Quantitative analysis of NO\textsubscript{x} emissions from Global Ozone Monitoring Experiment satellite image sequences

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Abstract. Nitric oxides (NO\textsubscript{x}) play a very important role among the anthropogenic trace gases. They affect human health and have an impact on ozone chemistry and climatic change. Here we describe a new method for the quantification of the global NO\textsubscript{x} budget from image sequences of the Global Ozone Monitoring Experiment (GOME) spectrometer on board the ERS 2 satellite. In contrast to measurements using ground-based or balloon- or aircraft-borne sensors, this instrument provides, for the first time, the possibility of observing global maps of NO\textsubscript{2} column densities. As part of this work, algorithms were developed to analyze GOME spectra numerically and to extract physically relevant parameters from the resulting maps using image-processing techniques. Column densities of NO\textsubscript{x} were determined using differential optical absorption spectroscopy (DOAS) [Platt, 1994]. By the combined use of an efficient B-spline interpolation and an inversion algorithm based on Householder transformations, the numerical algorithms accelerate the retrievals by a factor of 26 with respect to previous methods. Moreover, techniques are presented for separating tropospheric and stratospheric NO\textsubscript{2} columns and estimating the lifetime of NO\textsubscript{2} in the troposphere. This allows determination of regional NO\textsubscript{x} source strengths. Independent of traditional methods, a global source strength of \((43 \pm 20)\) Tg N yr\textsuperscript{-1} is estimated. The accuracy of this method is comparable to that of established statistical approaches.

1. Introduction

Within the last 100 years the chemical composition of the atmosphere has changed significantly due to anthropogenic influences. Among the emitted trace gases, oxides of nitrogen (notably NO and NO\textsubscript{2}) play a central role. Their natural concentration in most parts of the troposphere is believed to be below 10-20 ppt (parts per trillion), whereas concentrations up to 200 ppb (parts per billion) can now be found in cities. While NO\textsubscript{2} is itself toxic, its particular importance lies in its influence on atmospheric ozone chemistry. NO\textsubscript{2} may be also of interest with regard to radiative heating of the atmosphere.

The main sources for tropospheric NO\textsubscript{x} (= NO + NO\textsubscript{2}) are production by industry and traffic, forest and bush fires (biomass burning [Crutzen and Schmailzl, 1983], [Hao et al., 1990]), microbiological emissions by soil [Granli and Bokman, 1994], exchange with the stratosphere, lightning and air traffic. It is estimated that more than two third of the total NO\textsubscript{x} emissions are anthropogenic, dominated by the burning of fossil fuels for transportation and industrial activities.

Current production estimates for anthropogenic sources are very uncertain (see Table 1), and this uncertainty is mainly due to shortcomings in measurement techniques used [Lee et al., 1997]. The available ground-based and balloon- and aircraft-borne instruments make only local measurements, from which it is very difficult to estimate the global distribution of the trace gases of interest. This deficiency can best be resolved by the use of space-borne monitoring devices.

2. Global Ozone Monitoring Experiment

In April 1995 the ERS 2 satellite was launched by the European Space Agency (ESA). The satellite carries, in addition to other instruments, the Global Ozone Monitoring Experiment (GOME), an instrument designed to measure trace gas concentrations in the atmosphere. It consists of four spectrometers of moderate resolution that cover the spectral range from 290 nm to 790 nm with 1024 channels each. Analyzing the spectrum of sunlight reflected by the Earth (earthshine) using the technique of differential optical absorption spectroscopy (DOAS), quantitative information about trace gases in the atmosphere (e.g., NO\textsubscript{2}, BrO, OC\textsubscript{10}, SO\textsubscript{2}, H\textsubscript{2}O, O\textsubscript{3}, O\textsubscript{4}) is obtained.

The GOME instrument monitors the Earth in nadir view (looking downward approximately perpendicular to the Earth's surface) and records a spectrum every 1.5 s. Using a scanning mirror, the instrument records three pixels perpendicular to the direction of flight and one "back scan" pixel at the end of the scan. The size of the "ground pixel", which is defined as the footprint on the ground, is normally 320 x 40 km (see Figure 1). Additionally, a polarization
Table 1. Global Sources of NO\textsubscript{x} From Lee et al. [1997]\textsuperscript{a}

<table>
<thead>
<tr>
<th>Source</th>
<th>Best Estimate\textsuperscript{b}</th>
<th>Uncertainty\textsuperscript{b} [DLR]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lightning</td>
<td>5</td>
<td>2 - 20</td>
</tr>
<tr>
<td>Air traffic</td>
<td>0.8</td>
<td>0.59 - 0.95</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>7.9</td>
<td>3 - 15</td>
</tr>
<tr>
<td>Industry and traffic</td>
<td>22</td>
<td>13 - 31</td>
</tr>
<tr>
<td>Emissions from soil</td>
<td>7</td>
<td>4 - 12</td>
</tr>
<tr>
<td>Stratospheric production</td>
<td>0.64</td>
<td>0.4 - 1</td>
</tr>
<tr>
<td>Total</td>
<td>44</td>
<td>23 - 80</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Anthropogenic influences have a strong impact on the global NO\textsubscript{x} budget. The total emissions as well as their spatial distribution still show large uncertainties.

