ARTICLE

# Differential optical absorption spectroscopy as a tool to measure pollution from space

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## Introduction

If the total amount of a substance in a volume of gas or liquid is to be determined in the laboratory, absorption spectroscopy can often be used as a simple and reliable measurement technique. By comparing the intensity of a light source with and without the absorber in the light path, the integrated amount of the substance can be determined using Lambert–Beer's law and the absorption coefficient of the absorber. Depending on the absorption spectrum of the species of interest, light at ultraviolet, visible or near infrared (NIR) wavelengths can be used.

Over the last few decades, interest in measurements of the chemical composition of the Earth's atmosphere has increased significantly. This interest is prompted not only by scientific curiosity on how dynamics, chemistry, radiation and biology interact in this complex system, but also by the realisation that human activities already have altered air composition on a global scale. The ozone hole appearing in the stratosphere over Antarctica each spring, the rapid increase in atmospheric levels of $CO_2$ and other greenhouse gases, and air pollution in urban areas are just a few examples of how mankind is changing the atmosphere.

Absorption spectroscopy is routinely used for *in situ* measurements of, for example, ozone in the atmosphere in a way which is very similar to that used in the laboratory. For species present at lower concentration or with smaller absorption cross-sections, longer light paths are necessary to obtain the absorption strength needed to get results with the required accuracy. By using very intense lamps and collimated light beams, light paths of several kilometres can be realised, either over a long unobstructed distance or more locally using folding mirrors. However, this type of set-up is limited to measurements near the surface or on airborne platforms, and cannot be used to probe the upper atmosphere.

This problem can be solved by using the sun as a light source. All photons observed on the ground, from aircraft or balloons have passed through at least part of the atmosphere, and by combining the absorption measurement and a calculation of the light path, the average concentration of a substance along this light path can be determined. As it turns out, not only direct sunlight but also scattered light can be used, extending observation capabilities to cloudy situations and twilight, and thus increasing the number of possible viewing directions. As a result of the scattering geometry, observations of the zenith-sky at low sun provide very high sensitivity to the stratosphere, the atmospheric region between about 10 km and 50 km that contains the ozone layer. This is exploited by the ground-based Dobson and Brewer instruments, which have been used to monitor the atmospheric ozone abundance since the 1920s.[1]

The disadvantage of all these techniques is that they provide only local information, while global data sets are needed to characterise and monitor the Earth's atmosphere as a whole. The same measurement principle has therefore been adapted for satellite instruments. By tracking the sun (or the moon) rise or set, vertical profiles of atmospheric constituents can be measured, at least as long as the light path is not obstructed by clouds or strong scattering in the lower atmosphere. By pointing the instrument in the nadir direction towards the ground, light scattered from the surface or from the atmosphere is detected, providing information on the total column of trace species in the atmosphere. As the instrument orbits the Earth, a global picture is assembled strip by strip. An overview of the different viewing geometries is given in Figure 1.

While the basic principles of absorption spectroscopy apply for satellite measurements of scattered sunlight as for measurements in the laboratory, there are a number of complications that need to be taken care of. First of all, the atmosphere is a mixture of different gases at varying concentrations that all contribute to the absorption signal. In addition, scattering on air molecules, aerosols and clouds as well as absorption on the ground often dominate the extinction of sunlight, the atmospheric absorption signal being just a very minor part of the signal. To separate these various effects, measurements are taken at many different wavelengths simultaneously. Individual absorbers can be identified and separated through their characteristic variation of absorption with wavelength, their spectral fingerprint. In contrast, extinction by scattering and absorption on the

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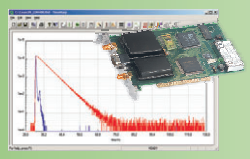

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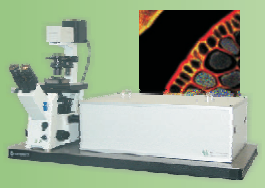

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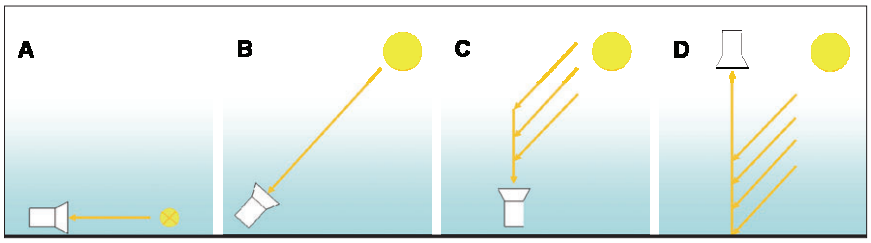



