

Case Study 4

Impacts of European Atmospheric Air Pollution on Water Nutrients in the Atlantic Ocean, Baltic Sea, and Mediterranean Sea

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4.1 Background Information

Combustion activities worldwide lead to atmospheric Nitrogen Oxides (NO_x) emissions which can be transported over long distances and, via dry and wet deposition, contribute to excess nutrient loads in the world's rivers, estuaries and oceans, leading to water pollution and impacts such as the commonly observed coastal algal blooms. Satellite imagery can be used to track these anthropogenic NO_x emissions and to study their potential impacts on water quality. This chapter provides a guide for obtaining and analyzing nitrogen dioxide imagery from the Ozone Monitoring Instrument (OMI).

The production of carbon, or primary productivity, by photosynthetic marine organisms provides the energy which ascends the marine trophic level ladder, from zooplankton to fish to whales, providing sustenance to the marine benthos when phytoplankton detritus descends to the seafloor. Phytoplankton productivity is controlled by the location and movement of these free-floating plants in oceanic currents, but their growth rate is determined primarily by the availability of sunlight and the necessary concentrations of vital nutrients. Enhanced phytoplankton productivity due to nutrient excess in waterways can lead to eutrophication, where organic detritus on the sea floor causes low dissolved oxygen, or zero dissolved oxygen concentrations in bottom waters due to bacterial decomposition. Increased nutrient levels may also cause species shifts from the common phytoplankton species to less desirable phytoplankton species, including species that are noxious or hazardous due to toxicity, otherwise known as harmful algal blooms.

The two primary marine macro-nutrients are familiar to many gardeners and

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grounds keepers as the basic elements of fertilizer: nitrate and phosphate. Macro-nutrients can enter water ways either via terrestrial sources or via direct or indirect atmospheric deposition. Terrestrial sources of nutrients can be divided into two categories: point and non-point sources. The main terrestrial non-point sources of nutrients are fertilizers from the agricultural sector and runoff from impervious surfaces. In some regions of the world, the agricultural sector contributes the largest fraction of the entire nitrogen load. Nitrate and phosphate are also produced as a result of various industrial processes and they are present in household chemicals such as dishwasher and laundry detergents. These pollutants are discharged into water ways via municipal water systems and they comprise the major point sources of nitrogen pollution. Although nitrogen and phosphate discharges from municipal waste water treatment plants today have been greatly reduced in some countries, nutrients continue to contribute to water pollution in rivers, estuaries and oceans worldwide.

In estuaries, nutrients are delivered by fresh water flow from rivers and streams into bays and sounds; where river flows enter the ocean directly, the nutrients from river waters can be transported hundreds of miles and foster enhanced productivity in their region of influence. Two fundamental processes, upwelling and mixing, bring deep-water nutrients to the surface, where they foster phytoplankton growth, such as the noteworthy Peru and Benguela upwelling zones. Because phytoplankton requires about 16 times as much nitrate as phosphate for optimum growth, nitrate is frequently the 'limiting nutrient', meaning that it controls the level of phytoplankton growth in ocean waters. Although nitrates are more commonly the limiting nutrient, there are times of the year and regions where it is possible for phosphate, iron, or silica to be the limiting nutrient.

Another important source of nitrogen to ocean waters is direct atmospheric deposition of nitrogen species. Atmospheric nitrogen species also contribute to nutrient loads in ocean waters through indirect deposition when nitrogen species deposit onto rivers that then feed into estuaries and open oceans. Combustion processes such as energy production from coal, vehicular emissions from gasoline and diesel fuel, other industrial activities, and fires lead to the emission of nitrogen oxide pollutants. Using the air shed for the Long Island Sound watershed as an example, the largest sources of nitrogen emissions are transportation (39%), electric utility (26%) and ammonia emitted from animal waste (16%). These nitrogen oxide species can undergo chemical modifications in the gas phase or liquid phase to species such as nitric acid and aerosol particles. When atmospheric nitrogen species are deposited on rivers, estuaries, or in the open ocean, they can also induce both surface water acidification and nitrification or excess nitrate. Sulfuric acid, which also has anthropogenic sources, is another contributor to water acidification. The deposited nitric acid is converted in surface seawater, which is basic (pH approximately 8.1 - 8.4), to nitrate, becoming biologically available.

