Voyages on the Atlantic – A Study of Oceanic Alkyl Nitrates

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DATA: BY THE NUMBERS

NUMBER OF YEARS TO GET DATA: 3
YES! FINALLY!

NUMBER OF YEARS TO INTERPRET DATA: 2
what does it all mean??

NUMBER OF YEARS TO WRITE ABOUT DATA: 1.5
blah blah blah blah...

NUMBER OF SLIDES TO PRESENT DATA: 1
RESULTS that's it?
The Big Picture

\[ \text{RO} + \text{NO}_2 \xrightarrow{\text{hv}} \text{RO} + \text{NO}_2 \]

\[ \text{NO}_2 \xrightarrow{\text{hv}} \text{NO} + \text{O} \]

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]

\[ \text{CDOM} \xrightarrow{\text{hv}} \text{ROD} \]

\[ \text{NO}_3 \xrightarrow{\text{hv}} \text{NO}_2 \xrightarrow{\text{hv}} \text{NO} \]

\[ \text{upwelling} \]

\[ \text{upwelling} \]

\[ \text{biolgy} \]
Reaction Mechanism

\[
\begin{align*}
\text{NO}_2^- & \xrightarrow{h\nu, H_2O} \text{NO} + \text{OH} + \text{OH}^- \\
\text{CDOM} & \xrightarrow{h\nu \text{ or } \text{OH}} \text{ROO}^- \\
\text{ROO}^- + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \text{ or } \text{RONONO}_2
\end{align*}
\]
The Cruise Track

- June 19 – Left Reykjavik, Iceland
- July 10 – Arrived Funchal, Madeira
- July 15 – Left Madeira
- August 11 – Arrived in Natal, Brazil
Goals of Study

• Measure depth profiles of C1-C3 alkyl nitrates.
• Incubation experiments to determine production rates of alkyl nitrates under ‘natural’ conditions.
How is Deep Water Sampled?

- Conductivity-Temperature-Depth (CTD) Rosette
- 35 bottles
Sampling Water for Gas Measurements

- Glass syringes
- Important to avoid bubbles.
Alkyl Nitrate Detection

- Purge and trap
- Trap on stainless steel w/liquid nitrogen
- Gas chromatograph for separation
- Quadrapole mass spectrometer to analyze
Surface Ocean Alkyl Nitrates

South 0 10 20 30 40 50 North

Latitude (degrees)

Alkyl Nitrates (ng/L)

- Methyl Nitrate
- Ethyl Nitrate
- Isopropyl Nitrate
- Total
Nitrite

\[
\text{NO}_2^- + h\nu, \text{H}_2\text{O} \rightarrow \text{NO} + \text{OH} + \text{OH}^- \\
\text{ROO}^- + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \text{ or } \text{RONO}_2
\]
Depth Profiles
Methyl Nitrate Depth Profiles

![Graph showing Methyl Nitrate Depth Profiles](image)
Isopropyl Nitrate Depth Profiles

[Diagram showing depth profiles with pressure on the y-axis and iPrONO₂ concentration on the color scale. The x-axis represents distance with South at 0 and North at 50. The y-axis ranges from 0 to 500 dbar, with pressure values indicated on the y-axis. The concentration ranges from 0 to 1.5 ng/L, with color scale on the right side of the diagram.]
Where do deep ocean alkyl nitrates come from?

- Bacterial processes?
- Free radical chemistry?
  - Calculated that 0.02 pM/day of OH formed from $^{40}$K decay in oceans
  - If every OH formed $\rightarrow$ RONO$_2$ will produce 10 pM in $\sim$500 days.
Incubation Experiments

• Collect water from surface
  - Filter to 0.2 µm or
  - Leave unfiltered

• Aliquot water and spike with nitrite.

• Why?
\[
\begin{align*}
\text{NO}_2^- \xrightarrow{h\nu, H_2O} & \text{NO} + \text{OH} + \text{OH}^- \\
\text{CDOM} \xrightarrow{h\nu \text{ or } OH} & \text{ROO}^\cdot \\
\text{ROO}^\cdot + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \text{ or } \text{RONONO}_2
\end{align*}
\]
Results of One Production Experiment

![Graph showing production rate vs. nitrite concentration. The graph includes data points for Methyl Nitrate, Ethyl Nitrate, and Isopropyl Nitrate.]
Methyl and Ethyl Nitrate Incubations

**Methyl Nitrate**

Production Rate (ng L$^{-1}$ s$^{-1}$) vs Nitrite (µM)

**Ethyl Nitrate**

Production Rate (ng L$^{-1}$ s$^{-1}$) vs Nitrite (µM)
Isopropyl Nitrate Incubations

![Graph showing the relationship between production rate (ng L\(^{-1}\) s\(^{-1}\)) and nitrite concentration (µM). The graph compares filtered and unfiltered samples.](image)
Conclusions

• Surface oceans can be explained by photochemical production.
• Source for deep ocean alkyl nitrates could be free radical chemistry.
• Alkyl nitrate production in natural waters is directly related to nitrite concentration.
Life Lessons
Anything can go wrong no matter how well prepared you are.
Anything can go wrong no matter how well prepared you are.

• Fortunately...
  - There is usually someone more seasoned than you are.
  - Ship’s Engineers

• And…
Always remember there is a light at the end of the tunnel.
In Port - Take advantage of local beverages
Don’t let a little matter of heights stop you from a cool picture.

*Cabo Girão* - The highest seacliff in Europe  
(alt 580 m)
Stop and smell the flowers.
Get blackmail photos when possible
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