**Figure 1.** Viewing geometry for absorption measurements in the atmosphere. A: long-path measurements using an artificial light source, B: solar or lunar occultation measurement from the ground, C: zenith-sky measurement of scattered sunlight and D: satellite nadir observation of scattered and reflected sunlight. The multiple arrows in panels C and D indicate that light scattered at different altitudes contributes to the observed signal.

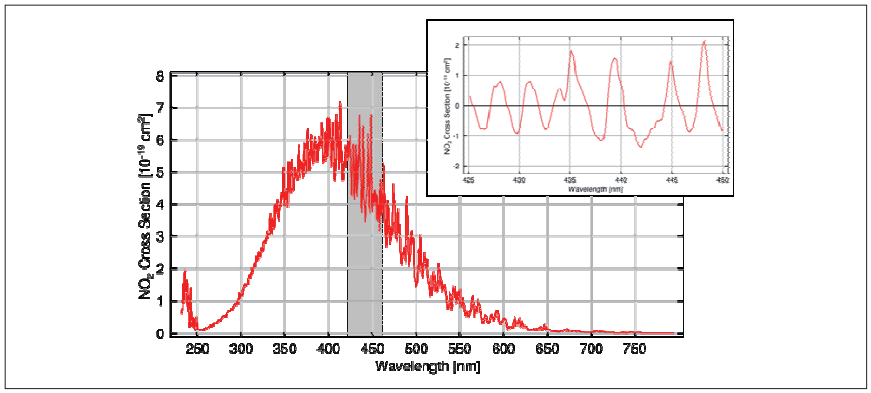



**Figure 2.** Absorption cross-section of $NO_2$ and the high-pass filtered part used in the retrieval of $NO_2$ from SCIAMACHY measurements (inset). The $NO_2$ cross-sections are shown at the spectral resolution of the instrument.

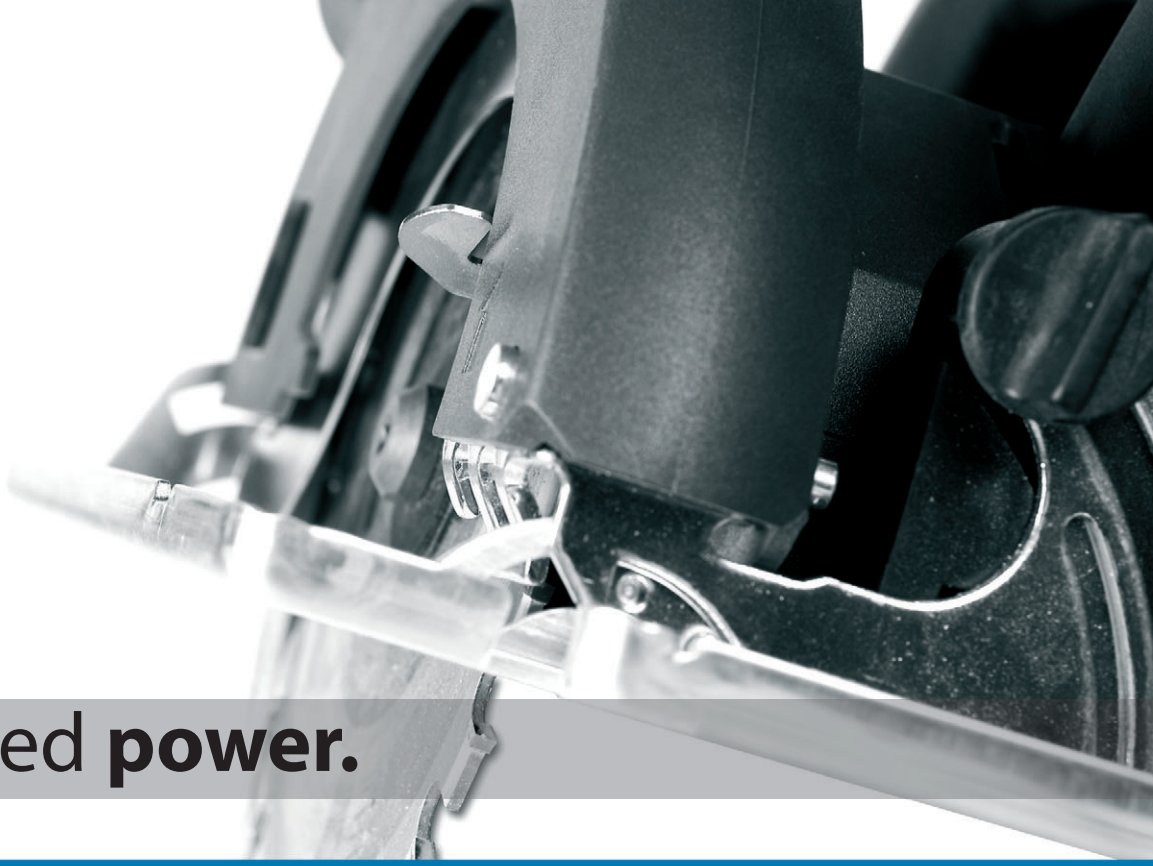
ground usually vary smoothly with wavelength and can be removed from the signal by applying high pass filters. The method thus becomes sensitive only to variations in absorption with wavelength and therefore is called Differential Optical Absorption Spectroscopy (DOAS).[2,3] An example of such a retrieval is shown in Figure 2. As in any application of absorption spectroscopy, the quality of the reference cross-sections used, including their temperature dependence and appropriate spectral resolution, is crucial for the accuracy of the results.

