Satellite image of Earth’s city lights - Defense Meteorological Satellite Program (DMSP) Operational Linescan System (OLS). The brightest areas of the Earth are the most urbanized (http://www.earthobservatory.nasa.gov/IOTD/view.php?id=896)

**Atmospheric NO₂ dynamics and impact on coastal ocean color retrievals**

M. Tzortziou, J. Herman, Z. Ahmad, C. Loughner
Tropospheric Nitrogen Dioxide ($NO_2$) data from SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) - Monthly for April 2007.

Measurements of tropospheric $NO_2$ are a good indicator of the geographical location of anthropogenic air pollution.

Major sources of NOx emissions: motor vehicles, electric utilities, other industrial, commercial, residential sources that burn fuels

Tropospheric Nitrogen Dioxide ($NO_2$) data from SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) - Monthly for April 2007. Measurements of tropospheric $NO_2$ are a good indicator of the geographical location of anthropogenic air pollution.
Major Causes of Wetland Loss and Degradation

- Human activities
  - Drainage
  - Dredging and stream channelization
  - Deposition of fill material
  - Diking and damming
  - Discharge of pollutants
  - Tilling for crop production
  - Logging
  - Mining
  - Construction
- Natural events
  - Air and water pollutants
  - Changing nutrient levels
  - Grazing by domestic animals
  - Erosion
  - Subsidence
  - Sea level rise
  - Droughts
  - Hurricanes and other storms

*The Land Loss between 1932-2000 is historical. The Land Loss between 2000-2010 is projected based on historical trends if no further action is taken as documented in the "Historical and Projected Coastal Louisiana Land Changes: 1932-2010" (www.Lacoast.gov/LandLoss/NewHistoricalLand.pdf)
The atmosphere contributes > 90% of satellite measured TOA signal in the blue-green, and it must be accurately modeled/removed for accurate ocean color measurements.

Herman, Ahmad and Tzortziou, 2007; Ahmad et al., 2007, Applied Optics
Nitrogen Dioxide Absorption Cross sections (at 293 °K)

Fig. 1. Relative NO\textsubscript{2} spectrum at 293 K measured by GOME FM between 231–794 nm. The spectral resolution is 0.2 nm at wavelengths below and 0.3 nm above 400 nm.
How much?

How variable?
GEO-CAPE CBODAQ Campaign in the Chesapeake Bay (11-20 July 2011)

CBODAQ: Chesapeake Bay Oceanographic Campaign with Discover-AQ

Atmospheric NO₂ dynamics and impacts on coastal ocean color
Atmospheric NO$_2$ dynamics and impacts on coastal ocean color

GEO-CAPE GOMEX campaign in the Gulf Of Mexico (9-22 September 2013)
Meteorological sensors

Pandora

Downwelling Irradiance Sensors for Ocean Color

O3, NO, NOy instruments (surface meas)

Filters for aerosol collection

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>280 to 525 nm</td>
</tr>
<tr>
<td>Spectral res</td>
<td>0.5 nm</td>
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<tr>
<td>Detector</td>
<td>2048 pixels CCD</td>
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<tr>
<td>Field of view</td>
<td>2.5° FWHM</td>
</tr>
<tr>
<td>Camera FOV</td>
<td>40.0°</td>
</tr>
<tr>
<td>Pointing Prec</td>
<td>0.01°</td>
</tr>
<tr>
<td>ND Filter</td>
<td>ND1 to ND3</td>
</tr>
</tbody>
</table>

Measurements of atmospheric composition and variability

Atmospheric NO₂ dynamics and impacts on coastal ocean color
DISCOVER-AQ: Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality

Three major observational components:

NASA UC-12 (Remote sensing)
Continuous mapping of aerosols with HSRL and trace gas columns with ACAM

NASA P-3B (in situ meas.)
In situ profiling of aerosols and trace gases over surface measurement sites

Ground sites
In situ trace gases and aerosols
Remote sensing of trace gas and aerosol columns
Ozonesondes
Aerosol lidar observations
Spatial & temporal variability in TCNO₂ - Washington DC/Chesapeake Bay area (July 18, 2011)

