

# Overview of tropospheric NO<sub>2</sub> vertical column density retrieval from space measurement

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**Abstract:** Nitrogen dioxide (NO<sub>2</sub>) plays a very important role among the anthropogenic trace gas. The tropospheric NO<sub>2</sub> vertical column density (VCD) maps derived have been used to study many scientific applications, such as pollution emissions and pollutant distribution. This paper reviewed the NO<sub>2</sub> inverse algorithm, Differential Optical Absorption Spectroscopy (DOAS), from satellite measurements, and also discussed the error analysis, validation and developing trends. Significant techniques are detailed for DOAS method, such as the ring effect algorithm, stratospheric NO<sub>2</sub> concentration algorithm and air mass factor (AMF). After displaying the different accuracies of NO<sub>2</sub> retrieved from satellite measurements, uncertainties are discussed for model parameters including cloud, a-priori NO<sub>2</sub> profiles, aerosol layer, and so on. There are many important issues needing to be improved. These include the tropospheric NO<sub>2</sub> retrieval algorithm, geostationary air quality satellite, and validation from ground-based measurements, Multi-Axis DOAS, and aircraft-based instruments.

**Key words:** NO<sub>2</sub>, SCD, VCD, AMF, tropospheric, DOAS

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## 1 INTRODUCTION

Nitrogen dioxide (NO<sub>2</sub>) plays a key role in the atmospheric chemistry. It participates in the control of the strong oxidant, ozone and the strongest atmospheric oxidizing agent. The main sources of troposphere NO<sub>2</sub> are emissions from fossil fuel combustion and biomass burning. But for a long time, the global distribution of NO<sub>2</sub> could only be analyzed by global chemistry transport models, because ground-based or air-borne measurement campaigns were temporally and spatially limited. An important step in filling the gap has been made by the Global Ozone Monitoring Experiment (GOME) instrument on the Second European Remote Sensing Satellite (ERS-2) launched in April 1995. It allows the retrieval of vertical column density (VCD) of NO<sub>2</sub> on a global scale. Since then, the similar instruments such as SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY), Ozone Monitoring Instrument (OMI) and GOME2 have been launched into sky. The tropospheric NO<sub>2</sub> VCD maps derived from these instruments have been used to study many scientific applications, such as pollution emissions and pollutant distributions.

After reviewing the satellite instruments, the NO<sub>2</sub> inverse

algorithm, the Differential Optical Absorption Spectroscopy (DOAS), from satellite measurements are presented in the third section. DOAS method determines the NO<sub>2</sub> state column density (SCD) along the light path through the atmosphere based on Lambert-Beer's law. It makes use of a differential absorption signal with respect to an extraterrestrial solar spectrum. The first step of this technique is the removal of aerosol scattering and surface reflecting effects by a low order polynomial function, then the Ring effects have to be considered, and finally the NO<sub>2</sub> SCD is derived based on a spectral fit of NO<sub>2</sub> to a reflectance spectrum. Based on the total SCD, the tropospheric NO<sub>2</sub> SCD is calculated by subtracting the stratospheric NO<sub>2</sub> concentration, and the tropospheric NO<sub>2</sub> SCD is converted to VCD by air mass factor (AMF). The Ring effect models, the stratospheric NO<sub>2</sub> concentration calculation methods and AMF calculation methods are revealed respectively.

As with all other remote sensing measurements, the retrieval of NO<sub>2</sub> columns from space borne instruments is based on a number of a priori assumptions and techniques that can introduce errors into the final NO<sub>2</sub> VCD product. This paper then displays the accuracies of NO<sub>2</sub> retrieved from different satellite measurements, and the analysis of errors caused by the uncertainty in model parameters such as clouds, surface albedo,

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and a priori profile shape, affecting the tropospheric air mass factor. In the following section, the validations of the satellite remotely sensed  $\text{NO}_2$  VCD using the ground in situ measurements and aircraft measurements are represented. Finally, in order to further promote the  $\text{NO}_2$  monitoring from space, three aspects are brought forward in the last section: (1) enhance different steps in DOAS method so as to promote the tropospheric  $\text{NO}_2$  VCD accuracies; (2) develop geostationary air quality satellite; (3) carry out wide validation of the  $\text{NO}_2$  column density retrieved from space by widely installing the MAX-DOAS instruments and developing aircraft-based instruments.

## 2 INSTRUMENTS

Environmental issues are of great worldwide concern. This was manifested especially by the United Nations First Conference on Environment and Development, held in Rio de Janeiro, Brazil in 1992. The hot topics range from global warming to the stratospheric ozone hole, and therefore all the issues are related to atmospheric trace constituents (Sigrist, 1994). As a trace gas, it has been recognized that nitrogen dioxide ( $\text{NO}_2$ ) contributes both directly and indirectly to the radiative forcing of climate (Solomon *et al.*, 1999; Velders *et al.*, 2001), and its direct contribution to global warming is relatively small (Solomon *et al.*, 1999), but  $\text{NO}_2$  plays a key role in the chemistry of the atmosphere. It participates in the control of the strong oxidant,  $\text{O}_3$  and the strongest atmospheric oxidizing agent, OH, which determines the oxidizing capacity of the atmosphere (Logan *et al.*, 1981; Thompson, 1992; Lelieveld *et al.*, 2004). In addition, the mixture of  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) with VOC produces photochemical smog.

The main sources of troposphere  $\text{NO}_x$  are emissions from fossil fuel combustion, mostly from power generation, road transport as well as marine shipping, and industry. Other important surface sources are emissions from biomass burning, mostly from savanna fires and tropical agriculture, and from microbial activity in soils (Lee *et al.*, 1997; Bradshaw *et al.*, 2000). The variability of  $\text{NO}_x$  concentrations in the lower troposphere is very large, so that the few available ground monitoring point observations of  $\text{NO}_x$  are difficult to produce regional scale concentrations (<http://www.temis.nl/products/no2.html>). So for a long time, the global distribution of nitrogen oxides could only be analyzed by model calculations, using global chemistry transport models (CTMs), because ground-based or air-borne measurement campaigns were temporally and spatially limited (Toenges-Schuller *et al.*, 2006).