The second main difference to measurements in the laboratory is the uncertainty in the light path. While simple measurement of the length of a cell is usually sufficient in the lab, the light path through the atmosphere depends not only on the position of the sun, the viewing angle of the satellite and the wavelength of the photon, but also on surface reflectivity, atmospheric visibility, the presence of clouds and other atmospheric parameters. Therefore, the relatively simple measurement of light intensities has to be combined with complex simulations of the radiative transfer in the atmosphere to convert the detected absorption signal to an atmospheric absorber column.

## Instruments

What are the technical requirements for the perfect satellite borne DOAS instrument? First, it should provide enough spectral coverage to facilitate the retrieval of as many trace species as possible. Typically, this includes wavelengths from the UV to the NIR. The spectral resolution must be sufficient to resolve the differential structures used in the retrieval, i.e. of the order of 0.2–0.8 nm. The sensitivity must be good enough to provide very high signal to noise (up to a few $10^3$) when measuring the scattered light over a dark surface and at the same time the dynamic range should be high enough to avoid saturation over bright clouds. Excellent straylight rejection is a key requirement for analysis of the measurements in the UV part of the spectrum as the measured intensity varies over two orders of magnitude as a result of the strong ozone absorption. In particular for tropospheric species, good spatial resolution and coverage is advantageous, implying the need for short integration times (of the order of a tenth of a second) and a large viewing swath. An additional complication arises from the fact that light scattered by molecules is polarised depending on the scattering angle, and the instrument efficiency usually varies with the polarisation state of the incoming light. Therefore, the polarisation of the light has either to be measured or to be efficiently "scrambled" at the instrument entrance. In general, the instrument has to be carefully characterised and calibrated before launch to facilitate accurate conversion of the measured signals into physical units under all operation conditions.

One practical example of a state-of-the-art satellite instrument designed for DOAS-type measurements is the SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) instrument, launched into a sun-synchronous orbit on the ENVISAT satellite in March 2002.[4] In nadir viewing mode, the instrument has a 960 km across track scan which typically is divided into ground pixels with a spatial resolution of $60 \times 30\,km^2$. It comprises a pre-dispersing prism with a grating that separates the spectrum into eight channels each with a 1024 pixel cooled diode array detector (Figure 3). Some technical details and the range of detectable species are given in Table 1 and Figure 4. In SCIAMACHY, the polarisation is measured at a spatial resolution of $7.5 \times 30\,km^2$ by broad-band detectors, which are also used to derive fractional cloud cover within one measurement scene. In addition to the nadir mode, the instrument also performs solar and lunar occultation as well as measurements of the limb radiance to derive vertical profiles of absorber concentrations in the stratosphere and upper atmosphere. More on the SCIAMACHY instrument and its mission can be found at http://www.sciamachy.de/#english. A smaller version of SCIAMACHY, GOME (Global Ozone