\textsuperscript{b}All values are in units of Tg N yr\textsuperscript{-1}.

The satellite scans the Earth in consecutive orbits that are not spatially contiguous (in the equatorial area) but leave a gap the width of two orbits (Figure 1). After cycling the Earth for a single day (14 orbits) it has covered approximately one third of the surface and scans on the following days the remaining regions. Every 3 days, global coverage is obtained. Approximately 30,000 spectra must be evaluated each day.

3. Retrieval of Trace Gas Concentrations

The applied method consists of several analysis steps which will be presented sequentially in the following sections (Figure 2).

1. The starting point of the analysis is the scaling of raw spectral data of the GOME instrument into calibrated radiances (level 1 data, see Figure 2, step 1a) by the Deutsche Zentrum für Luft- und Raumfahrt (DLR). Also, the PMD data are used for further calculations (Figure 2, step 1b). To deal with the huge data rate (approximately 6 GB per month), an analysis algorithm has been developed which is able to perform the analysis on standard PC hardware at about 26 times the acquisition rate.

2. On the basis of these data, apparent NO\textsubscript{2} slant column densities, SCDs, (Figure 2, step 2a) can be calculated from the NO\textsubscript{2} spectral signature using the DOAS method [Platt et al., 1979; Platt, 1994; Stutz and Platt, 1996] (see section 3.1). The spectral retrieval is the basis for generating time sequences of global NO\textsubscript{2} maps. The PMD information is used to deduce information about clouds and the surface albedo (Figure 2, steps 2b and 2c).

3. A satellite-borne instrument measures trace gas concentrations integrated along a light path through the whole atmosphere, that is, through both the troposphere and the stratosphere. Since these paths are in general not standing vertically on the ground and also do not represent a single physical path (they include scattering), they should be called "apparent slant column densities". In order to obtain column density data independent of the viewing geometry, the apparent slant column densities are transformed into "vertical column densities" (Figure 2, step 3a) using a conversion factor. The figures show an analysis flowchart and an example composite image. The conversion factor, called the "Air Mass Factor" (AMF), is particularly dependent on the solar zenith angle (SZA), that is, the location of the satellite, the scan angle of the instrument, the surface albedo, the viewing geometry, and the cloud cover (see section 4.4, equation (1), and Figure 2, step 3b).

\[ \text{AMF} = \frac{\text{SCD}}{\text{VCD}}. \] (1)
4. However, for the analysis of anthropogenic influences only the tropospheric fraction is of interest. In section 4 an algorithm is presented that discriminates between these two fractions by applying an image-processing approach (Figure 2, steps 4a and 4b). Moreover, the calculation of the NO\textsubscript{2} budget requires further processing: In general, the Earth is partially covered with clouds that hide portions of the NO\textsubscript{2} column from the view of the satellite instrument. This is especially true for the tropospheric column which is of particular interest for the analysis of anthropogenic emissions. Leue [1999] and Leue et al. [1999] demonstrated a technique to correct for this effect in the temporal mean. Using this, a map of annual mean NO\textsubscript{2} data near a coast with constant wind conditions can be used to estimate the atmospheric lifetime of NO\textsubscript{2} (see Figure 2, step 4c, also see section 5, and Figure 5).

5. Finally, we derive estimates for the global emissions and emission rates of nitric oxides. With this method we introduce a new procedure which is completely independent of standard approaches to calculate the NO\textsubscript{2} budget (generally based on statistical data of fuel use and emission factors). It can thus be used to reduce the uncertainty in current estimates.

### 3.1. Concept of DOAS

When light passes through an absorbing layer (e.g., the atmosphere) it will be attenuated by matter due to absorption or scattering. Both effects are described by the Lambert-Beer law, which in this application is given by

\[
I(\lambda) = I_0(\lambda) e^{-\sum_i \sigma_i(\lambda)SCD_i} A(\lambda),
\]  

where \( I(\lambda) \) describes the measured intensity and \( I_0(\lambda) \) the extraterrestrial light intensity. The sum in the exponential runs over all trace gases \( i \) in the light path \( l \) whose slant column density \( SCD_i = \int c_i(l) dl \), with \( c_i \) being the concentration of the trace gas \( i \), has to be calculated. The absorption cross sections \( \sigma_i(\lambda) \) are well known from measurements in the laboratory, and they are characteristic for each trace gas. The factor \( A(\lambda) \) describes additional attenuation by the optical system and by Rayleigh and Mie scattering in the atmosphere. Thus far, equation (2) can be transformed into a linear system of equations with respect to \( SCD_i \) by taking the logarithm of both sides:

\[
\ln I(\lambda) = \ln I_0(\lambda) + \ln A(\lambda) - \sum_i \sigma_i(\lambda)SCD_i. \tag{3}
\]

