

Measurements of O₃, NO₂ and BrO during the INDOEX campaign using ground based DOAS and GOME satellite data

A. Ladstätter-Weissenmayer, H. Altmeyer, M. Bruns, A. Richter, A. Rozanov, V. Rozanov, F. Wittrock, and J. P. Burrows

Institute of Environmental Physics, University of Bremen, P.O. Box 330440, D-28334 Bremen, Germany

Received: 24 July 2006 – Published in Atmos. Chem. Phys. Discuss.: 26 September 2006

Revised: 13 December 2006 – Accepted: 20 December 2006 – Published: 18 January 2007

Abstract. The INDIan Ocean EXperiment (INDOEX) was an international, multi-platform field campaign to measure long-range transport of air masses from South and South-East-(SE) Asia towards the Indian Ocean. During the dry monsoon season between January and March 1999, local measurements were carried out from ground based platforms and were compared with satellite based data. The objective of this study was to characterise stratospheric and tropospheric trace gas amounts in the equatorial region, and to investigate the impact of air pollution at this remote site. For the characterisation of the chemical composition of the outflow from the S-SE-Asian region, we performed ground based dual-axis-DOAS (Differential Optical Absorption Spectroscopy) measurements at the KCO (Kaashidhoo Climate Observatory) in the Maldives (5.0° N, 73.5° E). The measurements were conducted using two different observation modes (off-axis and zenith-sky). This technique allows the separation of the tropospheric and stratospheric columns for different trace gases like O₃ and NO₂. These dual-axis DOAS data were compared with O₃-sonde measurements performed at KCO and satellite based GOME (Global Ozone Measuring Experiment) data during the intensive measuring phase of the INDOEX campaign in February and March 1999. From GOME observations, tropospheric and stratospheric columns for O₃ and NO₂ were retrieved. In addition, the analysis of the O₃-sonde measurements allowed the determination of the tropospheric O₃ amount. The comparison shows that the results of all three measurement systems agree within their error limits. During the INDOEX campaign, mainly background conditions were observed, but in a single case an increase of tropospheric NO₂ during a short pollution event was observed from the ground and the impact on the vertical columns was calculated. GOME measurements showed evidence for small tropospheric contributions

to the BrO budget, probably located in the free troposphere and present over long periods of the year. The amounts of BrO have been investigated by the comparison of satellite pixels influenced by high and low cloud conditions based on GOME data which allows the determination of the detection limit of 3.8×10^{13} molecules cm⁻² of tropospheric BrO columns.

1 Introduction

The INDOEX project was an international scientific experiment with the main objective to study natural and anthropogenic climate forcing by aerosols and feedbacks on regional and global climate (Ramanathan et al., 2001). INDOEX field studies were carried out over the tropical Indian Ocean, which provides a unique natural laboratory for aerosol studies at the crossing point of pristine air masses from the southern Indian Ocean including Antarctica and rather polluted air masses from the Indian subcontinent. Regional consequences of global warming likely depend on the potentially large cooling effect of aerosols. Therefore, during the intensive field campaign of INDOEX, data were collected from airborne, ship-borne, ground - and satellite based instruments to analyse aerosol composition, atmospheric trace gases, and the long range transport of air pollution from SE Asia towards the Indian Ocean during the dry monsoon (Lelievre et al., 2001). The KCO, established by the Maldives government and the Scripps Institution of Oceanography is located in the tropics (5.0° N, 73.5° E). The KCO played a central role in the INDOEX campaign (Ramanathan et al., 2001). At KCO measurements with O₃-sondes and in-situ measurements of O₃, carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), CFCs, other chlorinated gases, nitrous oxide (N₂O) and sulfur hexafluoride (SF₆) were carried out alongside meteorological measurements of wind speed and direction, dry air temperature,

Correspondence to: A. Ladstätter-Weissenmayer
(lad@iup.physik.uni-bremen.de)