Over certain water bodies around the world, atmospheric nitrogen deposition

constitutes a large fraction of the total nitrogen load, such as open ocean areas close to large sources of air pollution, regions with little water upwelling, and regions with little influence from terrestrial sources of nutrients. This atmospheric contribution of nitrogen augments primary productivity, particularly in oligotrophic waters. According to Pryor and Sørensen (2002), dry deposition of nitric acid, nitric oxides, particulate nitrate, and ammonia comprises about 20 - 40% of the total nitrogen flux in oceanic study regions. Prospero et al. (1996) reported that anthropogenic nitrogen emissions cause the deposition rate of nitrogen oxide species " NO_y " to the North Atlantic Ocean to be about five times greater than pre-industrial levels; this increase is similar for reduced nitrogen species (" NH_x "). Prados et al. (1999) found that much of the NO_y in the North Atlantic is transported over long distances. Jickells (1998) wrote that approximately one-third of anthropogenic nitrogen emissions in the North Sea are comprised of nitrogen dioxides; this percentage is similar for the Kattegat in the Baltic Sea, but in the form of reduced nitrogen. For estuaries such as the Chesapeake Bay in the United States, with substantial terrestrial inputs of nitrogen, the importance of atmospheric nitrogen deposition is reduced compared to riverine input, but is still substantial. He also notes that airborne sea salt from sea spray contributes to the formation of large aerosol particles laden with nitrate, which increases the efficiency of atmospheric nitrate deposition substantially. According to Duce et al. (2008) atmospheric nitrogen deposition could account for up to 3% of new annual oceanic primary productivity, an increase that is 10 times larger than pre-industrial times, and this represents about one-third of the primary productivity caused by all external (water and air) nitrogen input to the oceans.

Atmospheric nitrogen deposition can also influence the oceanic release of nitrous oxide (N_2O), a greenhouse gas. According to Duce et al. (2008), "... the increase in AAN [anthropogenic atmospheric fixed nitrogen] has led to nearly an order of magnitude increase in anthropogenic N_2O emission from the oceans." Finally, atmospheric nitrogen deposition can shift the nitrogen/phosphate balance in surface waters. One of these areas is the North Atlantic Ocean, where Fanning (1989) documented, based on GEOSECS data, that while phosphate concentrations were depleted, nitrate and nitrite were detectable. He postulated that this was due to air pollution from the Eastern Seaboard, citing Levy and Moxim's (1989) map of global atmospheric combustion-produced nitrogen. In this area, phytoplankton productivity would have otherwise used up the available phosphate but atmospheric nitrogen provided an excess of nitrate, making phosphate the limiting nutrient.

This investigation uses atmospheric NO_2 satellite observations from the Ozone Monitoring Instrument (OMI) to examine its potential effect on water quality in the Atlantic Ocean, Mediterranean Sea, and Baltic Sea. The OMI NO_2 algorithm retrieval has been described by Bucsela et al. (2006). The product to be demonstrated is the total tropospheric column density in molecules/ cm^2 . This represents the integrated NO_2 amount from the surface of the earth to the tropopause (the atmospheric boundary between the troposphere and the stratosphere). Because OMI NO_2 is a