The basic drawback of equation (3) is that neither the initial light intensity \( I_0(\lambda) \) nor the attenuation factor \( A(\lambda) \) are known exactly, making it impossible to solve for the desired \( SCD_i \). The essential fact that permits the calculation of \( SCD_i \) without this knowledge is that these quantities only contain low frequencies with respect to \( \lambda \) whereas the absorption cross sections \( \sigma_i(\lambda) \) contain both low-frequency (LF) and high-frequency (HF) components. They can thus be split into two contributions \( \sigma_i = \sigma_i^B + \sigma_i^H \), where \( \sigma_i^B \) and \( \sigma_i^H \) are the low- and high-frequency components, respectively [Stutz and Platt, 1996]. If all low-frequency proportions are modeled by a set of appropriate basis functions \( \xi_j(\lambda) \),

\[
\ln I_0(\lambda) + \ln A(\lambda) - \sum_i \sigma_i^B(\lambda)SCD_i = \sum_j a_j \xi_j(\lambda), \tag{4}
\]

equation (3) becomes

\[
\ln I(\lambda) = \sum_j a_j \xi_j(\lambda) - \sum_i \sigma_i^H(\lambda)SCD_i, \tag{5}
\]

which is linear in the unknown quantities \( a_j \) and \( SCD_i \) and can be solved by a linear least squares method. In equation (5) the first summation represents the LF component, and the second summation represents the HF component. This approach is called differential optical absorption spectroscopy (DOAS).

#### 3.2. Practical Application of DOAS

In practice equation (5) has to be modified because the wavelength mapping between the absorption cross sections \( \sigma(\lambda) \) and the light intensity measured by the satellite \( I(\lambda) \) is not known exactly or can change due to changes in the spectrometer response during an orbit. The wavelength mapping can be accounted for by introducing an additional polynomial in the argument of the absorption cross section \( \sigma'(\lambda) = \sigma'\left(\sum_k b_k \lambda^k\right) \). This step transforms equation (5) from a linear to a nonlinear optimization problem:

\[
\ln I(\lambda) = \sum_j a_j \xi_j(\lambda) - \sum_i \sigma_i^H(\sum_k b_k \lambda^k)SCD_i, \tag{6}
\]

We next concentrate on solving the nonlinear problem in equation (6) in a very fast way, in contrast to the standard approach which is not sufficiently fast to process the spectra in real time. The major difficulties are the large number of unknown parameters (typically about 10) and the fact that the absorption cross sections \( \sigma(\lambda) \) are only known at discrete points and have to be evaluated at intermediate grid points due to the dispersion relation (the function that relates a specific spectrometer channel to the wavelength of the light recorded by this channel). To accomplish this, we rely on the following:

1. The adaptation of an efficient fitting algorithm from Ottow and Vansteenkiste [1981], taking into account that some of the parameters in equation (5) are linear and only those describing the dispersion relation are nonlinear, and
2. the application of a fast interpolation algorithm from Unser et al. [1991] that combines both interpolation accuracy and speed.

#### 3.3. Nonlinear Fitting Algorithm

In order to minimize the number of fitting parameters in the nonlinear fit of equation (6) an algorithm initially presented by Ottow and Vansteenkiste [1981] has been adapted. The algorithm is optimized for problems in which linear and nonlinear parameters can be separated. For this purpose we rewrite equation (6) in matrix-vector notation...
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\[ \psi(\lambda) = \Theta(b, \lambda) \cdot a , \]  

with the vector of the logarithm of the measured intensities \( \psi = \ln(I(\lambda_0), \ldots, \ln(I(\lambda_{n-1}))^T \) at the \( n \) discrete wavelengths \( \lambda_i \), the matrix of the reference spectrum

\[ \Theta = \left( \xi_0 \ldots \xi_m, \sigma'_0(b) \ldots \sigma'_{i-1}(b) \right) , \]  

and the linear parameters

\[ a = \left( a_0 \ldots a_m, \text{SCD}_0 \ldots \text{SCD}_{i-1} \right)^T . \]  

The direct approach attempts to solve equation (7) for the unknown parameters \( a \) and \( b \) by minimizing

\[ |\psi - \Theta(b) \cdot a|^2 , \]  

iterating both on \( a \) and \( b \). Ottoy and Vansteenkiste [1981] show that equation (10) can be solved alternatively by first solving the equation for the linear parameters \( a \) under the assumption that \( b \) are constant, giving

\[ a = \left( \Theta^T \Theta \right)^{-1} \Theta^T \psi , \]  

which is a chi-squared minimization assuming similar errors for all values (covariance matrix a multiple of \( \mathbb{I} \)). Substituting \( a \) in equation (10) and minimizing the resulting equation,

\[ |\psi - \Theta \left( \Theta^T \Theta \right)^{-1} \Theta^T \psi|^2 , \]  

is then equivalent to the original minimization problem, yielding the advantage that the linear parameters are fitted implicitly and iteration has only to be done on the remaining nonlinear parameters \( b \). This produces an effective reduction of fitting parameters by 30\%, resulting in faster convergence and less computational effort for each fitting step compared with the direct method.

