

Prior to this work, it was thought that $ClNO_2$ is formed only on sea salt ($\gamma \approx 2.5\times10^{-2}$, 100% yield).[8-15]
Our data show:
- $ClNO_2$ is a major product on conti-nental aerosol containing trace $Cl^-$.
- $ClNO_2$ is long-lived in the MBL.

$$NO_3^-(aq) + ClNO_2(aq) \rightleftharpoons ClNO_2(g) \xrightarrow{h\nu} NO_2(g) + Cl(g)$$

$$NO_2^+NO_3^-(aq) \xrightarrow{+Cl^-} ClNO_2(aq) \xrightarrow{H_2O} HCl(aq) + HNO_3(aq)$$

After sunrise, $ClNO_2$ is a source of Cl radicals and $NO_2$.

### Box model simulations

e.g., plume south of Galveston Bay, Aug. 18
Aerosol surface ~1.4% sea salt (mostly $(NH_4)HSO_4$)

$$[ClNO_2] \approx \int(\phi ¼ \gamma c S_{aerosol}[N_2O_5])dt$$

$\phi$ = yield, t = 1.5 hr

20% yield
expected <2% based on sea salt

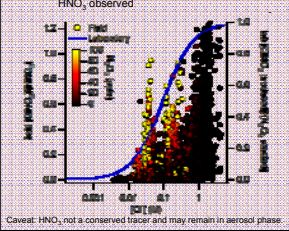
- also require large $\gamma$ (~0.03) and no $ClNO_2$ losses.
- several instances with ~100% yield.

### Yield experiments

Lab: $ClNO_2$ produced / $N_2O_5$ reacted as a function of $Cl^-$ content.




Field: $ClNO_2$ produced / $HNO_3$ observed vs. aerosol $Cl^-$




Caveat: $HNO_3$ not a conserved tracer and may remain in aerosol phase.

### Proposed mechanism

Mixing of continental with marine air

$$(NH_4)_{2-x}H_xSO_4(aq)$$

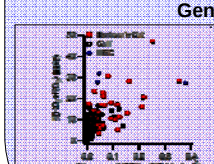
$$H_2SO_4, HNO_3 \xrightarrow{sea\ salt} HCl(g)$$

$$(NH_4)_{2-x}H_xSO_4 \bullet HCl(aq)$$

$$NO_x, O_3 \longrightarrow N_2O_5(g) \xrightarrow[(NH_4)_{2-x}H_xSO_4(aq)]{trace\ Cl^-} ClNO_2(g)$$

## Oxidation of VOCs by $NO_3$

### Generation of peroxy radicals

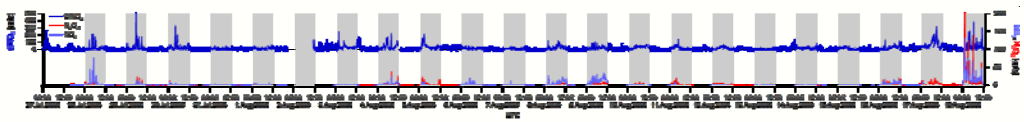
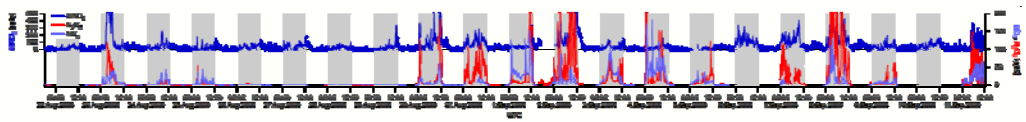


$\Sigma(HO_2+RO_2)$ measurements by PERCA
(see poster by R. Sommariva)

$$NO_3 + RH \longrightarrow R\bullet + HNO_3 \xrightarrow{O_2} RO_2\bullet + HNO_3$$

$$NO_3 + R_2C{=}CR_2 \xrightarrow{O_2} R_2C(O_2\bullet)\text{-}CR_2ONO_2 \longrightarrow ?$$

Further reactions lead to non-photochemical formation of OH radical, a primarily daytime species.[16]


**Acknowledgments**

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