Spatial & Temporal Variability of NO$_2$ and other trace gases over US coastal waters
Distribution, Air quality, Nitrogen-deposition and Ocean color

Maria Tzortziou, Jay Herman, Alex Cede, Nader Abuhassan
As the consequences of increasing air pollution, anthropogenic activities and climate variability are becoming more immediate and profound, understanding processes, feedbacks, interactions between the atmosphere and ocean components of the Earth System becomes increasingly important.

Need for detailed, integrated observations in the atmosphere-ocean system

Photograph of Gulf Coast of Texas and Louisiana (Gemini 11). Air pollution plumes from smokestacks can be seen in the Houston area.
Variability of NO₂ and other trace gases over US coastal waters

• Opportunity for interdisciplinary science ...

DISCOVER-AQ airborne observations over the Chesapeake Bay and the Gulf Coast
Variability of NO$_2$ and other trace gases over US coastal waters

*Opportunity for interdisciplinary science ...*

**Challenge in coastal areas and adjacent ocean:** ground-stations that monitor changes in tropospheric air quality (aerosols, NO$_2$, O$_3$, other trace gases) come to an abrupt end at the coastlines.
To address this issue ...

- We will extend measurements of the spatial and temporal patterns in traces gases and aerosols over estuarine and coastal waters in the Chesapeake Bay/Mid Atlantic Bight region

- Measurements performed using the Pandora spectrometers (NO$_2$, O$_3$, SO$_2$, HCHO, aerosols etc)

- Combine in-situ observations with Aura-OMI observations, aircraft measurements, and regional photochemical modeling (CMAQ and WRF-Chem)

Projects:
- NASA-NIP Award (PI: Tzortziou, Collaborators: Pickering, Herman, Mannino, Jordan, Dickerson)
- GEO CAPE activities (PIs: Tzortziou, Herman)
Evaluation of Satellite Products & Model Output in Coastal Regions

Weekly cycle of NO2 by GOME  Beirle et al., 2003
Apply Pandora measurements (NO2, O3, SO2, HCHO etc) over coastal waters to:

i) compare with collocated NASA-Aura OMI satellite NO2 retrievals in coastal areas, examine NO2 variability at scales smaller than OMI’s 12 x 24 km pixel (nadir view), and evaluate assumptions in satellite tropospheric NO2 retrievals (e.g. NO2 profile shape).

ii) evaluate air-quality model performance and emission inventories for improving model predictions of tropospheric NO2 amounts, distribution and transport over the studied estuarine/coastal region.

The CMAQ and WRF-Chem models will be used, enhanced with a new lightning NOx emission scheme and aircraft NOx emissions.
The large spatio-temporal variability in aerosols and other absorbing atmospheric constituents such as NO2 remains one of the largest sources of uncertainty for satellite ocean color retrievals, especially in coastal waters that are close to heavily polluted areas.
Improved Atmospheric Correction of Satellite Ocean Color

MODIS nLw(412) with NO₂ correction
→ **5-7% error in nLw(410)**, at low solar zenith angle (< 40°) and low look, for 0.5 DU change in NO₂ (typical variability of NO₂ close to Eastern US coastal areas).

→ **Error increases (reaching 15-20%)** for larger solar zenith and look angles, and as NO₂ is transported to higher altitudes.

→ This error is **spectrally dependant (from 350 to 500 nm with a maximum near 400 nm)**, so it does not cancel out when using band-ratios for ocean color retrievals.
Coastal Ocean Biogeochemical Processes

- Study exchanges of materials (carbon and nutrients) across land-ocean interface
- Resolve near-shore geophysical features
- Understand time and space scales of biological, biogeochemical and optical variability

GEO CAPE Ocean STM:
Threshold Spatial Res: 375x375 m
Threshold Temporal Res: < 3 hours

We need to understand atmospheric variability and accurately account for it in ocean color retrievals.

Otherwise it will lead to a false estimate of time-dependent underwater processes.

MODIS-Aqua:
water-leaving radiance at 645 nm and 250-meter resolution (mWcm⁻²mm⁻¹sr⁻¹.) (Reprinted from Franz et al. 2006).
Nitrogen Deposition in estuarine and coastal waters

The environmental impacts of NO$_2$ are not confined to the atmosphere.

NO$_2$ can act as an *acidifying and eutrophying agent in terrestrial and aquatic ecosystems* through dry/wet deposition of its oxidation products.

In the Chesapeake Bay, at least one third, and probably significantly more, of total nitrogen inputs comes from air deposition [STAC Publ. 09-001, 2009].
The environmental impacts of NO₂ are not confined to the atmosphere. NO₂ can act as an acidifying and eutrophying agent in terrestrial and aquatic ecosystems through dry/wet deposition of its oxidation products.
Nitrogen Deposition in estuarine and coastal waters

Many ground-based programs monitoring atmospheric deposition on various watersheds in the US.

**NADP/NTN (National Atm. Deposition Program /National Trends Network):** wet deposition data

**CASTNet (Clean Air Status and Trends Network):** ambient air pollution, estimates of dry deposition $D = CVd$

Concentrations of inorganic chemicals in precipitation (e.g. acidity (measured as pH), sulfate, nitrate, ammonium, chloride, and base cations).