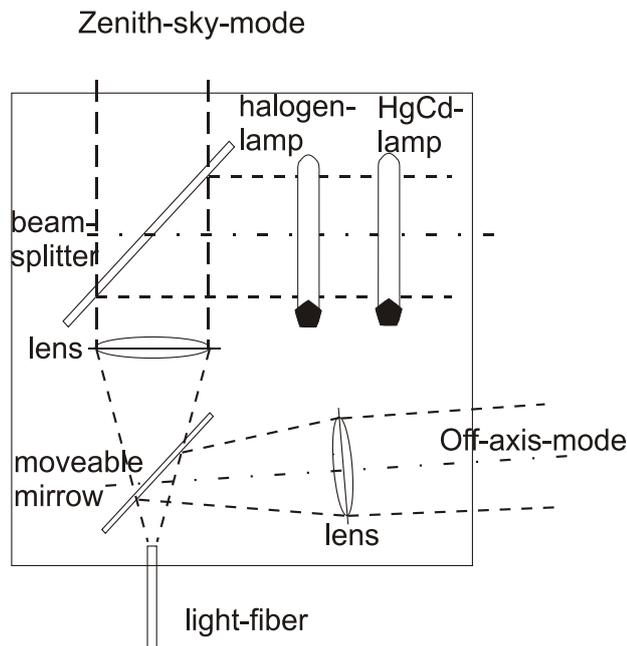


Fig. 1. Experimental setup of the DOAS telescope used in Kaashidhoo from 14 February to 16 March 1999 during the INDOEX campaign.

relative humidity, atmospheric pressure and rain amount during the intensive INDOEX campaign. During INDOEX, the Institute of Environmental Physics and Remote Sensing of the University of Bremen, Germany, performed remote sensing measurements using the technique of dual-axis-DOAS (off-axis and zenith-sky mode) at KCO. This instrument was a precursor of the multi-axis DOAS instrument described in (Wittrock et al., 2004) and (Heckel et al., 2005). Similar set-ups have been developed by other groups (Hoenninger et al., 2004), (Roozendaal et al., 2003). Simultaneous measurements of zenith-sky and off-axis scattered sunlight allow to distinguish stratospheric and tropospheric amounts of atmospheric gases. In this case the total and tropospheric column amounts of ozone (O₃), nitrogen dioxide (NO₂), as well as tropospheric amounts of BrO above KCO have been investigated. The results of our O₃ and NO₂ measurements were to be compared with those from GOME (Global Ozone Monitoring Experiment) (Burrows et al., 1999). The subject of this contribution is the validation of remotely sensed GOME data with ground based and O₃-sonde measurements above the Indian Ocean during INDOEX and also the synergistic use of all these measurements to exploit the advantages of the different methods (such as their different spatial and temporal resolution) to allow the best possible interpretation.

2 Experimental Set-up

2.1 Ground based DOAS measurements

During the intensive INDOEX campaign, DOAS measurements were carried out at KCO using two selected viewing geometries (dual technique: zenith and off-axis) (see Fig. 1). The dual-axis-DOAS-instrument is comprised off a Czerny Turner spectrometer (ARC 500, Acton Research Coporation) and a custom made telescope. High temporal resolution was achieved by switching between zenith-sky and 2° above the horizon direction within a short time interval (typically a few minutes). We can therefore assume essentially no change in the vertical column amount between the two recordings. For the observations at the elevation angle of 2°(angle between the horizontal direction and the viewing direction of the telescope) the light path through the boundary layer is extended and therefore the sensitivity to the lower atmosphere enhanced compared to the observation of zenith scattered sunlight (90°), which has a comparatively short path through the troposphere. These measurements were carried out each day between sunrise (average over the morning measurements = a.m.-value) and sunset (average over the evening measurements = p.m.-value) in the wavelength region of 327–492 nm with a spectral resolution of 0.5 nm. For this study, spectra in the wavelength region of 435–481 nm were analysed applying the DOAS technique (Platt, 1994), (Wittrock et al., 2004), (Heckel et al., 2005) to obtain the differential slant column (DSC). The DSC is the difference between the column amount of the absorber integrated along the light path through the atmosphere at the time of measurement (SC) and the absorber amount in the background spectrum (SC₀). For the background spectrum, a zenith measurement at high sun taken on the same day was used for both zenith-sky and off-axis observations. The absorber amount in the background spectrum (SC₀) is derived by assuming the mean value of the a.m. and the p.m. values for the vertical columns. A fifth order polynomial was fitted to the spectrum and absorptions by O₃ (Burrows et al., 1999), NO₂ (Burrows et al., 1998), the oxygen dimer O₄ (Greenblatt et al., 1990) as well as H₂O (Rothman et al., 1992) were taken into account. The effect of Raman scattering (Grainger and Ring, 1962) was compensated by fitting a synthetic Ring spectrum as an additional absorber (Vountas et al., 1998). Total vertical columns of the trace gases O₃ and NO₂ for the location Kaashidhoo can be derived by the division of the slant columns of the zenith measurements by the air mass factor (AMF). The AMF describes the light path through the atmosphere and is calculated with GOMETRAN/SCIATRAN (Rožanov et al., 1997). Error analysis revealed a maximum relative error of 5% for the total amount for either trace gas retrieval, taking into account the radiative transfer in the atmosphere for the AMF calculation including the assumed shape of the vertical profile of the absorber, the surface albedo, and the aerosol loading.