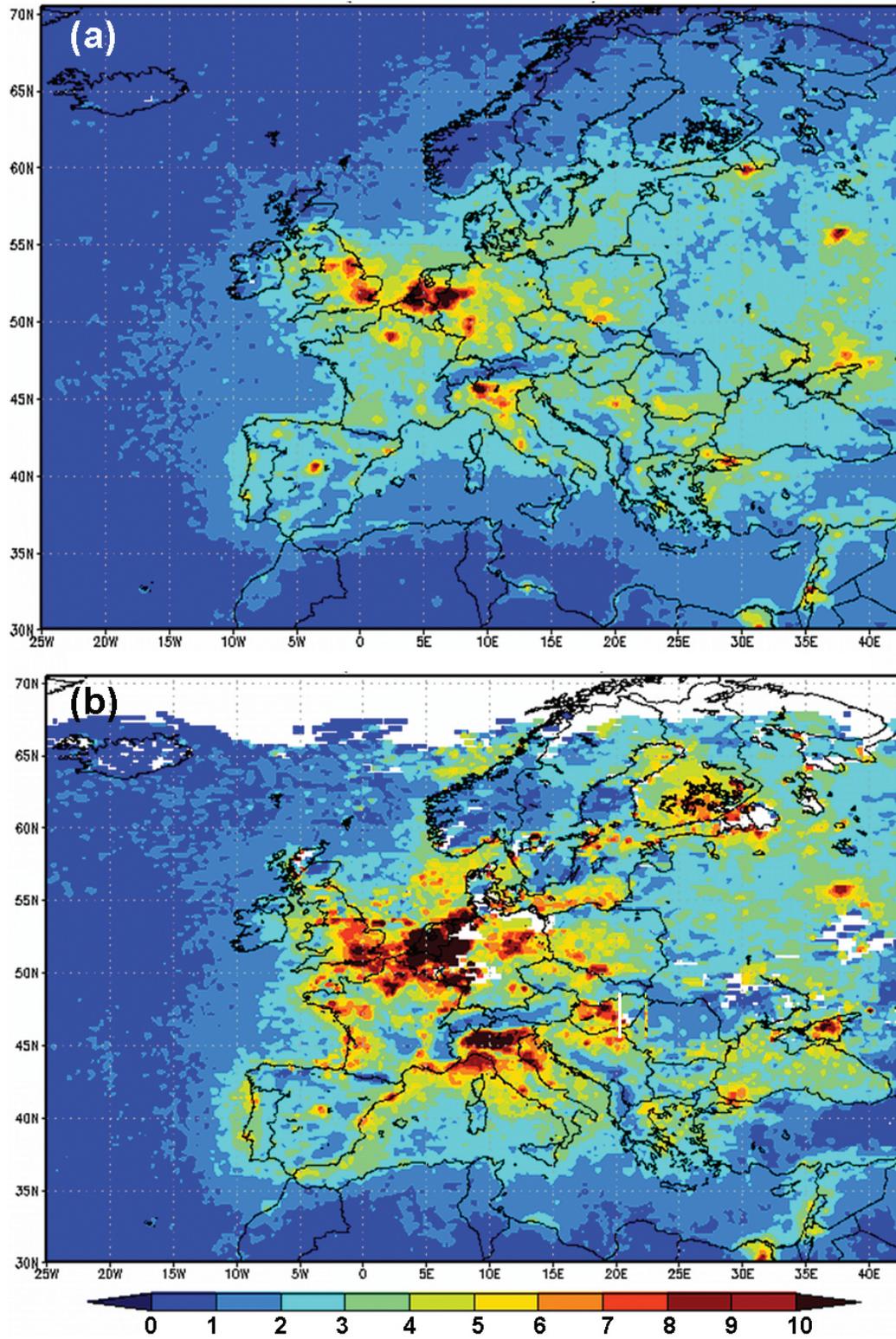


Figure 4.1 Giovanni mean monthly OMI (Ozone Monitoring Instrument) tropospheric NO₂ column for (a) July 2008 and (b) January 2008.

column measurement, it does not give us information regarding its vertical distribution. NO₂ has a relatively short photochemical lifetime (from hours to days) and tends to concentrate near the surface of the earth. OMI NO₂ tropospheric column measurements have been shown to be sensitive to boundary layer, concentration based, comparisons with measurements from ground based networks (Celarier et al. 2008; Lamsal et al. 2008). However, atmospheric convective processes can also lead to high NO₂ concentrations in the mid to upper troposphere (Prados et al., 1999).

OMI NO₂ tropospheric columns from 2005 until present are available globally from several sources. The Royal Netherlands Meteorological Institute (KNMI) Tropospheric Emissions Monitoring Internet Service (http://www.temis.nl/airpollution/no2col/no2regioomi_col3.php) has the advantage of providing near real-time imagery and maps for specific regions of the world. Another method for obtaining OMI NO₂ data is from the NASA GES DISC Interactive Online Visualization ANd aNalysis Infrastructure (Giovanni). Giovanni is a decision-support tool for air quality applications (Prados et al., 2010), among others, and it has the advantage of providing analysis tools, in addition to visualization capabilities.

This chapter will demonstrate how to access and interpret gridded 0.25 x 0.25 degree OMI NO₂ tropospheric columns through Giovanni. Visualizations are available both as jpg images and as a KMZ files which can be uploaded through Google Earth. Giovanni allows users to select areas of interest through an interactive map for the generation of latitude/longitude daily maps or temporally averaged maps. There are also a number of image analysis tools such as time series and correlation plots and maps.