Following the rules of Gaussian error propagation, the error of this calculation is

\[ \sigma^2(a_j) = \sum_i \sigma_i^2 \left( \frac{\partial a_j}{\partial \psi_i} \right)^2 , \]  

which can be seen by some simple calculations. These numerical errors were compared to an additional estimation of the fitting error. This estimation uses the highpass-filtered curve of the NO\textsubscript{2} SCDs along an orbit assuming that this noise is due to the known errors of the spectral data and the fitting error. Both estimates of the error term are in agreement, so the numerical error is used for further error propagation. The resulting errors are about 4.3\%. The fitting parameters for the NO\textsubscript{2} DOAS algorithm used in this work were taken from Wagner [1999]. The spectral range between 430 nm and 450 nm was selected, and the reference spectra were taken from Burrows et al. [1998] and Rothman [1992].

### 3.4. B Spline Interpolation

During the fitting process it is necessary to evaluate the absorption cross sections \( \sigma(\lambda) \) at arbitrary wavelengths \( \lambda \) due to the unknown dispersion relation in equation (6). As the absorption cross sections are only known at discretely sampled spectral positions, we require an interpolation algorithm.

The most suitable interpolation algorithm is the B spline interpolation. B splines of order \( n \), \( \beta_n(\lambda) \), are piecewise continuous polynomial functions that form a base for all piecewise continuous polynomial functions. The signal can thus be decomposed in B splines and so can be evaluated at arbitrary wavelengths

\[ \sigma'(\lambda) = \sum_{i=-\infty}^{\infty} c_i \beta^n(\lambda) . \]  

Unser et al. [1991] showed that the decomposition can be done very efficiently using a recursive filter scheme and also described an algorithm that calculates the evaluation at intermediate grid points with only four additions and four multiplications for B splines of order 3. As an additional advantage, once the decomposition has been performed, the derivatives of the signal with respect to \( \lambda \) (which are required during the fitting algorithm) can be computed directly using the coefficient determined in the spline process \( c_i \) [see Jähne, 1999].

### 3.5. Comparison to Previous Approaches

In order to estimate the impact of the methods described in sections 3.3 and 3.4, we compare the new algorithm to our standard analysis software MFC [Gomer et al., 1996]. The comparison includes the evaluation of NO\textsubscript{2} data for one 600 MB CD-ROM of GOME data. This showed that the new algorithm is approximately 26 times faster than the standard approach, mainly because of the use of the efficient interpolation algorithm described in section 3.4 and the reduction of the fitting parameters described in section 3.3.

### 4. Separation of Stratosphere and Troposphere

The next step in the analysis is the separation of the stratospheric and the tropospheric contributions to the total NO\textsubscript{2} column as we are only interested in the tropospheric NO\textsubscript{2} emissions. These emissions occur mostly near the ground and largely determine the tropospheric NO\textsubscript{2} column. Often the high concentrations near the ground are hidden by clouds. In this case the measured columns can be dominated by the stratospheric contributions. In the following, for simplicity, we use the terms tropospheric and stratospheric column meaning the column below and above the cloud layer, respectively. The separation step will be executed with an image-processing approach on 3-day composite NO\textsubscript{2} vertical column density images considering the following assumptions of the spatial distribution of stratospheric NO\textsubscript{2}.

#### 4.1. Discrimination Criteria

Plate 1 shows a typical distribution of the vertical column density (VCD) of NO\textsubscript{2} for September 15, 1998. On this map the basic assumptions used to discriminate between tropospheric and stratospheric NO\textsubscript{2} are as follows:
1. The total column varies on a much larger spatial scale than the tropospheric fraction, due to the longer lifetime of nitric oxides in the stratosphere and the fast horizontal mixing there. The tropospheric emissions usually take place on a scale of only several hundred kilometers as they are mainly caused by rather localized emissions from industrial sources, or biomass burning events. This can be observed very well over European and North American regions in Plate 1, as well as, for example, in South Africa near Johannesburg.

2. It can be observed that the stratospheric distribution is less variable in the longitudinal direction than in the latitudinal direction, where it is apparent that a distinct latitudinal pattern is established. This is mainly due to the wind system in the stratosphere which flows from east to west. The anisotropy is amplified by the latitudinal dependency of the solar radiation which causes high stratospheric NO2 concentrations in the summer hemisphere. The diurnal variation of stratospheric NO2 does not affect the GOME observations because the GOME overpass appears always at the same local time (about 1030) for a given latitude.

3. More than 90% of the tropospheric NO2 is produced by industrial emissions, biomass burning events, and emissions from the soil (see Table 1). Practically all emissions occur over land masses, with the remaining 10% produced over the oceans from aircraft plumes and lightning. It is therefore expected that the observed NO2 columns over the oceans will be dominated by the stratospheric component, because the tropospheric column can be neglected there (see Plate 2). Typical stratospheric NO2 VCDs over the oceans around noon range from $2 \times 10^{15}$ to $6 \times 10^{15}$ cm$^{-2}$ (see, for example, Senne et al. [1996]), whereas typical tropospheric VCDs are about 1 order of magnitude smaller (see, for example, Torres and Thompson [1993]). This is due to the short lifetime of NO2 in the troposphere of approximately 1 day (see below), which leads to a rapid decay of the nitric oxides in the absence of emission sources.