The total vertical column of the trace gases consists of a tropospheric as well as a stratospheric part. Using both observation modes and appropriate AMF calculations, tropospheric vertical columns and/or profiles can be deduced from the measurements (Heckel et al., 2005), (Wittrock et al., 2004), as carried out in this study for the trace gas O₃. The analysis of the tropospheric amount of NO₂ is based on the results of dual-axis-DOAS measurements combined with model assumptions. The following simplifying assumptions were made for the calculation of tropospheric NO₂: (a) a polluted and well mixed air mass (air masses with higher amounts of NO₂ than in the surroundings air) follows the wind from north to south, (b) this air parcel passes both observing modes without any exchange with the environment and (c) the air mass is box shaped with homogeneously high amounts of NO₂ (see Fig. 2). With these assumptions the analysed air parcel is passing first the off-axis observing mode and then the zenith observing direction (see Fig. 2).

2.2 GOME and O₃-sonde measurements

GOME was launched in April 1995 onboard the European satellite ERS-2 in a sun-synchronous near polar orbit at a mean altitude of 795 km for measuring the sunlight scattered from the Earth's atmosphere and/or reflected by the surface in nadir mode in a wavelength region of 240 to 790 nm with a spectral resolution of 0.2–0.4 nm. The local equator crossing time is 10:30 a.m. With 14 orbits per day, global coverage at the equator is reached after three days for a 960 km swath width (the size of one GOME ground pixel is 40×320 km²) (Burrows et al., 1999). For this study GOME data reprocessed with WFDOAS (Weighting Function Differential Optical Absorption Spectroscopy) Version 1 (Coldewey et al., 2005) and (Weber et al., 2005) were extracted with a maximum distance of 300 km away from the location of interest to obtain vertical columns of O₃. The analysis to derive slant columns of NO₂ (Richter and Burrows, 2002) in the 425–450 nm and of BrO in the 344–359 nm wavelength region (Richter et al., 2002) was carried out using the IUP Bremen DOAS algorithm. The retrieval method is similar to that used for ground-based zenith-sky measurements. For the comparisons with ground based DOAS measurements, only GOME lv1-spectra with a maximum distance of 300 km around Kaashidhoo were extracted. GOME observes both, the troposphere and the stratosphere (Burrows et al., 1999), and in cloudy conditions it is impossible for GOME to detect the exact trace gases amount below the cloud layer. For the comparison of the tropospheric column amounts from GOME with ground based DOAS measurements, only GOME-pixels under cloud free conditions (using measurements with a cloud fraction of less than 0.2 as determined by the FRESKO algorithm (Koelemeijer, et al., 2001)) were included in the analysis. The tropospheric trace gas columns were derived by applying the tropospheric excess method (TEM) or reference sector approach. The