An important step in filling the knowledge gap of  $\text{NO}_x$  global distribution was made by the GOME instrument on the Second European Remote Sensing Satellite (ERS-2) (Burrows *et al.*, 1999). GOME launched in April 1995 allows the retrieval of VCDs of  $\text{NO}_2$  on a global scale (Burrows *et al.*, 1999). Since GOME could provide global coverage  $\text{NO}_2$  maps in a rough week after cloud filtering, it demonstrated the ability to

provide a full global mapping of the atmospheric composition (Richter, 2002; Martin, 2002; Velders, 2001). GOME is a nadir-viewing spectrometer operating in the ultraviolet and visible part of the spectrum, and has a forward-scan ground pixel size of 320 km across track by 40 km along track. The global coverage of the observations is reached within three days. Global tropospheric  $\text{NO}_2$  columns was retrieved from GOME for the period January 1996—June 2003. Since 22 June 2003 data coverage has been limited due to the failure of the ERS-2 tape recorder. Higher resolution tropospheric  $\text{NO}_2$  retrieval data have become available since SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) launched in March 2002 on board the ESA Envisat satellite (Bovensmann *et al.*, 1999). The OMI(Ozone Monitoring Instrument) launched in 2004 can provide the full global coverage of tropospheric  $\text{NO}_2$  once a day. OMI continues the TOMS record for the total ozone and other atmospheric parameters such as  $\text{NO}_2$ , BrO, OCIO, etc., related to ozone chemistry. The instrument is a contribution of the Netherlands Agency for Aerospace Programs (NIVR) in collaboration with the Finnish Meteorological Institute (FMI) to the EOS Aura mission.

Now satellite instruments, such as SCIAMACHY, OMI and GOME2, can measure atmospheric trace gas concentrations with global coverage and fixed spatial and temporal resolution over a long period of time. This kind of measurements are the integrated tropospheric column of  $\text{NO}_2$ , and the  $\text{NO}_2$  column values are dominated by the amounts in the lower troposphere as a result of the relatively short lifetime of  $\text{NO}_x$ . The  $\text{NO}_2$  maps derived from these measurements have been used to study the  $\text{NO}_2$  fields on both global and regional scales (Burrows *et al.*, 1999; Leue *et al.*, 2001; Richter & Burrows, 2002; Martin *et al.*, 2002; Edwards *et al.*, 2003; Beirle *et al.*, 2003; Schaub *et al.*, 2005). The analysis of the retrieved  $\text{NO}_2$  revealed the spatial and temporal distribution of troposphere  $\text{NO}_2$  that can be used to indicate the areas of intense pollution. The troposphere  $\text{NO}_2$  can also be used for many scientific applications, as for example to study the emissions, distribution and abundance of tropospheric  $\text{NO}_2$  accounting for regional and seasonal variability (Leue *et al.*, 2001; Richter & Burrows, 2002; Beirle *et al.*, 2003), for instance, analyzing the weekly cycle in tropospheric  $\text{NO}_2$  column densities from GOME for 1996—2001. Over different regions of the world as well as over individual cities, a clear signal of the ‘weekend effect’ with reductions on rest days typically between 25%—50% was found. Another outstanding example is the analysis of inter-annual variability in biomass burning and the detection of trends in industrial emissions on the basis of tropospheric  $\text{NO}_2$  column densities from GOME over the period 1996—2002 (Richter *et al.*, 2004, 2005).

Space borne  $\text{NO}_2$  measurements have also been combined with other tools, for instance, the EDGAR 3 emission inventory and nighttime images to study the distribution patterns of the corresponding anthropogenic emissions (fossil, industrial, waste) (Toenges-Schuller *et al.*, 2006), to describe intercontinental or transboundary transport events of  $\text{NO}_2$  and to identify

sources (Spichtinger *et al.*, 2001; Stohl *et al.*, 2003; Wenig *et al.*, 2003; Schaub *et al.*, 2005). The troposphere NO<sub>2</sub> columns from space measurements have showed the significance for the assessment of regional, transnational and intercontinental air pollution. The troposphere NO<sub>2</sub> VCDs from satellite instruments have been used to evaluate global and regional models on their capability of simulating tropospheric NO<sub>2</sub> (Velders *et al.*, 2001; Lauer *et al.*, 2002; Kunhikrishnan *et al.*, 2004; Konovalov *et al.*, 2005). An international, multi-platform field campaign including ground based platforms and satellite based measurements, the INdian Ocean EXperiment (INDOEX) was carried out to measure the long-range transport of air masses from South and South-East (SE) Asia towards the Indian Ocean (Ladstatter-Weissenmayer, *et al.*, 2007). Over eastern China the large increase in NO<sub>2</sub> VCD was shown from GOME and SCIAMACHY measurements for the years 1996–2004 (Richter *et al.*, 2005, Van der A *et al.*, 2006), but it needs wide validation in the future, which was also admitted by the authors.

### 3 NO<sub>2</sub> INVERSE ALGORITHMS FROM SATELLITE MEASUREMENTS

#### 3.1 NO<sub>2</sub> Retrieval algorithms

It is very complicated to retrieve NO<sub>2</sub> troposphere VCD from space borne measurements. 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. Based on a spectral fit of NO<sub>2</sub> to a reflectance spectrum, Bremen University (Richter & Burrows, 2002; Richter *et al.*, 2005), Dalhousie University/SAO (Martin *et al.*, 2003) and BIRA/KNMI (Boersma *et al.*, 2004) three groups developed the same general approach to retrieve NO<sub>2</sub> tropospheric VCD (Van Noije *et al.*, 2006), but the European retrievals use the Differential Optical Absorption Spectroscopy (DOAS) technique (Platt *et al.*, 1979) while the SAO algorithm used a direct spectral fit (Van Noije *et al.*, 2006). The following is a brief introduction to the DOAS NO<sub>2</sub> tropospheric VCD retrieval method.