4. As described by Wenig et al. [1999], clouds hide the portion of the NO2 column that lies below the cloudy layer (in the troposphere) from the view of GOME. Therefore the NO2 column observed over cloudy regions will be dominated by the stratospheric contribution. Taking into consideration typical values of the stratospheric and tropospheric NO2 VCDs over the ocean (see above), we find that the relative contribution of the tropospheric VCD to the total NO2 signal is of the order of only a few percent. Therefore cloudy pixels located over the sea should represent the stratospheric NO2 column in that region. Our approach might overestimate the stratospheric NO2 VCD by about a few percent. However, compared to the large contributions of tropospheric NO2 to the total atmospheric NO2 VCD over the continents, this effect is negligible.

These considerations will now be exploited in order to estimate the total stratospheric NO2 column. The method consists of two major steps: First, maps of the total vertical NO2 column density are generated, and the pixels of interest (i.e., cloudy pixels over the sea) are taken. Second, the emerging gaps are interpolated using an image-processing filter that considers the frequency of the spatial distribution in the stratosphere (i.e., the filter mask mainly expands in the latitudinal direction).

4.2. Estimation of the Stratospheric Background

The observation described in section 4.1 can be exploited to estimate the stratospheric background following an image-processing approach. First, land regions are masked out to avoid errors in the stratospheric signal due to tropospheric contributions. To avoid influences from emissions near coastlines a region of approximately 200 km offshore is disregarded as well. Using a threshold we segment pixels with a cloud fraction of at least 50% and mask out the cloud-free pixels. On the remaining pixels the stratospheric proportion of the total column will dominate. The cloud fraction of the GOME pixels is detected using the cloud detection algorithm introduced by Wenig [1998], which uses the data of the three PMD channels to deduce the fractional cloud cover for each GOME pixel. Using a threshold we segment pixels with a cloud fraction of at least 50% and apply the resulting mask on the trace gas map. This procedure yields an image of NO2 column densities with pixels that very likely represent the stratospheric NO2 column but contain large gaps due to the masking process.

These gaps have to be interpolated in order to estimate the total stratosphere. To provide boundary conditions we have to account for the different structure of the stratospheric distributions in latitudinal and longitudinal directions discussed in section 4.1. An interpolation algorithm has to be chosen which does not simply calculate the interpolated value for every pixel but also slightly takes into account the average over the neighboring region, for the values do not exactly represent the stratosphere but contain noise and also remnants of the tropospheric NO2 column.

We use for this purpose the concept of "normalized convolution" by Knutsson and Westin [1993]. If G denotes the original image, where $G(x, y)$ is the NO2 concentration, M the mask for each pixel in the interval $[0, 1]$, which is given by $1/a_2^2$ and is 0 for the gaps, then the interpolated image $G'$ is given by:

$$G' = \frac{B(G \cdot M)}{B(M)}$$

where "\cdot" denotes the multiplication for each pixel separately. The low-pass filter operator $B$ can be of different size in any coordinate direction.

The advantage of this filter type lies in its efficiency and the fact that it combines interpolation and averaging. The resulting numerical errors are dependent on the size of the gaps and are typically between 3.0% and 20.0%, the resulting stratospheric NO2 VCDs range from $1 \times 10^{15}$ to $4 \times 10^{15}$ cm$^{-2}$ (see Plate 2).

4.3. Tropospheric Column

The result of the interpolation is now operationally defined as the stratospheric background of the total NO2 column. An example can be seen in Plate 2, which also illustrates the intermediate steps in the discrimination algorithm. The image shows that the background could be estimated...
very well and is smoothly interpolated over the land regions which had been masked out for the calculation of the latitudinal sections.

The tropospheric contribution can now be estimated by forming the difference between the original image and the estimated stratosphere. In the resulting image Plate 2c we see that localized emission sources appear pronounced, whereas the global stratospheric trend is almost completely suppressed. Moreover, it emerges that the NO2 column over land is systematically higher than that over the oceans, which confirms our assumptions that the main sources are over land.

4.4. Significance of the Ground Albedo

Although the tropospheric residual calculated in section 4.3 qualitatively represents the overall distribution of the tropospheric column density of NO2, it does not provide quantitative values. This is because the air mass factor depends not only on the solar zenith angle and scan angle, but also on several further atmospheric parameters including the trace gas vertical profile and ground albedo. The error of the air mass factor (AMF) has been analyzed with Monte Carlo simulations [see Marquard et al., 2000]. Because of the strong solar zenith angle dependence, the assumption for the Gaussian error propagation is not fulfilled. Assuming an error of 1 degree for the solar zenith angle, 50% for the profile height, and 25% for the ground albedo leads to uncertainties between 3% and 10%. The albedo error has been calculated by comparing albedo maps (see Wenig [1998] and Leue [1999]) from different months to the albedo data from Li and Garand [1994].