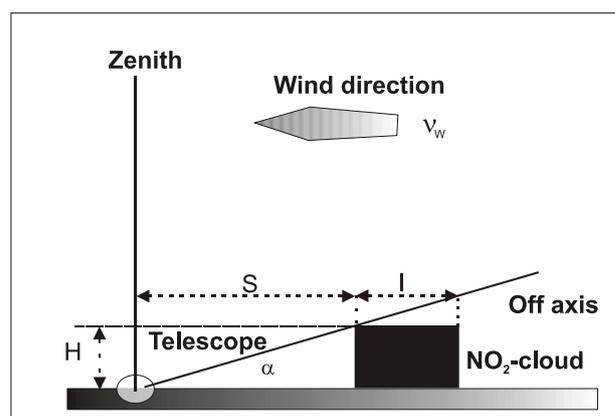


Fig. 2. The conceptual model used for describing a plume with high NO₂ amounts as observed with zenith and off axis geometry.

TEM is based on the assumption that the columns of stratospheric trace gases such as NO₂ and O₃ are approximately constant at a given longitude. This is a large over simplification but appears to work well for tropical and sub tropical conditions for O₃ and NO₂ and to higher latitudes mainly for NO₂. A number of studies have been published focusing on the retrieval of tropospheric NO₂ (Leue et al., 2001), (Richter and Burrows, 2002), (Martin et al., 2002) and O₃ (Ladstätter-Weißmayer et al., 2004) from GOME data. The error on the resultant tropospheric O₃ is estimated to be 4 DU (Ladstätter-Weißmayer et al., 2004) and on the tropospheric columns of NO₂ approximately 1.5×10^{15} molecules cm⁻² (Richter and Burrows, 2002) based on GOME data. During the INDOEX campaign in January to March 1999, in addition to the Vaisala radio sondes (Komhyr et al., 1995) 55 electrochemical cell (ECC) ozone soundings (Lobert et al., 2002) and (Thompson et al., 2003) were launched about once per day at approximately 14:00 local time (09:00 Universal Time (UT)) at the KCO by the Scripps Institution of Oceanography. In order to obtain the tropospheric vertical columns of O₃, the sonde data were summed up to the height of the tropopause defined in this case study to be at 4 PV (potential vorticity) Units.

3 Results and Discussion

3.1 Total column amounts of O₃ and NO₂

The ground based DOAS measurements were used to determine a.m.-, and p.m.-, values for O₃ and NO₂ total columns. The latter were determined from the observations at SZA between 83 and 90° in the morning and afternoon. The analysis of the zenith-sky ground based measurements of O₃ showed almost no difference between a.m. and p.m. values (Fig. 3a). Indicating that there was no detectable diurnal variation for the vertical columns of O₃ during the whole INDOEX