The DOAS method uses the narrow molecular absorption bands to identify trace gases and their absorption strength to retrieve tropospheric and stratospheric trace-gas concentrations. Based on the space borne measurements, the DOAS method determines the NO<sub>2</sub> SCD along the light path through the atmosphere in a given spectral window between 425 and 450 nm. The DOAS method NO<sub>2</sub> SCD inversion is based on Lambert-Beer's law and it is interpreted as the NO<sub>2</sub> column density along the average photon path from the Sun through the atmosphere to the satellite instrument, so the radiance received by satellite sensor describes the extinction of the solar radiation

in an absorbing atmosphere. The absorption of radiation is quantitatively expressed by Lambert-Beers law as follows:

$$I(\lambda) = I_0(\lambda) \exp \left[ - \left( \sum_i \text{SCD}_i \cdot \sigma_i + P(\lambda) \right) \right] + N(\lambda) \quad (1)$$

where  $I(\lambda)$  presents the solar spectrum after absorption (earthshine radiance) received by satellite instrument,  $I_0(\lambda)$  is the extraterrestrial solar spectrum (solar irradiance),  $\text{SCD}_i$  are the unknown species column densities,  $\sigma_i$  are the relevant cross sections of the absorbing species, with wavelength and temperature dependent structures,  $P(\lambda)$  is the polynomial in wavelength  $\lambda$  and  $N(\lambda)$  is the photon noise depending on  $I(\lambda)$ . DOAS makes use of a differential absorption signal with respect to a baseline or background absorption, which in case of satellite observations is usually provided by an extraterrestrial solar spectrum. The logarithm of the ratio of the irradiance spectrum and the earthshine spectrum is denoted as optical density (or optical thickness),

$$\lg[I_0(\lambda)/I(\lambda)] = \sum_i \text{SCD}_i \cdot \sigma_i + P(\lambda) \quad (2)$$

In the DOAS approach, the contribution of molecular (Rayleigh) and aerosol scattering to the attenuation of sunlight, which varies slowly with wavelength, is separated from the higher frequency signal due to molecular absorption. For that purpose, the reflectance spectrum is divided into a spectrally smooth part (broadband absorption and scattering) and a differential part. The smooth part can be modeled by a low order polynomial function  $P(\lambda)$ , the second term in the right side of Equ. (2). NO<sub>2</sub> information is retrieved from the first term in the right side of Equ. (2) (Burrows *et al.*, 1999; Richter & Burrows, 2002; Boersma *et al.*, 2004).

In addition, Ring effects have to be considered for the NO<sub>2</sub> retrieval. The so-called Ring effect arises in the atmosphere due to inelastic scattering processes, mainly rotational Raman scattering by molecular O<sub>2</sub> and N<sub>2</sub>. Roughly speaking, it manifests itself by a broadening of the solar and atmospheric spectral features present in the satellite earthshine backscattered spectra. This broadening typically reduces the depth of thin solar and atmospheric absorption features by several percents. Hence, it has a strong impact on spectroscopic measurements using the DOAS method and requires appropriate correction to be implemented in retrieval algorithms. In DOAS, the Ring effect is usually accounted for as an absorber. Ring cross sections can be obtained from different sources (Vountas, 1998; Chance, 1997).

After removing the smooth part (broadband absorption and scattering) and the Ring effect, NO<sub>2</sub> SCD is derived based on a spectral fit of NO<sub>2</sub> to a reflectance spectrum (Toenges-Schuller *et al.*, 2006). At present, fitting windows in the visible part of the spectrum (425–450nm) is used to retrieve the slant column densities of NO<sub>2</sub>. The visible window is optimised for NO<sub>2</sub>. After getting the SCD, it is necessary to convert SCD to a total VCD by using the air mass factor (AMF) (Rozanov *et al.*, 1997).

As the satellite observes both the troposphere and the

stratosphere, tropospheric NO<sub>2</sub> column concentration is derived by subtracting stratospheric NO<sub>2</sub> column concentration from total VCD (Burrows *et al.*, 1999). More details of the retrieval of troposphere NO<sub>2</sub> VCD from satellite data were given by Burrows *et al.* (1999) and Richter and Burrows (2002).

### 3.2 The Ring effect algorithm

The Ring effect refers to the filling in of Fraunhofer lines, which is known as solar absorption lines caused almost entirely by rotational Raman scattering. The inelastic component of the molecular scattering results in a net increase of radiance in the line because more radiation is shifted to the wavelength of an absorption line than shifted from this wavelength to other wavelengths. A systematic underestimation can be caused due to the filling in of telluric lines in the retrieved amount of the absorber (Sioris, 2001).

N. N. Shefov, the astronomer of the Academy of Sciences of the USSR, stated in 1958 that shallower Fraunhofer lines in the scattered light from the terrestrial atmosphere in the blue-violet part of a twilight sky spectrum was found, which was compared to a spectrum of direct solar light. However, the phenomenon was named after another astronomer James Ring, who published the first English language paper with J. R. Grainger (Grainger & Ring, 1962). A number of mechanisms contributing to the Ring effect, such as aerosol fluorescence (Noxon & Goody, 1965), Rotational Raman Scattering (RRS) (Brinkmann, 1968), earth's albedo (Hunten, 1970) and Rayleigh Brillouin scattering in addition to RRS (Kattawar *et al.*, 1981) have been suggested; but RRS is now generally agreed to be the primary source. As the first scientist to attribute the filling in of solar Fraunhofer lines to rotational Raman scattering, Brinkmann (1968) developed a simple single scattering model based on measuring rotational Raman spectra of N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> to predict the filling in of the terrestrial and Venusian atmosphere. For satellite-based UV-visible measurements Rayleigh-Brillouin scattering was rejected for the considered instrument resolution and assumed that only RRS contributes to the Ring effect. The results agreed with observations from the Shuttle Solar Backscatter Ultraviolet (SSBUV) Radiometer (Joiner *et al.*, 1995).