For profile heights corresponding to a stratospheric distribution, the dependency of the AMF on the ground albedo is very weak, so we neglected it when estimating the stratospheric background. The remaining residual, however, strongly depends on the albedo and has to be corrected according to its influence. The procedure for this correction is illustrated in Plate 3. Before applying the correct tropospheric air mass factor AMFtrop, we have to remove the influence of the previously applied stratospheric air mass factor AMFstrat. So the correct transformation is given by

\[
\text{VCD}_{\text{trop}} = \left( \text{VCD}_{\text{meas}} - \text{VCD}_{\text{strat}} \right) \times \frac{\text{AMF}_{\text{strat}}}{\text{AMF}_{\text{trop}}}. \tag{16}
\]

Because the input parameters for the calculation of AMFtrop (i.e., solar zenith angle and ground albedo) strongly depend on space and time (season) we use correction maps (see Plate 3) to transform the tropospheric columns into quantitative values. From Plate 3c it can be seen that the largest correction factors appear in regions with weak reflectivity and are as large as 2.5. This is especially true for oceanic regions where the tropospheric residual is near zero. Typical correction factors for land range from 1.5 to 2.0 with a typical ground albedo of between 0.05 and 0.15. Only over areas with high albedo, for example over deserts, can the correction factor be close to unity. It should be noted here that most recently indications were found that the ground albedo in the blue spectral range over land might be systematically smaller than applied here (A. Richter and J. Burrows, Retrieval of tropospheric NO2 from GOME measurements, submitted to Advances in Space Research, 2000). For such smaller values the corresponding tropospheric NO2 VCDs would be systematically larger. Plate 3e shows the quantitatively correct map of the tropospheric NO2 distribution. After all corrections have been applied, it can be seen that areas of high emission appear more pronounced and have better contrast. In regions with large emissions of tropospheric NO2, columns of up to 3.0 \times 10^{15} \text{cm}^{-2} are seen. The errors are between 25% (for Europe) and 50% (for the Commonwealth of Independent States). These differences are due to the normalized convolution which produces higher errors for pixels lying in the middle of larger gaps (see [Leue, 1999]).

5. Estimation of the Mean NO2 Lifetime

For the determination of the mean NO2 source strength from the tropospheric maps, knowledge of the NO2 lifetime \( \tau \) is necessary. In this section it will be estimated from the decay curve of NO2 on the off-wind side of coasts with strong tropospheric emissions.

On the image of the annual mean tropospheric NO2 residual shown in Plate 4 high NO2 columns over the ocean in the downwind direction from the coast can be seen, whereas off coasts with opposite wind directions no such features can be found. This behavior is due to the chemical decay of NO2 over the ocean where there is no emission (see Plate 5). From this decay curve we estimate the mean NO2 lifetime from a case study in North America.

The basic assumption underlying the method is that in the annual mean the wind speed \( u \) and the lifetime \( \tau \) can be substituted by their mean values and that the chemical decay can be described by a linear model (first-order decay). In this approach the spread of the plume by (turbulent) diffusion does not have to be taken into account because in the vertical case it is invisible to GOME, which only measures the integrated concentrations (vertical columns). Additionally, lateral diffusion does not play a role if we can assume a similar NO2 distribution in the neighborhood of the measured case owing to the conservation of mass.

The decay curve of NO2 then shows a static behavior and can be expressed by the following equation (taking the mean air movement as \( x \) direction)

\[
\frac{dc}{dt} \equiv 0 = u_x \frac{\partial c}{\partial x} + \frac{1}{\tau} c, \tag{17}
\]

where \( c \) denotes the NO2 concentration and \( u \) the wind velocity. From integration it follows directly that:

\[
c(x) = c_0 \exp \left( -\frac{x}{u_x \tau} \right). \tag{18}
\]

The mean NO2 lifetime \( \tau \) over 1 year can thus be calculated by the determination of the 1/e length of the decay curve. From a nonlinear fit (see Plate 5) the 1/e length is found to be \( x_e = 670 \pm 75 \text{ km} \). This fit has been done for each
row of pixels of the marked area (see Plate 5), and the variation of the results has been used to determine the uncertainty for $x_e$. Information on the wind vector field with a temporal resolution of 6 hours was taken from the NILU database (ftp://zardoz.nilu.no). The annual mean wind speed in the $x$ direction for 1997 was found by calculating the average over these data to be $u_x = 6.8 \pm 0.5 \text{ m s}^{-1}$ for the lower troposphere.

From this information we calculate a resulting lifetime $\tau = 27 \pm 3 \text{ hours}$ which agrees well with values of approximately 1 day found in the literature.

6. Correction for the NO Fraction of NO$_x$

Using the image derived of the annual mean tropospheric NO$_2$ vertical column density (VCD) and an estimate of the mean NO$_2$ lifetime, we can attempt an estimate of the global NO$_x$ budget. However, to do this we need to derive quantitative values of the NO$_2$ vertical column densities from the NO$_2$ VCDs.