1) Significant temp variability (0.7 DU)
2) Significant spatial variability (~0.7-0.8 DU)
3) Diurnal patterns are different at different sites

= 123 km
= OMI satellite footprint at large viewing angles

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
Spatial & temporal variability in TCNO$_2$ - Washington DC/Chesapeake Bay area (July 2011)

1) OMI does not capture spatial variability in NO2 (rural vs urban sites)
2) OMI does not capture temporal variability in NO2 (diurnal or weekly patterns)

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
Spatial & temporal variability in TCNO$_2$ – Helsinki Finland

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
Spatial & temporal variability in TCNO₂ – Helsinki Finland (Sept 2011 – Nov 2012)

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
Atmospheric NO$_2$ dynamics and impacts on coastal ocean color
Spatial & temporal variability in TCNO$_2$ – Seoul and Busan in Korea

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
Spatial & temporal variability in TCNO₂ – Seoul and Busan in Korea (March 2012-April 2013)

With a coarse resolution and an overpass at around 13:30 local time, OMI → cannot detect this strong variability in NO₂ → missing pollution peaks from industrial and rush hour activities.

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
What is the impact on ocean color?
Radiative Transfer Code

Ahmad and Fraser (1982) and Mobley (1988; 1994).

- Both codes have been extensively validated
- We have linked the two codes, so that output from one code is provided as input to the other for a more complete and accurate description of the ocean-atmosphere system.

Hydrollight simulations: $Rrs$ spectra

- $[\text{Chla}]=23 \text{ mgm}^{-3}$
- $[\text{TSS}] = 20 \text{ mgm}^{-3}$
- $a_{\text{CDOM}}(300) = 2.1 \text{ m}^{-1}$

Ahmad-Fraser (AF) code: TOA reflectance, $\rho_{\text{TOA}}(\lambda)$

- 300 nm - 3.0 $\mu$m
- Includes aerosols and trace gases
- Vandaele et al. (1998) values of NO$_2$ absorption cross-section
- RT calculations for SZA: 1.5°, 18°, 30°, 42° and 60°, varying azimuth angles depending on geometry, and look angles of 36°, 42° and 48°
- homogeneous NO$_2$ vertical distribution within the first (i) 2 km and (ii) 3 km from the ground, based on air-quality model simulations (CMAQ).

Tzortziou et al 2014, JGR-Oceans, 119, 3834–3854
Percent change in TOA signal, caused by a change of 1 DU of NO₂

\[
\% \text{ change } L_{TOA}(\lambda) = \frac{L_{TOA}(\lambda)_{(NO₂ = 1 \text{ DU})} - L_{TOA}(\lambda)_{(NO₂ = 0 \text{ DU})}}{L_{TOA}(\lambda)_{(NO₂ = 0 \text{ DU})}}
\]

The impact on \(L_{TOA}\)

- has a strong spectral dependence: **max in 400-420 nm**, due to spectral shape in NO₂ abs. cross sections
- has a SZA dependence: because of the larger slant path with increasing SZA, which results in more scattering and, hence, more absorption
- depends on NO₂ vertical distribution, and becomes larger as the NO₂ is distributed at higher altitudes
Percent error in $R_{rs}$ caused by not accounting for 1 DU of atmospheric NO$_2$
(or, error when a change in TOA is wrongfully attributed to a change in ocean contribution)

$L_w / L_{TOA} = 2.5\%$ at 412 nm and SZA=30°

The error in $R_{rs}$
- has a strong spectral dependence: **max in 350-400 nm**, due to spectral dependence of $L_w / L_{TOA}$
- has a SZA dependence: because the error in $L_{TOA}$ increases with increasing optical path, and because the relative contribution of $L_w$ to the TOA signal decreases with increasing solar zenith and look angles
- depends on NO$_2$ vertical distribution, and becomes larger as the NO$_2$ is distributed at higher altitudes
False variability (%) in retrieved Chla due to unaccounted variability in NO$_2$ using MODIS OC3M