4.2 Demonstration

STEP 1: Go to the main Giovanni web page <http://giovanni.gsfc.nasa.gov>

STEP 2: Access Giovanni OMI NO₂

Go to the table in the main Giovanni page and click on 'Aura OMI L3' link.

STEP 3: Generate Maps of OMI NO₂

In this section, you will generate several latitude/longitude plots to help with your image analysis.

1. Spatial Selection: Click on the map and with the mouse select a box that includes Europe, the North Atlantic Ocean, the Baltic Ocean, and the Mediterranean Ocean. Alternatively, enter these latitudes and longitudes in the boxes below the maps: North: 70.5; South: 30; East: 42.5; West: -25
2. Parameter Selection - select the box with the following parameter: NO₂ Tropospheric Column (Cloud-Screened at 30%).
3. Temporal Selection: Begin Date = 2008, July 1; End Date = 2008, July 31

4. Under "Select Visualization," select "Lat-Lon Map, Time-Averaged" and then click on "Generate Visualization". It will take a few moments for Giovanni to create the figure. Your image should look similar to the one shown in Figure 4.1a.
5. Repeat the above for the following Time period: January 1 - January 31, 2008. Your image should look similar to the one in Figure 4.1b.

STEP 4: Visualize images on Google Earth and download of GIF images

1. From the results page for the January 2008 visualization you just created, click on the "Download Data" tab at the top of the page.
2. To download a KMZ or other data files click on the items on the last column.
3. To view the image on Google Earth, click on the KMZ icon, then upload to Google Earth directly or you can choose to save the file, then open Google Earth, and then open the file after you start Google Earth.
4. Zoom in the country of Spain and make a note of where the OMI NO₂ is the highest. Your image should look similar to Figure 4.2, which shows the OMI NO₂ over Spain overlaid on Google Earth.
5. To download a gif image click on the file name at the bottom of the first column.

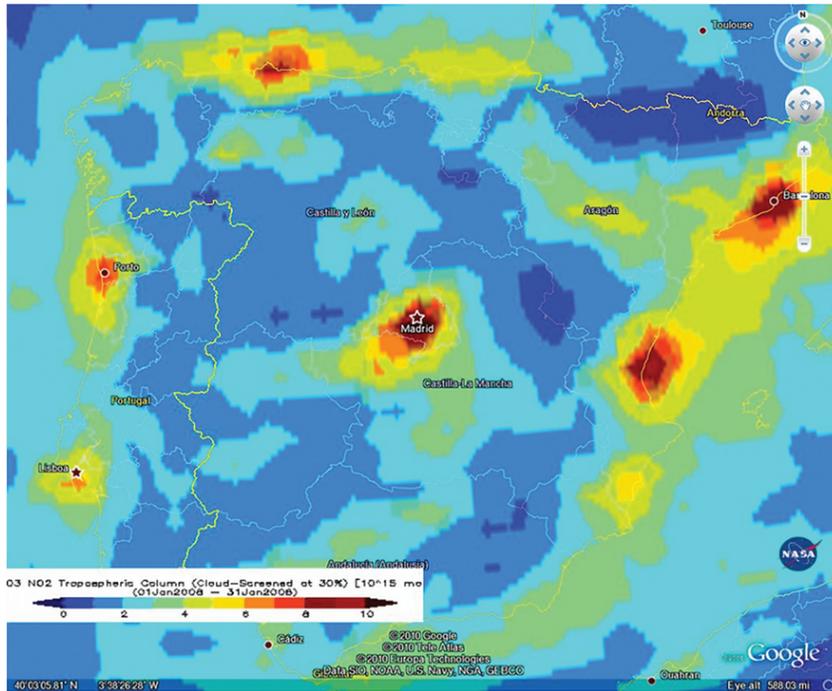


Figure 4.2 Giovanni mean monthly OMI tropospheric NO₂ column for July 2008 over Spain using a KMZ output data file from Giovanni on Google Earth.

STEP 5: Generate Animation Plots of NO₂

1. Now go back to the 'OMI AURA L3' page (click on Home in the tab above the map).
2. Leave the same Spatial and Parameter Selections as in STEP 3
3. Temporal Selection: Begin Date = 2008, February 1 End Date = 2009, February 29
4. Under "Select Visualization," select "Animation" and then click on "Generate Visualization". You can use the tabs at the bottom of the plot to advance images one by one or to visualize all the images as an animation. We will be focusing on the images for February 12 - 14 (Figure 4.3).