To obtain these, we note that NO$_2$, as measured by GOME, is in a photochemical-stationary state with NO. The ratio (known as the Leighton ratio) is given by

$$L = \frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k[\text{O}_3]}{J(\text{NO}_2)} ,$$  

(19)

with the ozone concentration $[\text{O}_3]$, the NO$_2$ photolysis frequency $J(\text{NO}_2)$ and the rate coefficient of the reaction of $\text{O}_3 + \text{NO}_2$, $k = 1.7 \times 10^{-12} \exp(-1310/T) \text{cm}^3 \text{s}^{-1}$ [see Atkinson et al., 1997]. These parameters were estimated assuming typical conditions near ground level:

$$T = 270 \pm 20 \text{ K} ,$$

$$\Rightarrow k = (1.33 \pm 0.48) \times 10^{-14} \text{cm}^3 \text{s}^{-1} ,$$

and $[\text{O}_3] = (1.25 \pm 0.5) \times 10^{12} \text{ cm}^{-3} .$

The photolysis frequencies (see Table 2) were calculated with a program from Ruggaber and Dlugi [1994], which requires as input the ground albedo, solar zenith angle, and a vertical NO$_2$ profile. For this calculation a typical tropospheric NO$_2$ profile was used. With these data, wavelength and albedo-dependent correction factors are calculated:

$$f_{\text{NO}_2} = \frac{[\text{NO}] + [\text{NO}_2]}{[\text{NO}_2]} = \frac{J(\text{NO}_2)}{k \cdot [\text{O}_3]} + 1 ,$$

(20)

Table 2. Photolysis Frequencies $J(\text{NO}_2)$ for Different Albedos and Solar Zenith Angles and a Profile Height of 1.5 km, Calculated With a Program From Ruggaber and Dlugi [1994]$^a$

<table>
<thead>
<tr>
<th>Albedo</th>
<th>SZA 40°</th>
<th>SZA 50°</th>
<th>SZA 60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>8.7</td>
<td>7.9</td>
<td>6.7</td>
</tr>
<tr>
<td>10%</td>
<td>9.2</td>
<td>8.3</td>
<td>6.9</td>
</tr>
<tr>
<td>15%</td>
<td>9.7</td>
<td>8.7</td>
<td>7.1</td>
</tr>
<tr>
<td>20%</td>
<td>10.2</td>
<td>9.7</td>
<td>7.4</td>
</tr>
</tbody>
</table>

$^a$Data are in units of $10^{-3}$ s$^{-1}$

which is, for example, for an albedo of 20% and a SZA of $40^\circ$: $f_{\text{NO}_2} = 1.61 \pm 0.34$.

7. Cloud Correction

Pixels observed by GOME are nearly never cloud-free, rather they are (at least partially) covered with clouds with a probability of above 99.8%, [see Kurosu, 1997], which partially hide the observed NO$_2$ column. We assume that in the annual mean clouds have a shielding effect, so with increasing cloud cover the average NO$_2$ VCD should decrease. We plotted the average tropospheric NO$_2$ VCD versus the cloud cover (CC) in order to investigate the magnitude of the shielding effect. Compared to the clear sky GOME pixel the NO$_2$ decreases with increasing CC as expected. On average, we derive a cloud correction factor close to the factor of 4.0 calculated by G. Velders et al. (Global tropospheric NO$_2$ column distributions: Comparing 3-D model calculations with GOME measurements, submitted to Journal of Geophysical Research, 2000). This factor was used to correct for the shielding effect of clouds.

8. Estimation of the Mean NO$_2$ Source Strength

The estimation of the source strength (production rate) $\lambda$ can now be done from the data of the annual mean image of the tropospheric NO$_2$ residual considering the correction factor mentioned above. Assuming that the production rate is constant over the year, as well as the lifetime $\tau$, the temporal development of the NO$_2$ concentration is then described by

$$\frac{dc}{dt} = \lambda - \frac{1}{\tau} c ,$$

(21)

$$\Rightarrow c_T = \frac{1}{T} \int_0^T c(t) dt ,$$

(22)
Plate 1. Three-day composite image of the vertical column density of NO$_2$ for September 14-16, 1998.

Plate 2. Visualization of the discrimination algorithm described in section 4.2. Starting with map (Plate 2a), we mask out land masses and cloud-free pixels and estimate the stratosphere (Plate 2b) using normalized convolution. The tropospheric residual (Plate 2c) can then be estimated by calculating the difference between Plates 2a and 2b. It shows pronounced maxima in industrialized regions (please note the different scales of the maps).
Plate 3. Illustration of the correction process for the tropospheric residual with the tropospheric air mass factor. The correction factor (Plate 3c) is calculated from the SZA (Plate 3a) and the ground albedo (Plate 3b) which we estimate directly from the GOME PMD data. Applying Plate 3c to the original tropospheric residual (Plate 3d) we gain the corrected tropospheric NO$_2$ column in Plate 3e.