Basically, the Ring effect is considered as a pseudo-absorption process. Several methods have been suggested in order to obtain an effective Raman cross-section for the DOAS fitting process. Fish (1994) assumed the spectrum of the Raman scattered light is unstructured, thus the Ring spectrum can be approximated as the reciprocal of the reference spectrum. Another method is to assume single scattering is valid and using spectra of the parallel and perpendicular polarization components. A Ring cross section can be calculated on the assumption that RRS is unpolarized (Solomon *et al.*, 1987; Fish, 1994). Both assumptions of these two methods are questionable. In the reciprocal reference spectrum method, the spectrum of inelastically scattered light is structured; while in the measured polarization method, RRS is slightly polarized. In 1995, Fish and Jones developed the first radiative transfer with calculated RRS

parameters and performed measurements using a Beer's law formalism (Fish & Jones, 1995). The model is also questionable due to their incorrect calculation of O<sub>2</sub> RRS cross sections. A fourth approach was developed by Chance and Spurr in 1997. They convolved the combined N<sub>2</sub> and O<sub>2</sub> mixing ratio weighted rotational Raman scattering cross-sections with a high-resolution solar spectrum to produce an effective Ring cross-section (Chance & Spurr, 1997). Single-scattered GOMETRAN (the radiative transfer model designed for the GOME instrument) simulated spectra including Raman scattering was used to test accuracy in the retrieval of NO<sub>2</sub>. The result shows that using this type of Ring cross-section is accurate to 2% for solar zenith angle (SZA) is less than 70° and 4% for SZA<90° (McLinden, 1998). After removing the smooth part of the effective Ring cross-section, the differential cross-section is determined.

### 3.3 The stratospheric NO<sub>2</sub> concentration algorithm

The total NO<sub>2</sub> SCD includes two parts of contribution, one from stratosphere and the other from troposphere, so the tropospheric NO<sub>2</sub> column concentration is derived by subtracting the stratospheric part from the total NO<sub>2</sub> SCD. In principle, several methods can be used to distinguish between tropospheric and stratospheric parts from space borne observations, each having its own advantages and problems.

Richter and Burrows (2002) estimated the stratospheric NO<sub>2</sub> SCD from NO<sub>2</sub> columns over the remote Pacific Ocean with very low contamination from tropospheric NO<sub>2</sub>. This technique is known as troposphere excess or reference sector method (Richter & Burrows, 2002). For this method, the stratospheric NO<sub>2</sub> is assumed to have only a weak longitudinal dependency, and the column in an area remote of the known sources are assumed to be of stratospheric origin at each latitude (Toenges-Schuller *et al.*, 2006). In order to avoid the impact of polluted air masses, a clean region in the Pacific (5°S—5°N, 130°—170°E) was selected and for this area a vertical column of  $2 \times 10^{15}$  molecules (molec) cm<sup>-2</sup> was appropriate and independent of season (Richter *et al.*, 2002). To account for the small amount of tropospheric NO<sub>2</sub> over the Pacific, a correction is applied based on the output from the GEOS-CHEM model (Bey *et al.*, 2001) for the day of observation (Martin *et al.*, 2002). The advantage of the method is its simplicity, while the main drawback is the fact that variations in the stratospheric NO<sub>2</sub> can not be distinguished from the variations in the tropospheric columns.

The stratospheric part of the NO<sub>2</sub> can also be estimated using an image processing algorithm (IPA) (Leue *et al.*, 2001). In this method, it is assumed that the columns over the oceans over cloudy pixels are of stratospheric origin and also the longitudinal homogeneity (Sierk *et al.*, 2006). Clouds are used to distinguish between tropospheric and stratospheric absorptions, because clouds effectively block the view to the parts of the troposphere below cloud top height for a satellite based instru-

ment. The main problem with this method is that both stratospheric and tropospheric concentrations need to be constant in time for a simple interpretation of the correlation plot between cloud cover and NO<sub>2</sub> column.

In addition, temperature method has been used to separate cold stratospheric from warm tropospheric NO<sub>2</sub> contributions in ground-based observation, because the differential absorption cross-section is smaller at stratospheric temperatures than at room temperature. This method is based on the distribution information of NO<sub>2</sub> between troposphere and stratosphere coming from the temperature dependence of the absorption cross-section of NO<sub>2</sub> (Richter *et al.*, 1997). The stratospheric column can also be taken from the results of a global chemical transport model. The 3D-CTM SLIMCAT (Chipperfield, 1999) was used to simulate the daily stratospheric NO<sub>2</sub> column for the time of the satellite overpass. To account for differences between the model and measurement, the SLIMCAT data are scaled to the GOME data over a clean region (180°–210° longitude) (Richter *et al.*, 2005), they are consistent with the GOME observations in the Pacific Ocean reference sector (Savage *et al.*, 2004; Richter *et al.*, 2005). In addition, an assimilation approach was developed to force the stratospheric distribution of NO<sub>2</sub> of the TM<sub>4</sub> model to be consistent with the observations (Boersma *et al.*, 2004). This approach depends crucially on the accuracy of the model results and has to be investigated further.

### 3.4 The AMF calculation methods

AMF is used to convert the SCD to VCD in the troposphere NO<sub>2</sub> column concentration retrieval method from satellite measurements. AMF represents the ratio of the effective optical path through the atmosphere to the vertical optical path and is given by the ratio SCD/VCD (Noxon *et al.*, 1979; Solomon *et al.*, 1987; Perliski & Solomon, 1993).