STEP 6: Generate an OMI NO₂ Time Series Plot

1. Go back to the 'OMI AURA L3' Page (click on Home in the tab above the map).
2. Now we will want to narrow our frame to observe NO₂ over the North Sea between England and Norway. Select a region of the North Sea or alternatively, enter these latitudes and longitudes in the boxes below the maps: North: 59.6; South: 52.6; East: -84; West: -96 3.
3. Parameter Selection (select the box for the following parameter): NO₂ Tropospheric Column (Cloud-Screened at 30%).
4. Temporal Selection: Begin Date = 2008, Feb 1; End Date = 2008, Feb 29
5. Under "Select Visualization," select "Time Series" and then click on "Generate Visualization". It will take a moment for Giovanni to create the plot. If you chose the same latitudes and longitudes above, your plot should look similar to Figure 4.4. Write down the days in February in which OMI NO₂ is the highest over this region.

STEP 7: Image Interpretation

In order to interpret the images, look at the colour bar at the bottom of each map, which has a scale from 1 to 10×10^{15} molecules/cm². Values over 7 indicate moderately polluted conditions. Keep in mind that these are column measurements. We do not know whether the pollution is closer to the surface, where it can have greater impacts on human health, or higher in the atmosphere. OMI data, however, are not always available. One of the main reasons for lack of data is cloudiness. The OMI data available through Giovanni have been automatically screened (the region appears white in the map because the data are not available) when the cloud cover is 30% or greater. The last figure you created (Figure 4.4) is called a time-series, and it shows the averaged NO₂ tropospheric column (y-axis) over the regions (square) you selected in Giovanni for each day. The day of the month is shown in the x-axis.

4.3 Questions

Q 1: Look at the July 2008 map you generated (Figure 4.1a). Which countries have the highest NO₂ emissions and why? Think about what kinds of human activities