Plate 4. Mean tropospheric residual of the NO$_2$ vertical column density for the year 1997. The map shows a clear correlation between emission peaks and industrialized regions.
Plate 5. Example for the decay curve along a latitudinal section through an NO$_2$ plume at the eastern shore of the United States. The $1/e$ distance of the curve can be calculated using a nonlinear regression with an exponential function. Combined with the average wind speed ($6.0 \pm 0.5$ m/s) an average NO$_2$ lifetime of $27 \pm 3$ hours is derived.

Plate 6. Estimate of the mean NO$_x$ burden (in $10^9$ g nitrogen) and emission (in $10^{12}$ g nitrogen per year and in kg N km$^{-2}$ y$^{-1}$) for 1997 for different parts of the world.
Table 4. Overview of the Errors of the Different Evaluation Steps

<table>
<thead>
<tr>
<th>Evaluation Step</th>
<th>Type of Data</th>
<th>Relative Error</th>
<th>Typical Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOAS fit</td>
<td>NO$_2$ SCD</td>
<td>2 - 5%</td>
<td>4.5 - 60.0$^b$</td>
</tr>
<tr>
<td>Conversion of SCD to VCD</td>
<td>AMF</td>
<td>3 - 10%</td>
<td>1.0 - 10.0</td>
</tr>
<tr>
<td>Interpolation from ocean to land</td>
<td>NO$_2$ VCD</td>
<td>3 - 20%</td>
<td>0.5 - 5.5$^b$</td>
</tr>
<tr>
<td>Tropospheric estimation</td>
<td>trop. frac. of VCD</td>
<td>25 - 50%</td>
<td>0 - 3.0$^b$</td>
</tr>
<tr>
<td>NO$_x$ correction</td>
<td>factor</td>
<td>10 - 25%</td>
<td>1.0 - 2.0</td>
</tr>
<tr>
<td>Cloud correction</td>
<td>factor</td>
<td>10 - 25%</td>
<td>4.0</td>
</tr>
<tr>
<td>Analysis of NO$_2$ decay in coastal regions</td>
<td>NO$_2$ VCD</td>
<td>10%</td>
<td>27 ± 3 hours</td>
</tr>
<tr>
<td>Estimation of source strengths</td>
<td>emission rate maps</td>
<td>30 - 50%</td>
<td>43 Tg N yr$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$The DOAS error is the numerical error of the fitting process (see section 3.1). The interpolation error of the normalized convolution step is dependent on the size of the gap which has to be closed for the estimate of the stratosphere (see section 4.2). The tropospheric estimation is described in section 4.3 and has to be corrected by several factors like the NO$_x$ correction factor and the cloud correction factor (see section 6). The calculation of the NO$_2$ lifetime is described in section 5. The shown emission rate is the global source strength for the year 1997.

$^b$These values are in units of $10^{15}$ molecules NO$_2$ cm$^{-2}$.

\[
\frac{c_T}{\lambda} = \frac{\lambda T}{e^{\frac{\lambda}{T}} + e^{\frac{\lambda}{T} \left(e^{\frac{-\lambda}{T}} - 1\right)}}
\]

with the mean concentration $c_T$ for the time period $T$. By comparison with the measured values $c_T$ (see Figure 4) and the lifetime $\tau$ from section 5 we can now estimate the global NO$_2$ budget and the mean production rate $\lambda$ over one year.

Results of the determination of the global source strength and NO$_2$ emission budgets are presented in Plate 6. It shows that the global emission strength is as large as $(43 \pm 20)$ Tg N yr$^{-1}$, which is in good agreement with values found in the literature (see section 9 and Table 3). Although the absolute values have uncertainties of approximately a factor of 2 (see error analysis in Table 4), they clearly identify the regions emitting the most NO$_2$. Emission by geographic region is shown in Plate 7 and it can be seen that Africa, although it is a sparsely industrialized region, has the highest NO$_2$ emissions, presumably due to biomass burning. However, by looking at the relative emission rate per unit area values shown in Plate 8, it can be seen that the higher emission densities occur in the more industrialized countries.

9. Conclusions

Our new method to discriminate the tropospheric and stratospheric NO$_2$ contribution to the vertical NO$_2$ column measured by the GOME satellite instrument uses only intrinsic image information and can thus be applied self-consistently to each global NO$_2$ map of an image sequence (see section 4). From the tropospheric NO$_2$ images, information about the mean NO$_2$ lifetime can be obtained by an-
alyzing its decay behavior in coastal regions (see section 5). The estimated lifetime of 27±3 hours corresponds very well to values found in the literature of about 1 day. This leads to a first estimation of the mean NOx budget for the year 1997, and the calculations also will be done for the following years. Though the errors are relatively high, this method is a good alternative to traditional ground-based measurements.

We realize that in each of the evaluation steps described above substantial improvements are possible and necessary. While work is under way in our institution to make these improvements, this paper is focused on presenting preliminary results which, nevertheless, clearly demonstrate the power of this new technology, and making them available to the scientific community. Examples where uncertainties and systematic errors can be significantly reduced include better characterization of the effect of clouds and aerosol on the tropospheric NOx column seen by GOME. Also the estimate of the NOx lifetime can clearly be improved beyond our simple assumption of a global average value.

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