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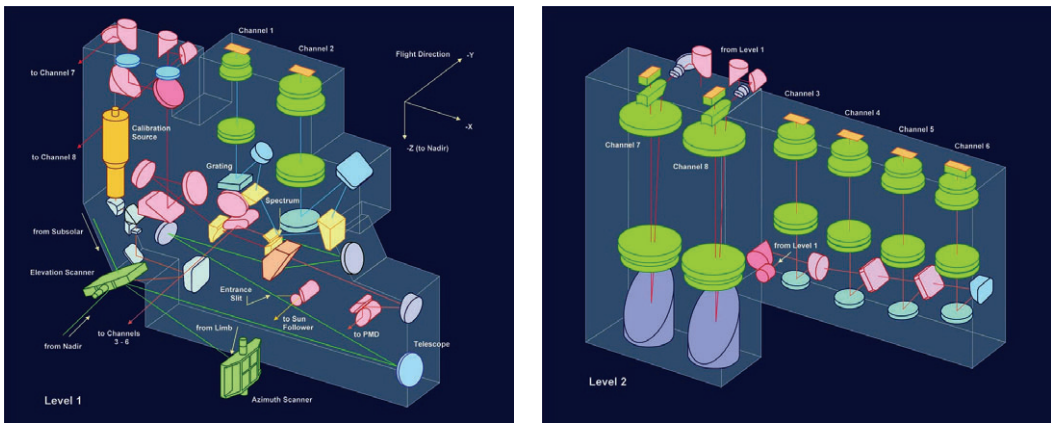


**Figure 3.** Optical configuration of the SCIAMACHY instrument. Entrance optics, calibration unit and channels 1 and 2 (left) and channels 3–8 (right). The nadir view of the instrument is to the bottom of the sketch. (Graphics: DLR-IMF, modified after SJT 1996.)

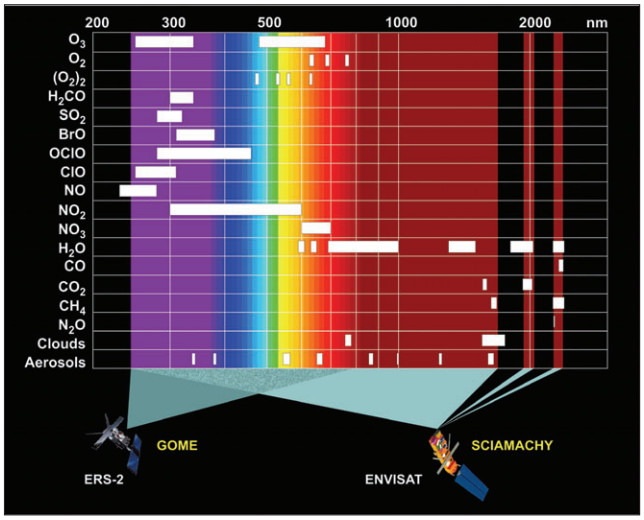


**Figure 4.** Overview on atmospheric species that can be detected with GOME and SCIAMACHY and the spectral intervals which can be used for the retrieval (white bars). SCIAMACHY covers the same wavelength region as GOME but has additional channels in the NIR.

**Table 1.** Some specifications of the eight SCIAMACHY measurement channels.

| Channel | Spectral range (nm) | Resolution (nm) | Detector | Temperature (K) |
|---|---|---|---|---|
| 1 | 214–334 | 0.24 | Si | 204–210 |
| 2 | 300–412 | 0.26 | Si | 204–210 |
| 3 | 383–628 | 0.44 | Si | 222–228 |
| 4 | 595–812 | 0.48 | Si | 223–224 |
| 5 | 773–1063 | 0.54 | Si | 221–222 |
| 6 | 971–1773 | 1.48 | InGaAs | 197–203 |
| 7 | 1934–2044 | 0.22 | InGaAs | 146–156 |
| 8 | 2259–2386 | 0.26 | InGaAs | 144–150 |

Monitoring Experiment[5]) is focusing on nadir measurements in the UV and vis and a series of GOME is now flying on the European operational meteorological satellite METOP (http://www.eumetsat.int).