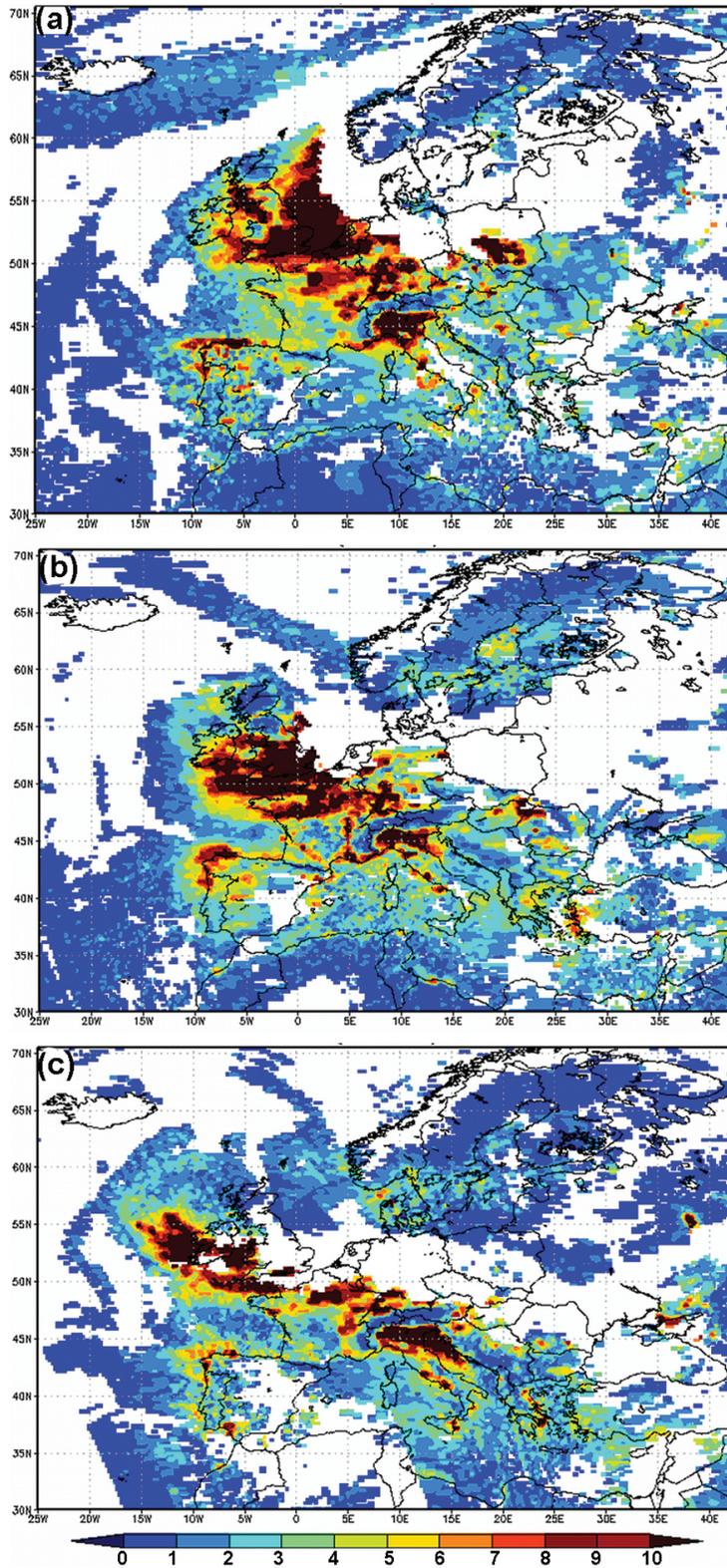


Figure 4.3 Giovanni daily OMI tropospheric NO₂ column on (a) 12 February 2008, (b) 13 February 2008 and (c) 14 February 2008.

in those countries may be contributing to the higher NO₂ levels compared to other countries.

Q 2: Look at the January 2008 map you generated (Figure 4.1b). How do the mean values in January compare to those in July? Explain why the NO₂ tropospheric column over land is higher in one month than in the other.

Q 3: During which month (January or July) would one expect a greater amount of NO₂ atmospheric deposition over the Baltic Sea, Mediterranean Sea, and the Atlantic Ocean?

Q 4: Look at the NO₂ values in Spain on January, 2008 (Figure 4.2). Which parts of Spain have the highest NO₂ concentrations and why? List several locations and activities in those locations which could be contributing to those high NO₂ concentrations. Why are some parts of Spain more polluted than others?

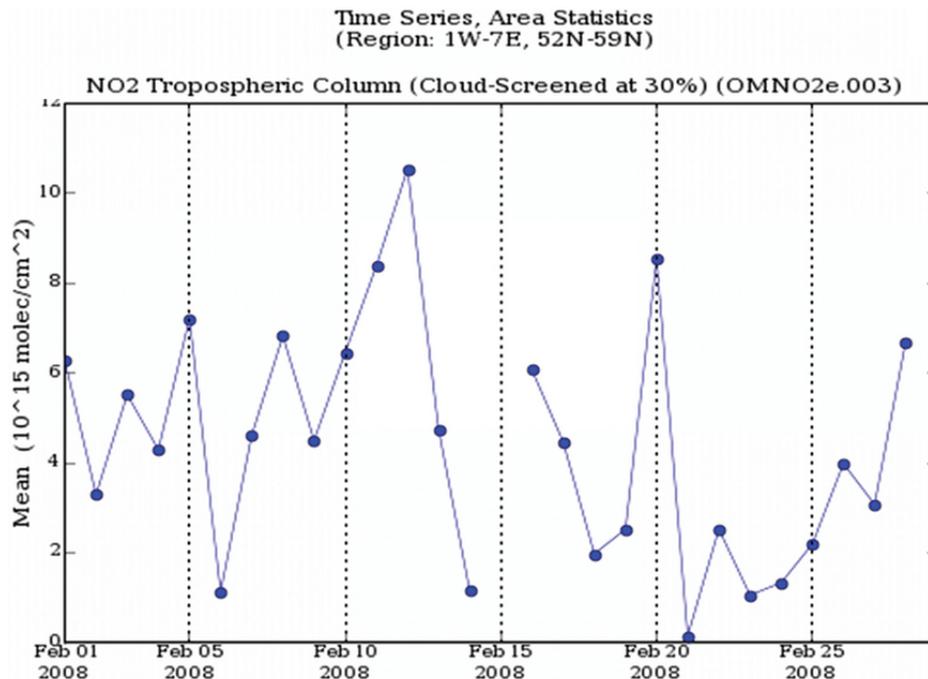


Figure 4.4 Giovanni time series of OMI tropospheric NO₂ column over the North Sea for February 2008.

Q 5: What are the main differences between land and the surrounding oceans in Figures 4.1a and b? Which coastal areas in Europe and surrounding oceans would we expect to have the greatest problems with ocean productivity and water pollution impacts such as algal blooms?