Impact of using the OMI value (0.75 DU) instead of the TCNO$_2$ measured by Pandora (0.4 to 2.4 DU)
False variability (%) in retrieved CDOM due to unaccounted variability in NO₂

\[ a_{CDOM}(\lambda) = \ln \left[ \frac{R_{rs \text{ ratio}} - a}{b} \right] / (-c) \]

R_{rs \text{ ratio}}: \( R_{rs}(490)/R_{rs}(555) \) for SeaWiFS
\( R_{rs}(490)/R_{rs}(551) \) for MODIS-Aqua


The error in CDOM is spectral dependent: it affects the CDOM absorption spectral shape \( S_{CDOM} \)

\( \rightarrow \) Impact of using the OMI value (0.75 DU) instead of the TCNO₂ measured by Pandora (0.4 to 2.4 DU)
Nearshore environments are particularly vulnerable to atmospheric pollution,
**Build-up of air pollution** along shorelines during sea/lake/bay- breeze events

Prior to the development of the bay/sea breeze
Offshore winds transport pollutants from urban areas out over the surface waters of the estuary.

As the bay/sea breeze develops
Winds start changing direction, stagnation develops over the estuary – accumulation of pollutants

Once the bay breeze forms
- Onshore winds transport the high concentrations of surface pollutants towards the coastline.
- Converge with freshly emitted urban pollution
- Maxima in concentrations of pollutants at the land-ocean interface...

Strong, prolonged bay breeze
Produces stronger convergence resulting in pollutants being transported upward, out of the BL to the free troposphere.
Pollutants in the free troposphere:
→ gain a longer lifetime
→ have a larger impact on climate
→ are susceptible to long range transport

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Loughner et al. 2011; Loughner, Tzortziou et al., 2013
Banta et al., 2005, BAMS

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Atmospheric NO$_2$ dynamics and impacts on coastal ocean color
Atmospheric pollutants accumulation at the land-water interface

2 July 2011 - DISCOVER-AQ and CBODAQ campaigns over the Chesapeake Bay

WRF (Weather Research and Forecasting) simulations

Atmospheric NO$_2$ dynamics and impacts on coastal ocean color
Atmospheric pollutants accumulation at the land-water interface

2 July 2011 - DISCOVER-AQ and CBODAQ campaigns over the Chesapeake Bay
CMAQ (Community Multi-scale Air Quality) simulations run at high (1.3 km) horizontal spatial resolution

Stagnation and low deposition rates result in pollutant buildup over the estuarine waters, and along the shorelines.

Total atmospheric nitrogen near the surface
CMAQ - 1:00 PM EST

Loughner and Tzortziou, In Prep
Summary

- To account for the known strong NO₂ variability in coastal ocean color retrievals, requires measurements of NO₂ at a spatial & temporal resolution relevant to the satellite ocean color observations.

- NO₂ observations from coarser resolution atmospheric sensors (e.g., OMI 12km x 24 km at nadir) do not capture the strong temporal and spatial variability of NO₂ in coastal waters.

- 0.7 DU unaccounted variability in NO₂, resulted in an error in coastal water Rrs(412) as large as 40% at low SZAs (< 30°), while it gets as large as 70-80% for large SZAs.

- The error in Rrs gets larger:
  - at larger NO₂ amounts (e.g., Busan: 2 DU change in NO₂: > 150% error in Chla and CDOM abs coeffs)
  - at shorter wavelengths (350-400 nm)
  - at larger solar zenith and look angles
  - as the NO₂ is distributed at higher altitudes

- Accurate atmospheric correction for NO₂ requires information on NO₂ vertical distribution.

- Meteorological processes such as bay/sea/lake breezes often result in accumulation of atmospheric pollution over estuarine and coastal waters, as well as transport of pollutants out of the BL in the free troposphere and over long distances and over the coastal ocean, further away from emission sources.

- More shipboard measurements are needed over the ocean to understand NO₂ dynamics, vertical distribution, dispersion, and gradients in coastal environments.