Several aspects of a satellite DOAS instrument can be varied. For example, active scanning with a mirror across the track (whisk broom scanner) could be replaced by an imaging spectrometer combined with a two-dimensional detector that maps wavelength in one direction and space in the second. This concept has been realised in the Ozone Monitoring Instrument (OMI, http://aura.gsfc.nasa.gov/instruments/omi/) and has the advantage of fewer moving parts and higher throughput as a larger detector can be used. However, the geometry of the ground pixels is more complex and some instrument properties vary for different parts of a scene, which complicates data analysis. Diode array detectors can be replaced by CCDs, which provide higher sensitivity but have less dynamic range and suffer from the harsh radiation environment in orbit. And as mentioned above, the polarisation of the incoming light can be scrambled, superseding the need for polarisation measurements.

## Examples of applications

A number of relevant atmospheric species can be measured from space using the DOAS method. They include pollutants such as ozone, nitrogen dioxide ($NO_2$), sulphur dioxide ($SO_2$), formaldehyde (CHCHO), carbon monoxide (CO), methane ($CH_4$) and several other trace gases (see Figure 4). For the lower atmosphere (the troposphere), determination of nitrogen dioxide amounts is the most mature application. The detection of $NO_2$ is based on its strongly structured absorption spectrum around 430 nm (see Figure 5), a spectral region where most other atmospheric absorption signals are small. At these wavelengths, the measurements are sensitive down to the surface, enabling detection of $NO_2$ from pollution sources. As $NO_2$ is also

present in the stratosphere, this part of the signal has to be removed to isolate the information from the lower atmosphere. This is achieved by using measurements over unpolluted regions and results from global chemistry transport models of the atmosphere on the spatial distribution of $NO_2$ in the stratosphere.

Nitrogen oxides (NO and $NO_2$, usually referred to as $NO_x$) are emitted not only from all combustion sources but also during lightning and from microbial activities in soils. In the industrialised parts of the world, fossil fuel combustion is the dominating source. Biomass burning and large wildfires also produce large amounts of nitrogen oxides, and locally, thunderstorms can contribute significantly. From an air quality point of view, nitrogen oxides are relevant not only because they adversely affect human health, but also because they are a key ingredient for the formation of summer ozone smog in large cities and increasingly also in rural parts of the industrialised world. In addition, nitrogen dioxide also contributes to acidification, for example, in the form of acid rain. Therefore, local and international laws regulate emissions and environmental levels of nitrogen oxides.

First, global maps of tropospheric $NO_2$ amounts have been derived from measurements of the GOME instrument (see news item in http://www.spectroscopyeurope.com/news13_1.html) but SCIAMACHY measurements provide much improved spatial resolution. An example is shown in Figure 6 for a global field and zoom-ins over some industrialised areas. The signature of anthropogenic pollution can clearly be identified, highlighting the large $NO_2$ concentrations over regions such as the Po valley, the Ruhr area, in Europe, the Ohio River valley in the US and the densely populated parts of China. Elevated levels of $NO_2$ are also observed in tropical regions where burning of forests and Savannah are the main sources.

Most of the sources of $NO_x$ are land-based, but international shipping is increasing and so are the emissions of pollutants such as $NO_x$ or sulphur dioxide ($SO_2$) into the otherwise pristine maritime boundary layer. For the shipping routes with the largest numbers of vessels the $NO_2$ pollution signal can even be picked up from satellite as shown in Figure 7.

With the continuous satellite based measurements now covering many years, first attempts to quantify changes in $NO_2$ levels have been undertaken. The results are shown in Figure 8, where the annual change in $NO_2$ amount between 1996 and 2002 is plotted as derived from GOME measurements. Over Europe and parts of the US, $NO_2$ levels have

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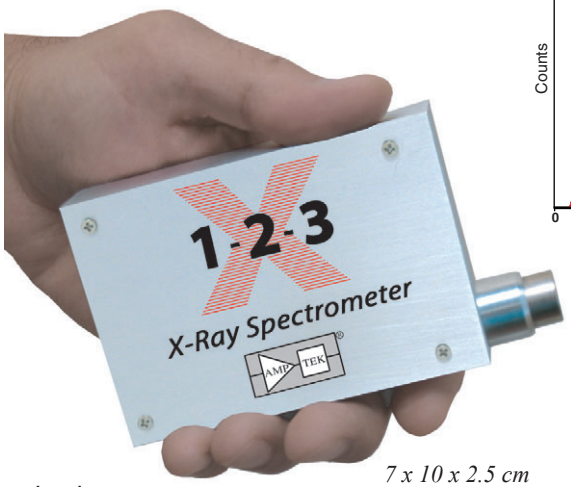