AMF values are generally in the range of 0.8–1.5 over land and 1.5–2.5 over oceans, reflecting a larger relative contribution of the boundary layer to the tropospheric NO<sub>2</sub> column over land, however relatively high AMFs are found over continental regions that are arid (deep, intensely convective, or snow covered) (Randall *et al.*, 2003). When Irie *et al.* (2005) used the DOAS technique to derive total NO<sub>2</sub> at sunrise and sunset from the spectra measured, the high constant AMF values of 17.0, 16.5 and 15.86 over 1996–2002, which were taken from the Network for the Detection of Stratospheric Change (NDSC) database, were used for three different places in East Asia respectively. It should be noted that the use of constant AMF values may contribute to the uncertainty in total NO<sub>2</sub>, because AMF can vary depending on season (Irie *et al.*, 2005). AMF is usually calculated by a radiative transfer model SCIATRAN (Rozanov *et al.*, 1997; Richter, *et al.*, 2005) based on a priori information, for example a seasonally varying surface albedo (Koelemeijer *et al.*, 2003), surface altitude, aerosol loading and

vertical NO<sub>2</sub> profiles from the chemistry-transport Model of Ozone and Related Tracers (MOZART) (Horowitz *et al.*, 2003). A global tropospheric chemistry model CHASER with 32 vertical layers (surface to 5 hPa) and T42 horizontal resolution (2.8° latitude × 2.8° longitude) (Sudo *et al.*, 2002) was also used to derive AMF values. In fact, AMF depends not only on the observing geometry (scanning angle and solar zenith angle), but also on the vertical profile of the absorbing trace gas, surface albedo, cloud coverage, cloud height, and aerosol loading. As explained in detail by Richter and Burrows (2002) and summarized by Heland *et al.* (2002), the main sources of error in the AMF calculation are the assumptions made on the NO<sub>2</sub> vertical profile, the surface albedo and the aerosol loading.

Besides the atmospheric radiative transfer models, the backward Monte Carlo method (Palazzi *et al.*, 2005) has also been used to simulate AMF. What Monte Carlo method uses to calculate AMFs is the mean path of the photons in the atmosphere layer by layer, averaged on all the photon histories and the a priori vertical profile of the absorber of interest (Palazzi *et al.*, 2005), which is

$$\text{AMF} = \frac{\sum_0^{\text{TOA}} \Delta S_i \cdot \rho_i}{\sum_0^{\text{TOA}} \text{VCD}_i} \quad (3)$$

where  $\Delta S_i$  and  $\rho_i$  refer to the averaged path and the trace gas concentration in the layer  $i$  and the sum is carried out from the surface to the TOA (top of the atmosphere) (Wagner *et al.*, 2007).

In addition, box-AMFs which characterise the ratio of the partial SCD to the partial VCD of an atmospheric layer was put forward. The box-AMFs are identical to the so called weighting functions (Rodgers, 1976, 2000). The great advantage of calculating box-AMFs is that they can serve as an universal data base to calculate appropriate (total) AMFs for arbitrary species with different height profiles and total AMFs can be easily calculated from the box-AMFs (AMF<sub>*i*</sub>), as

$$\text{AMF} = \frac{\sum_0^{\text{TOA}} \Delta \text{AMF}_i \cdot \text{VCD}_i}{\sum_0^{\text{TOA}} \text{VCD}_i} \quad (4)$$

here AMF<sub>*i*</sub> and VCD<sub>*i*</sub> refer to the box-AMF and the partial VCD for layer  $i$ , within which layer the trace gas concentration is assumed to be constant.

An inter-comparison exercise between six different radiative transfer (RT) models had been carried out in the framework of QUILT, an EU funded project based on the exploitation of the Network for the Detection of Stratospheric Change (NDSC) (Hendrick *et al.*, 2006). The models include the Combined Differential-Integral (CDI) approach (UBRE model) (Rozanov *et al.*, 2000 and 2001), the Discrete Ordinate method (NILU and IASB models) (Lenoble, 1985; Stamnes *et al.*, 1988; Spurr, 2001), the backward Monte Carlo method (UHEI model) (Lenoble, 1985), and single scattering ray tracing method (ISAC-CNR and NIWA models) (Solomon *et al.*, 1987). The

complete set of initialization data and results have been made publicly available through the QUILT project web site (<http://nadir.nilu.no/quilt/>), enabling the test of other RT codes designed for the calculation of SCDs/AMFs. RT modeling is an important step in the interpretation of DOAS observations. It allows the conversion of SCDs into VCDs using calculated AMFs.

#### 4 ERROR ANALYSIS FOR TROPOSPHERIC NO<sub>2</sub> RETRIEVAL FROM SPACE

As with all remote sensing measurements, the retrieval of NO<sub>2</sub> columns from space borne instruments is based on a number of a priori assumptions and techniques that can introduce errors into the final NO<sub>2</sub> VCD product.

Uncertainty in a single NO<sub>2</sub> value was estimated to be  $15 \times 10^{14}$  molec·cm<sup>-2</sup> (Richter & Burrows, 2002) or 35%—60% under highly-polluted conditions (Boersma *et al.*, 2004), suggesting that there is much smaller uncertainty in the monthly-averaged NO<sub>2</sub> data (Irie *et al.*, 2005). Just the same as this uncertainty estimation, a more quantitative but still rough estimate of the uncertainties is to assume an absolute error of the order of  $4 \times 10^{14}$  molec·cm<sup>-2</sup> and a relative error of the order of 30%—50% (Savage *et al.*, 2004). The error in the NO<sub>2</sub> retrieval due to spectral fitting and determination of the tropospheric column is about  $1\text{--}10^{15}$  molec·cm<sup>-2</sup> and dominates the overall retrieval error over the oceans and remote continental regions (Randall *et al.*, 2003). Martin *et al.* (2002) showed that the total error in the retrieval of tropospheric NO<sub>2</sub> columns over continental source regions is largely determined by the AMF calculation. They derived through propagation of errors an overall error of 53% on the AMF calculation including contributions from errors in surface reflectivity, the NO<sub>2</sub> profile, aerosols, cloud cover, and radiative transfer (Randall *et al.*, 2003). Taking the air-mass factor correction for temperature into account may reduce the slant-column error of approximately 7% to a vertical column error of approximately 5% (Chance, 2002). Boersma *et al.* (2004) divided the retrieval uncertainty for vertical tropospheric NO<sub>2</sub> columns from satellite observations into three categories: (1) errors caused by measurement noise and spectral fitting, affecting the slant column density; (2) errors related to the separation of stratospheric and tropospheric NO<sub>2</sub>, affecting the estimate of the stratospheric slant column; (3) errors due to uncertainty in model parameters such as clouds, surface albedo, and a priori profile shape, affecting the tropospheric air mass factor. Just as the third uncertainty mentioned above, the main uncertainties related to the vertical distribution of the NO<sub>2</sub>, the impact of aerosols and clouds were presented in his work using GOME NO<sub>2</sub> satellite data to examine regional differences in TOMCAT model performance (Savage *et al.* 2004). The followings describe the main uncertainties in detail.