Q 6: Pick a coastal region or ocean and list countries which are likely to contribute

to excess nutrients and algal blooms in that particular coast or ocean?

Q 7: Now look at Figure 4.3. We will be focusing on the North Sea, which is the part of the Atlantic Ocean between England and Norway. We will also be looking at the North Atlantic west of Ireland. What do you observe in comparing the images for February 12, 13, and 14? You can also go back to the Giovanni session and use the controls to slow down the loop or view each image individually.

Q 8: Look at Figure 4.4. This figure shows the average NO₂ tropospheric column over the area you selected over the North Sea. Which days had the highest NO₂ pollution levels?

Q 9: Now compare the individual Giovanni NO₂ maps for each day in February and compare them to the time series (Figure 4.4). Is there a correspondence between the two? What is the source of the variability in the OMI tropospheric NO₂ over the North Sea in February 2008?

4.4 Answers

A 1: The Netherlands in northern Europe have some of the highest NO₂ concentrations. England has very high concentrations as well. These are the countries in Europe with the highest concentrations of industrial activity.

A 2: The July levels are generally lower. There is greater photochemical destruction of NO₂ in the summer due to higher ozone concentrations. Moreover, heating sources that depend on fossil fuel combustion, such as coal, are used in the winter but not in the summer. Coal is a fossil fuel and a large source of NO₂.

A 3: We would expect greater atmospheric NO₂ deposition in the winter. This would be true for all the oceans surrounding Europe where the atmospheric deposition is dominated by the sources (countries) shown in Figures 4.1a and b, and where there is little contribution from sources further away that are not shown in the map.

A 4: Spanish cities are more polluted than rural areas because they have more cars and industrial activities. Cars and other equipment that burn gasoline or diesel lead to NO₂ emissions. Industrial activities also use up a lot of energy that leads to NO₂ emissions.

A 5: The land areas are generally more polluted than the oceans. However, some of the coastal areas can be just as polluted as the land. This is because of their close proximity to atmospheric pollution sources. For example, there are values of NO₂ along the Southern Coast of France and along the coast of Italy that approach 6 to 7 x 10¹⁵ molecules/cm². Some of the oceans (Figure 4.1b) have values of NO₂ that can be quite large. This is because under certain atmospheric conditions, atmospheric

NO₂ can also travel long distances over oceans. The Baltic Sea north of Poland has high pollution levels in January 2008. The Atlantic Ocean also experienced levels of NO₂ that were comparable to land, particularly in the North Sea. The oceans where we would expect the worst problems with algal blooms would be those affected by large terrestrial or atmospheric sources of nutrients, including NO₂ from both. Phosphorus and sediments, when in excess, also contribute to water pollution and impacts such as algal blooms. Based on these maps, we would expect the Baltic Ocean and the North Sea in particular to receive a strong influence from atmospheric sources, and therefore these bodies of water would be more vulnerable to water pollution. Some portions of the Mediterranean Ocean such as coastal areas of Northern Italy would also be more vulnerable to water pollution due to atmospheric NO₂ deposition.

A 6: Over the Baltic, we would expect several contributing sources. All land areas that surround the Baltic Sea would contribute terrestrial sources of nutrients, including NO₂ from the rivers that feed into the Baltic Sea. Atmospheric sources of nutrients would be dominated by the surrounding countries with the highest levels of OMI tropospheric NO₂, primarily Germany, Poland, and Finland.

A 7: If you look at these figures in sequence you can see a plume of NO₂ over the North Sea on February 12th. On February 13th the plume moved west over the United Kingdom and Ireland, and by February 14th it has moved primarily offshore west of Ireland. The pollution over the North Sea on February 12th likely originated over northern Europe (the Netherlands, Belgium).

A 8: The highest NO₂ levels are on February 12th, 2008. However, there are other days later in the month, when the NO₂ tropospheric column increased again.

A 9: Go back and forth between the time series (Figure 4.4) and the maps for February 2008. There should be a correspondence between the two. If the map shows that the areas you selected had large NO₂ values, that should also be reflected as a peak in the time series. This variability is due to shifting meteorological patterns which cause varying degrees of transport of atmospheric NO₂ from land to the North Atlantic Ocean. You can select different regions (oceans) to create animation plots and time series and study the variability of atmospheric NO₂ and expected variability in water nutrient inputs.

4.5 References

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