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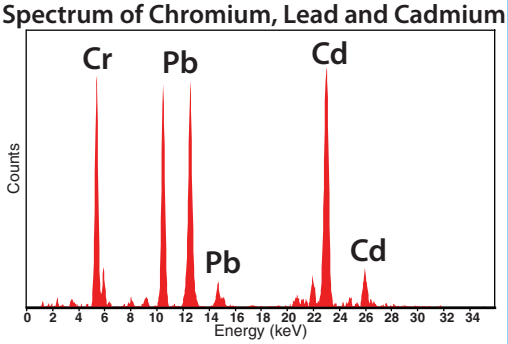


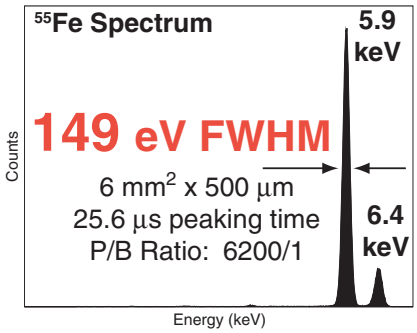


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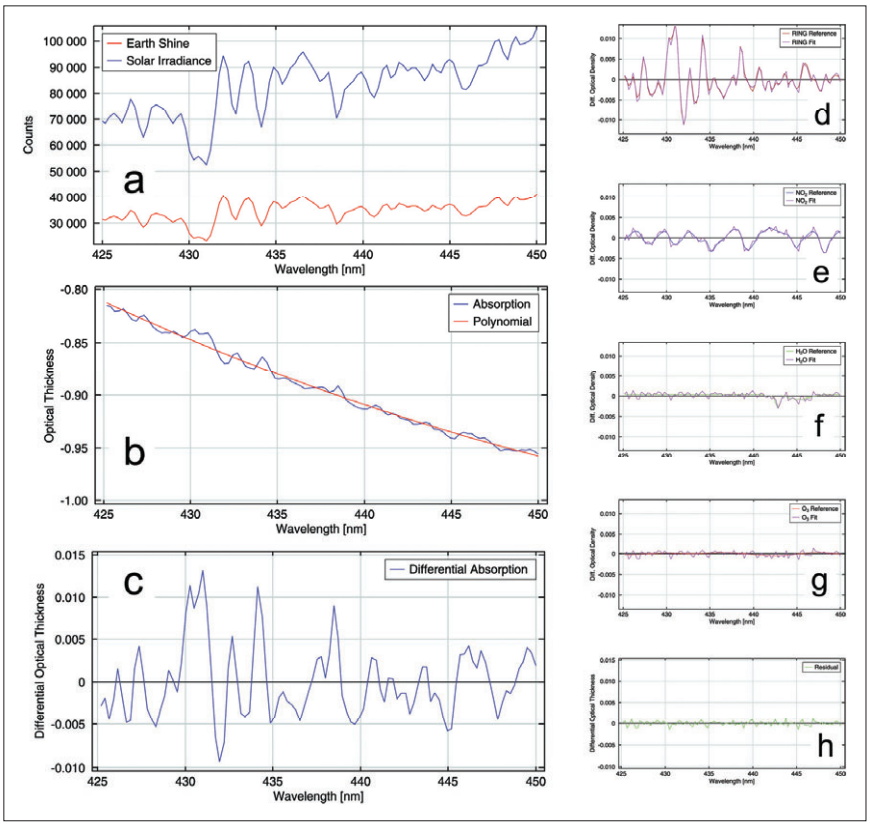


**Figure 5.** Example of a $NO_2$ DOAS evaluation on a SCIAMACHY measurement over a polluted part of Europe. Left column: a) The measurements of unattenuated solar irradiance and the light scattered back from the surface and atmosphere, b) optical thickness and polynomial for high pass filtering, c) resulting differential signal. Right column: individual contributions to the differential signal as determined in the DOAS analysis: d) signature of inelastic scattering, e) $NO_2$ absorption, f) $H_2O$ absorption, g) $O_3$ absorption, h) residual after removing all known components.