##### 4.1 Cloud

The largest uncertainties are due to clouds. As a result of the large footprint of the space borne instruments, for instance the least one is  $24 \times 13.5 \text{ km}^2$  for OMI instrument, the number of truly cloud free pixels is limited, and most measurements are contaminated by residual clouds. The space borne measurements are usually low in the presence of clouds, as the pollution below the clouds is shielded from the view of satellites (cloud shielding effect). The NO<sub>2</sub> column density retrieval depends very sensitively on the presence of clouds, as discussed in several papers (Velders *et al.*, 2001; Richter & Burrows, 2002; Martin *et al.*, 2002). Even relatively small cloud fractions (between 5% to 20%) can have a significant effect on the result, leading to underestimations of up to 40%, in particular in industrialized regions in winter. The OMI NO<sub>2</sub> product document also shows the vertical column error as large as 20%—50% caused by the presence of pollution and clouds (Chance, 2002). However, low clouds or fog can also enhance the space borne instruments' sensitivity toward trace gases (cloud albedo effect), that is clouds can also lead to an overestimation of NO<sub>2</sub> columns if a significant amount of NO<sub>2</sub> is located above or within a low cloud layer (Savage *et al.*, 2004). So in order to reduce the uncertainty of NO<sub>2</sub> quantitative retrieval introduced by cloud, high quality observations of the cloud properties (at least cloud fraction and cloud top height) are necessary (Boersma *et al.*, 2004). To minimize the shielding effects of clouds on the retrieval, based on a cloud retrieval algorithm (FRESCO) (Koelemeijer *et al.*, 2001), the GOME data with a cloud fraction less than 0.2 was used (Irie *et al.*, 2005).

##### 4.2 A-priori NO<sub>2</sub> profiles

Uncertainty in NO<sub>2</sub> arises primarily due to errors in the a-priori NO<sub>2</sub> profiles used and the tropospheric air mass factor calculations. In Houweling's work, a globally (13:30 local time) averaged tropospheric NO<sub>2</sub> profile from the TM3 chemical transport model (Houweling *et al.*, 1998) for 20 known industrial areas was used. Savage *et al.* (2004) gave a conclusion that the NO<sub>2</sub> retrieval is self-consistent and any such errors can be introduced by TOMCAT profiles using vertical profiles from the TOMCAT model run in the data analysis (Savage *et al.* 2004). In fact, profiles of NO<sub>2</sub> are characterized by a large range of variability. In emission areas the NO<sub>2</sub> concentration peaks at the surface, while downstream of such areas the pollution plume peaks at higher altitudes. The profile of NO<sub>2</sub> will be determined by aspects like the distribution of emission sources, the stability and height of the boundary layer, wet removal of nitric acid, deep convection and long-range transport by the wind (Boersma *et al.*, 2004). All these aspects strongly varies in time and space, so the assumed NO<sub>2</sub> profile in the AMF calculation causes errors to NO<sub>2</sub> VCD values.

### 4.3 Aerosol layer influence

Under unpolluted background conditions, aerosol optical depth (AOD) is expected to be small, and the influence of aerosols can mostly be removed from the radiance received by space borne measurements by separating the smooth part and higher frequency part with wavelength in the NO<sub>2</sub> SCD retrieval mentioned in the second section. But for high polluted conditions, aerosol AOD is often enhanced as well, and the aerosol's effect on the air mass factor may be significant (Chance, 2002). However, aerosol layers does influence the radiation field and the sensitivity of space borne instruments for near-surface NO<sub>2</sub>, aerosol also contributes uncertainty to NO<sub>2</sub> column retrieval from satellite measurements through AMF calculation. For instance, it is reported that aerosols reduce the AMF by up to 40% over the biomass burning regions, largely due to obscuration of the NO<sub>2</sub> column by black carbon (Randall *et al.*, 2003) and reduce the AMF by 10%—20% in dusty regions. By contrast, aerosols increase the AMF by 5%—10% over industrial regions (Randall *et al.*, 2003). Because of the big variation of aerosol and the lack of aerosol information directly retrieved from trace gases instruments, the aerosols' vertically resolved optical properties were used in the AMF calculation within the LIDORT model (Randall *et al.*, 2003); only a few different aerosol scenarios, e.g. maritime, rural and urban, have been taken into account in the retrieval. It was also reported in literatures (Chin *et al.*, 2000, 2002; Ginoux *et al.*, 2001) that the monthly mean fields of aerosol mass concentration from the Global Ozone Chemistry Aerosol Radiation and Transport (GOCART) model were chosen to be used.

### 4.4 Other factors

Other factors, for example the fitting window, NO<sub>2</sub> cross section spectrum, the temperature and surface albedo, all affect the NO<sub>2</sub> SCD inversion accuracies. The following presents the brief overview about these factors.