Ambient measurements of gaseous $SO_2$, $HNO_3$, and $O_3$, particulates (sulfate, $SO_4^{2-}$, nitrate, $NO_3^-$, ammonium, $NH_4^+$, other relevant ions), and meteorological parameters.
Despite the importance of dry NOx deposition in urban areas, atmospheric NOx is among the most important parameters currently missing from CASTNet. This significantly inhibits accurate model estimates of oxidized-N dry deposition [e.g. Dennis, 2007].

### Dry Deposition of Reactive N is Important

#### Important Fraction of Dry Deposition Not Being Measured

<table>
<thead>
<tr>
<th>Specie</th>
<th>Kg-N (x10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>4.22</td>
</tr>
<tr>
<td>NO₂</td>
<td>14.53</td>
</tr>
<tr>
<td>PAN’s</td>
<td>5.42</td>
</tr>
<tr>
<td>Other</td>
<td>5.71</td>
</tr>
<tr>
<td>HNO₃</td>
<td>55.12</td>
</tr>
<tr>
<td>aNO₃⁻</td>
<td>1.63</td>
</tr>
</tbody>
</table>

- **Not Being Measured (34%)**
- **Dry Ox-N > Wet Ox-N**
- **Dry Red-N < Wet Red-N**

**Not Being Measured (82%)**

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From Robin L. Dennis (Atmospheric Sciences Modeling Division, ARL/NOAA)
Our measurements of NO₂ over coastal areas, and at atmospheric deposition monitoring sites in the Chesapeake Bay watershed can be applied to:

- complement current measurements at these sites with detailed (currently missing) NO₂ information

- combined with satellite information and aircraft observations, can be applied to constrain photochemical models and evaluate model performance and emission inventories (including new schemes for lightning and aircraft NOx emissions) for improving model predictions of tropospheric NO₂ amounts, distribution and transport over coastal regions

- compare model estimates of atmospheric dry/wet N-deposition with in-situ measurements and apply results to better understand observed spatial and temporal patterns of nitrogen deposition in the studied coastal region.
Variability of NO₂ and other trace gases over US coastal waters

NASA/GSFC:
- moderately polluted site
- long-term/on-going monitoring of atmospheric composition from CIMEL, Brewer, lidars, Pandora, Cleo

UMBC:
- close to the Baltimore urban area.
- CIMEL, lidars etc

Wye:
- Eastern CB shore
- NADP/NTN station (MD13) monitoring wet deposition since 1983.

UMCP:
- surface NO₂ measurements using a commercial cavity ring-down spectroscopy NO₂ detector modified for enhanced sensitivity (R. Dickerson)

Beltsville:
- NADP (MD99) and CASTNet (BELL116) sites monitoring deposition since 2004

SERC:
- Western CB shore
- long-term (1970s-now) and on-going monitoring program of wet N-deposition (nitrate, ammonium, and total Kjeldahl N, TKN).
- Ancillary data: Na and Cl in deposition, Aerosols (CIMEL site)
- Meteorological parameters.
Variability of NO$_2$ and other trace gases over US coastal waters

**OASIS (Ocean Atmosphere Sensor Integration System)** platform
solar-powered (battery stored) Autonomous Surface Vessel (ASV)

**Table: Measured on OASIS**

<table>
<thead>
<tr>
<th>Location</th>
<th>Measured on OASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper (200m) ocean profiling</td>
<td>horizontal velocity</td>
</tr>
<tr>
<td>Surface ocean</td>
<td>pCO$_2$, temperature, salinity,</td>
</tr>
<tr>
<td></td>
<td>fluorescence (chlorophyll-a, CDOM,</td>
</tr>
<tr>
<td></td>
<td>phycoerythrin)</td>
</tr>
<tr>
<td>Surface atmosphere</td>
<td>pCO$_2$ profile, air-sea flux of CO$_2$</td>
</tr>
<tr>
<td></td>
<td>(x4), 3D wind velocity, air pressure,</td>
</tr>
<tr>
<td></td>
<td>temperature, humidity, downward</td>
</tr>
<tr>
<td></td>
<td>solar radiative and IR flux</td>
</tr>
<tr>
<td>Atmosphere aerosol and trace gas</td>
<td>Surface CO$_2$ concentrations.</td>
</tr>
<tr>
<td>observations</td>
<td>NO$_2$, HCHO, O$_3$, SO$_2$, AOD</td>
</tr>
</tbody>
</table>

John Moisan (NASA/Wallops)
Variability of NO$_2$ and other trace gases over US coastal waters
Variability of NO₂ and other trace gases over US coastal waters

Pandora onboard the NOAA Ship Delaware II, cruises in N. Atlantic as part of on-going Ecosystem Monitoring (EcoMon) field program sponsored by NOAA –NMFS (John Hare).

- 16-18 day cruises quarterly each year
- typically surveys 120 randomly selected stations
- next cruises: May-June and August in 2011
- measurements of ocean biogeochemical and optical parameters will be performed (e.g. PP, POC, particulate nitrogen (PN), DOC, pigments, DIC, inorganic N, P,Si compounds, TDN,TDP, $a_{CDOM}$, $a_{ph}$, chl-a)
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