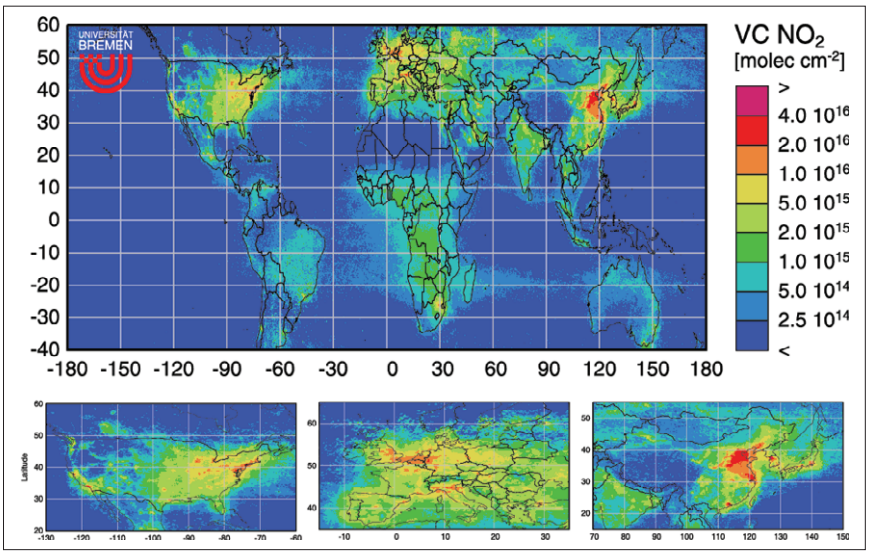


**Figure 6.** Tropospheric $NO_2$ columns retrieved from SCIAMACHY measurements for 2005. Large values are found over industrialised areas in Europe, Asia, North America and South Africa. Elevated $NO_2$ is also observed over regions with intense biomass burning such as Central Africa, Brazil or the Northern part of Australia.

been reduced (blue colours), mainly as result of improved emission controls, e.g. through catalytic converters in cars. At the same time, a large increase in $NO_2$ is observed over China, where use of fossil fuels has much increased over the last decade as result of rapid economic development. Analysis of SCIAMACHY data from recent years shows that the increase in $NO_2$ levels over China is still continuing.

The examples presented demonstrate the potential of space borne measurements of atmospheric composition using the DOAS method. No other approach can currently provide this wealth of global data on, e.g. $NO_2$ pollution, and the results highlight the truly global nature of the problems we are facing.

## Outlook

Although results obtained with the current generation of UV/vis satellite spectrometers have already changed our view of the Earth's troposphere, much more could be learned with improved instrumentation.

Ideally, the measurements should not be taken only once per day or even less frequently but several times per day to follow the diurnal changes in emissions and chemistry (e.g. the morning rush hour in cities or the effect of lightning in late afternoon thunderstorms). More measurements per day would also increase the amount of cloud free data. This could be achieved for Europe and Africa by either having an instrument in geostationary orbit or for global hourly observations by using a fleet of identical sensors in different orbits.

Further improvements in spatial resolution are needed to address air quality in urban areas and to better localise emission sources. In addition, decreasing the size of the ground scenes should help to have more measurements down to the surface by looking between clouds.

For many applications, not the column amount but the vertical distribution of the trace species is of interest. Different approaches are currently being evaluated to retrieve this information, including the comparison of measurements over clouds at different altitudes and synergistic use of measurements at different wavelengths. The latter method relies on the fact that the altitude region to which a measurement is most sensitive varies with wavelength as result of scattering