In the DOAS algorithm, the optimal wavelength window for the NO<sub>2</sub> detection accuracies must have high sensitivity to the NO<sub>2</sub> absorption signature and minimal sensitivity to geophysical and instrument-related spectral features. In the selection of the two fitting windows for OMI NO<sub>2</sub> tropospheric SCD, a compromise had to be found between an optimum in difference in the sensitivity towards the troposphere and good NO<sub>2</sub> detection accuracies, so the windows 345—359nm and 490—540nm were selected. Below 345nm, NO<sub>2</sub> retrieval is noisy and subject to interference by ozone absorption, while above 540nm water vapour absorptions interfere strongly with the NO<sub>2</sub> fit (Chance, 2002).

Secondly, the NO<sub>2</sub> cross section spectrum is an uncertainty. According to Vandaele *et al.* (1998), the accuracy of the NO<sub>2</sub> cross section is estimated to be 2%. since this 2% primarily represents offset errors, and the error in the NO<sub>2</sub> slant column density is estimated to be less than 2%. But due to temperature

dependency of NO<sub>2</sub> cross section spectrum, optimized fit window should be chosen for minimal temperature dependence. Now in fitting NO<sub>2</sub> to a reflectivity spectrum in OMI NO<sub>2</sub> product algorithm, a 220K effective temperature is assumed for NO<sub>2</sub>. It was also described that a 10K temperature perturbation in the fitting temperature would result in a slant column error <4 % in NO<sub>2</sub> slant column calculations (Chance, 2002).

Thirdly, the surface albedo directly influences the sensitivity of space borne instruments for boundary layer NO<sub>2</sub>. High quality albedo maps in the relevant spectral range are essential (Boersma *et al.*, 2004).

## 5 VALIDATION OF RETRIEVED NO<sub>2</sub> FROM SATELLITE

Now there are different tropospheric NO<sub>2</sub> retrieval algorithms for satellite measurements, but more extensive validations of the tropospheric NO<sub>2</sub> retrieval from satellite measurements are needed for different regions, seasons and meteorological conditions. Since the launching of the first space borne instrument GOME for trace gases monitoring, many campaigns have been carried out to validate the retrieved results. Firstly, the tropospheric NO<sub>2</sub> VCDs are proved to be reasonably well correlated with the near-surface measurements, which are performed by standard molybdenum converter instruments under cloud free conditions (Winer *et al.*, 1974). Their results showed that the slope of the tropospheric NO<sub>2</sub> VCDs versus ground measurements seems to be unreasonable in winter since the low mixing heights would be expected to possibly yield lower tropospheric columns versus ground measurements in comparison to summer. As a consequence, the NO<sub>2</sub> measurements from these instruments represent an upper limit for the real NO<sub>2</sub> concentrations (Grosjean & Harrison, 1985). Secondly, the ground based NO<sub>2</sub> column concentration measurements were used to validate the satellite retrievals. In fact, at the ground level, column NO<sub>2</sub> has a long history of ground-based measurements. Noxon(1975) published the first measurements and established the basic latitudinal and seasonal behavior of column NO<sub>2</sub>. Since that time, several stratospheric trace gases like NO<sub>2</sub>, BrO, and OClO have been monitored from the ground using the DOAS technique (Platt, 1994). A significant part of this monitoring effort was carried out through the framework of the Network for the Detection of Stratospheric Change (NDSC) started in January 1991, and the Network has been providing a long term measurements of trace gases for detecting atmospheric change and validating space-borne sensors (Hendrick *et al.*, 2006). The ground-based NO<sub>2</sub> measurements were used to validate the tropospheric NO<sub>2</sub> VCDs derived from GOME (Petrinoli *et al.*, 2004) in the Po basin, and tropospheric NO<sub>2</sub> VCDs for the period 1996—2002 were compared with near-surface measurements of NO<sub>2</sub> from 99 ground stations in the Lombardy region in northern Italy. Thirdly, the aircraft NO<sub>2</sub> profile measurements were used for the tropospheric NO<sub>2</sub> VCD validation. During a GOME overpass over Austria under

cloud-free conditions, the aircraft NO<sub>2</sub> profiles measured had been used to validate the tropospheric NO<sub>2</sub> VCDs from GOME (Heland *et al.*, 2002). Martin *et al.* (2004) also evaluated the tropospheric measurements of NO<sub>2</sub> from GOME, using in situ measurements over eastern Texas and the southeast United States from two aircraft campaigns carried out in summer. These studies reported good agreement with both GOME and in situ measurements of NO<sub>2</sub> under certain meteorological conditions.

In China, the long path active DOASs, made by Anhui Institute of Optical and Fine Mechanism in Chinese Academy of Sciences, was developed to monitor the ground level air quality in many cities by Chinese EPA (Liu, *et al.*, 2004). Recently, more than 10 sets of Max-DOAS have been produced to monitor tropospheric NO<sub>2</sub> VCDs in order to evaluate the air quality for Beijing Olympic Game. Multi-Axia DOAS (Max-DOAS) measurements, based upon the DOAS technique (Platt, 1994) provide a methodology to resolve spatial distributions of various trace gases using scattered light from the sun or other non-artificial sources.

## 6 THE DEVELOPING TRENDS OF NO<sub>2</sub> MONITORING FROM SPACE

Since the GOME instruments had shown its advantage in the applications for regional and global scale trace gases monitoring, the SCIAMACHY, OMI and GOME-2 satellite instruments were gradually launched into sky and provided large amount of data on global air quality and air pollution, including tropospheric NO<sub>2</sub> VCDs. These instruments can provide the NO<sub>2</sub> VCD distribution in global scale and have really given great impact to atmospheric chemistry research and some applications, just like the regional and seasonal emissions and distribution of tropospheric NO<sub>2</sub> variability. However, there are some aspects existed for further improvement.