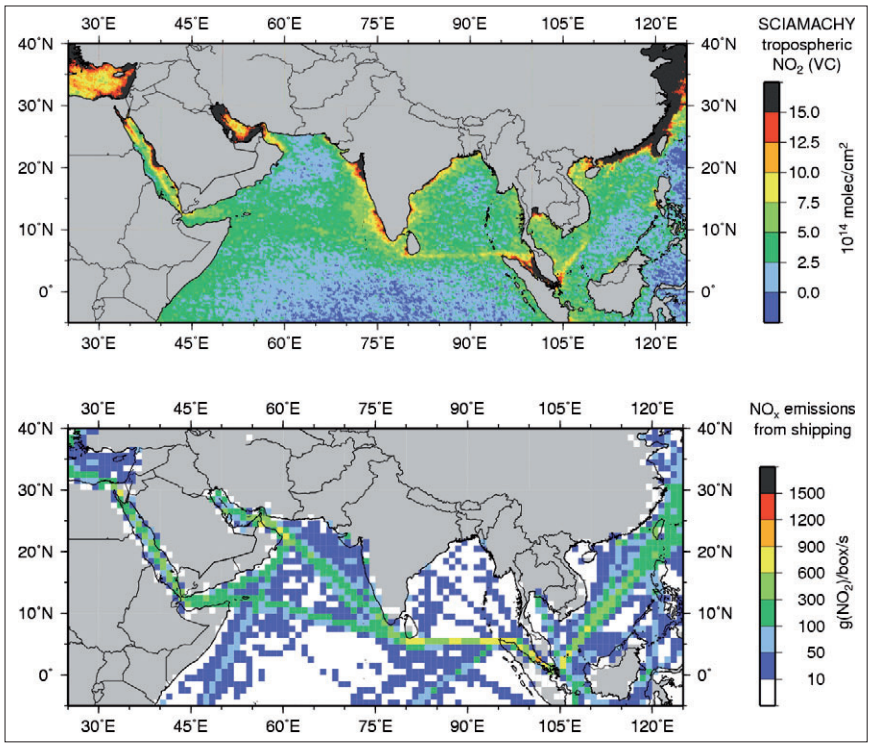


**Figure 7.** $NO_2$ signature of shipping. (a) Tropospheric $NO_2$ columns derived from SCIAMACHY data from August 2002 to April 2004 using the Differential Optical Absorption Spectroscopy (DOAS) technique. (b) Estimated distribution of $NO_x$ emissions by shipping in the same region based on global distribution for vessel traffic densities. Figure taken from Reference 7. Copyright 2004 American Geophysical Union.

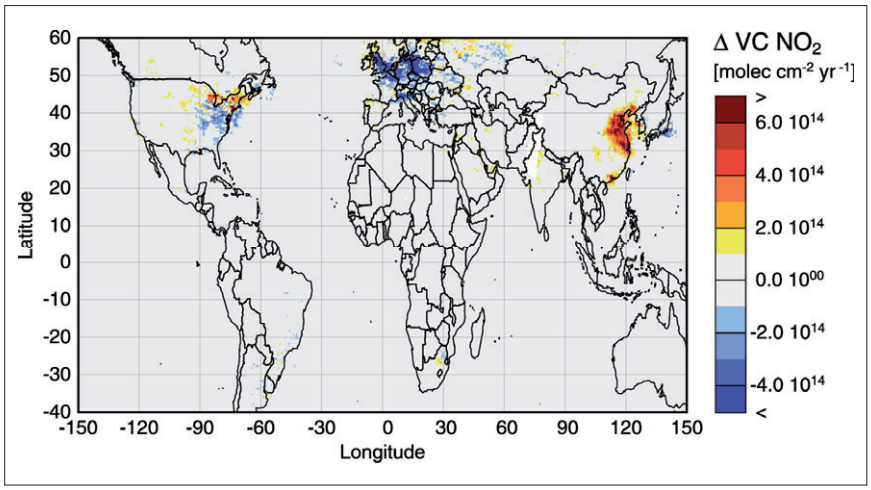


**Figure 8.** Average annual changes in tropospheric $NO_2$ as observed by GOME from 1996 to 2002. The gradient obtained from a linear regression of the annual averages of tropospheric GOME $NO_2$ columns, from 1996 to 2002 is shown. Reductions in $NO_2$ are observed over Europe and the Central East Coast of the United States, while large increases are evident over China. Figure taken from Reference 6.

in the UV/vis and temperature contrast in the thermal infrared. Combination of a UV/vis with an infrared nadir looking instrument should provide several independent layers in the troposphere for some species.

While these and many other ideas will be followed on in the coming years, it is at the same time important to also provide continuity of existing measurements. Unlike the situation in the laboratory, a measurement of atmospheric composition cannot simply be repeated at a later time, and given the speed of atmospheric changes we are witnessing, continuous global monitoring of the atmosphere should have a high priority.

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