### 6.1 The tropospheric NO<sub>2</sub> VCD retrieval algorithm

The DOAS method is widely used to retrieve the NO<sub>2</sub> concentration from the ground level long path DOAS measurements and space borne measurements, but tropospheric NO<sub>2</sub> VCD retrieval accuracies are influenced by many relative factors such as the removal of the aerosol and surface albedo scattering, the cloud effect, the Ring effect, the AMF calculation and stratospheric NO<sub>2</sub> concentration calculation. Among those factors, the cloud and AMF play big roles in the inversion method. Because it is difficult to separate the cloud free part even from the least spatial pixel of OMI instrument to improve the accuracies of retrieved tropospheric NO<sub>2</sub> VCD. So from this point, to improve the spatial resolution of the satellite sensor from recent fine scale of 13×24km<sup>2</sup> to 5×5km<sup>2</sup> even 1×1km<sup>2</sup> is the exigent requirement for the NO<sub>2</sub> VCD monitoring from satellite measurements. Secondly, it is necessary to pay more attention to the AMF calculation. Because the AMF values are

sensitive to many parameters such as the observing geometry, the NO<sub>2</sub> profiles, the surface albedo and the aerosol models, which are the important inputs for the tropospheric AMF calculated. For instance, the spring/summer aerosol models or the fall/winter models are not enough to calculate AMF. It is necessary to study the AMF uncertainties and sensitivities caused by the different parameters, and estimate their influences on retrieved tropospheric NO<sub>2</sub> VCD. So it is also essential to establish a systemic AMF look-up-table, which covers different kind of NO<sub>2</sub> profile distributions, aerosol models, surface albedos and the observing geometries, for regional or global scale tropospheric NO<sub>2</sub> VCD monitoring.

In addition, the first step of DOAS algorithm is the removal of the contribution from surface reflecting and aerosol scattering by a low order polynomial model. However, the different order of polynomial models will result in different level errors to the final NO<sub>2</sub> VCD. Accordingly, the influences on NO<sub>2</sub> VCD accuracies brought by different order polynomial models need further studies. Besides, a more accurate Ring effect correction is required for the retrieval of trace gas concentrations. Especially for the weaker absorbers, it is absolutely necessary that the Ring effect should be removed to ensure proper analysis of observed spectra.

### 6.2 To develop geostationary air quality satellite

Though the instruments such as GOME, SCIAMACHY, OMI and GOME-2 on polar orbits have provided the global scale of tropospheric NO<sub>2</sub> VCD distribution within one day or several days, they can not meet the high spatial and high frequent temporal requirements for emission inventory and the regional pollutant transport monitoring. We know the meteorological geostationary satellite such as the FY-2 and GOES (geostationary operational environmental satellites) in the orbit of 36,000 km height can provide one third area of the Earth surface within half an hour. From this point, the geostationary air quality satellite will also show its advantages for regional pollutants transport monitoring if the new specific instrument for geostationary platform would be successfully designed and produced in the near future. Now we begin to implement a project for the scientific demonstration on air quality instrument specific for geostationary satellite platform. We hope to discuss with other scientists about its advantages, disadvantages and concerned issues compared to the polar orbit air quality satellite instrument. There is a similar idea to develop geostationary air quality satellite reported by Japanese Akimoto in the Fourth DOAS International Workshop held in early April, 2008 in Hefei, Anhui province in China (Akimoto *et al.*, 2008).

### 6.3 The validation of NO<sub>2</sub> column density retrieved from space

Generally, NO<sub>2</sub> column density retrieved from space borne data needs validation. MAX-DOAS is an efficient approach to



derive some tracegases tropospheric concentration. Based on the combination of different viewing directions, MAX-DOAS uses the sunlight scattered in the zenith sky as the light source to derive column amounts of absorbers, like NO<sub>2</sub> and O<sub>3</sub>. MAX-DOAS instruments should be widely installed to develop a network suitably for the improvements in minimizing errors of NO<sub>2</sub> column density result retrieved from space borne data because of the large scale footprint of satellite image pixel. Even if the smallest OMI nadir pixel is large enough for any single ground based NO<sub>2</sub> concentration measurement, such as MAX-DOAS, it can not meet the scale of OMI image pixel.

Another method to validate the space-based NO<sub>2</sub> column density result comes from aircraft-based instruments. There are several advantages to develop air borne NO<sub>2</sub> column density measurement instrument. Firstly, other than ground based measurements, aircraft-based measurements principle and approach are the same as space-based measurements. Secondly, the air borne NO<sub>2</sub> measurements can provide large area measurements to meet the comparison with the big footprint of satellite sensor nadir viewing pixel. Thirdly, its flexible campaign can be used to monitor the urgent pollutants situation of chemical plant blast accident. Nevertheless, due to the higher temporal and spatial resolutions, air borne trace gas concentrations measurements are more accurate. Moreover, air borne measurements can provide 3-D trace gas distributions. To sum up, not only ground-based measurements but also aircraft-based measurements improvement is very helpful to space borne NO<sub>2</sub> concentration measurements validation.

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## 对流层 NO<sub>2</sub> 柱浓度卫星遥感反演综述

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**摘 要:** NO<sub>2</sub> 是主要的大气痕量气体, 对流层 NO<sub>2</sub> 垂直柱密度分布图已经用于诸如污染排放和污染物分布的科学应用研究。就 NO<sub>2</sub> 柱浓度的卫星差分光谱吸收反演算法(DOAS)进行了评述, 包括误差分析、验证和发展趋势。对 DOAS 算法中的主要技术环节进行了详细的阐述, 如 ring 效应算法、平流层 NO<sub>2</sub> 浓度算法和大气质量因子(AMF)问题。论文描述了影响卫星反演 NO<sub>2</sub> 浓度, 如云、NO<sub>2</sub> 廓线的先验数据和气溶胶等不确定性因素。针对 NO<sub>2</sub> 反演应用需求提出了今后应该加强的内容, 如进一步加强 NO<sub>2</sub> 算法研究、发展空气质量探测的静止卫星、重视基于地基多轴被动 DOAS 和机载平台成像 DAOS 观测对卫星反演结果的验证。

**关键词:** NO<sub>2</sub>, SCD, VCD, AMF, 对流层, DOAS