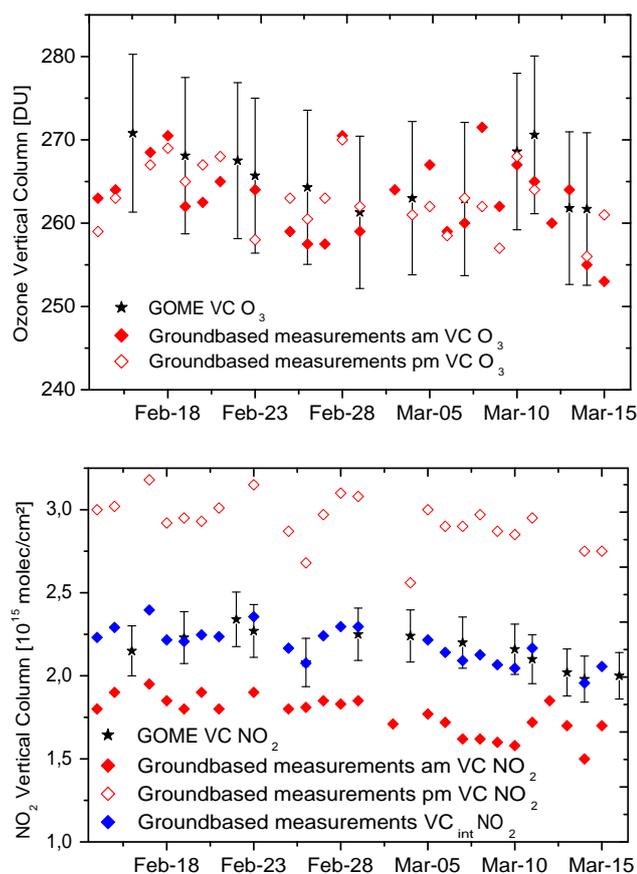


Fig. 3. Total columns of O₃ (a) and NO₂ (b) measured by the ground based DOAS system and with GOME during the INDOEX campaign from 14 February to 16 March 1999. VC_{int} is the ground-based vertical column of NO₂ interpolated to the GOME overpass time. (c) Model calculation of the diurnal cycle of NO₂ for 20 March 1999 including the measuring time of ground based a.m. and p.m. as well as the overpass time of GOME.

campaign. A mean value of 263 DU (Dobson Units) was determined using both a.m. and p.m. data. Deviations of up to 10 DU from the mean value which can be attributed to the transport of different air masses, are observed. Comparison of these data with the results of satellite based GOME measurements shows agreement within 3% for the total columns. This value is smaller than the combined errors of the ground based measurements and the satellite based measurements of 5%. Figure 3b shows the a.m. and p.m. values for NO₂ vertical columns (given in molecules cm⁻²) from the ground based DOAS measurements compared to the GOME results. The difference between the a.m. (around 6:30 a.m.) and the p.m. (around 17:30 p.m.) values of the ground based measurements was significant for NO₂. The p.m. values were almost a factor of 1.7 higher than the a.m. values. This behavior is attributed to the photolysis of N₂O₅ in the stratosphere. The influence of the diurnal cycle is more intense in

the tropics compared to mid-latitudes where the factor is typically 1.4 (Solomon et al., 1987) for ground based measurements. An average NO₂ daytime increase of $1 \times 10^{14} \text{ cm}^{-2}/\text{h}$ can be calculated from our ground based measurements. A similar result is obtained comparing ground based measurements carried out in the morning and GOME data. The retrieved a.m. columns of NO₂ show roughly 25% lower values compared to the GOME results. In comparison to the ground based measurements, the total columns of NO₂ from GOME are $4 \times 10^{14} \text{ cm}^{-2}$ (mean value) higher because of its later overpass time of 10:30 a.m. at KCO compared to the ground based measurements carried out 4 h earlier. This increase of $1 \times 10^{14} \text{ cm}^{-2}/\text{h}$ compared to the output of a photochemical model (Sinnhuber et al., 2005) based on the chemistry scheme from the SLIMCAT model (Chipperfield, 1999), with reaction rate constants taken from the JPL-2002 recommendations (Sander et al., 2002) (see Fig. 3c) which predicts an increase of $8 \times 10^{13} \text{ cm}^{-2}/\text{h}$. This increase, which is almost linear during the times of ground based and GOME measurements (as can be seen from Fig. 3c), is in a good agreement with the result calculated from the ground based measurements ($1 \times 10^{14} \text{ cm}^{-2}/\text{h}$). The interpolation of the retrieved a.m. and p.m. columns of NO₂ from ground based measurements to the overpass time of GOME, depicted in blue in Fig. 3b, shows differences of around 3% compared to the GOME results. In summary, both O₃ and NO₂ columns derived from GOME measurements agree well with the values obtained from the ground based measurements within their error bars. While for O₃ no diurnal variation could be observed, NO₂ significantly increases over the day in good agreement with results from a photochemical box model.

3.2 Tropospheric column amounts of O₃

The second scientific aim of this study was to determine the influence of pollution events on the tropospheric column amounts of O₃ and NO₂.

Figure 4 shows the comparison between the tropospheric column of O₃ determined as described above from GOME data and that derived from the ozone sonde measurements. The results of tropospheric amounts of O₃ from both instruments are in the range of background conditions because the tropical Indian Ocean is dominantly influenced by pristine air masses from the southern Indian Ocean including Antarctica during this time of the year. The following comparison shows the results of two selected case studies, for which the atmospheric circumstances were especially favourable for the DOAS technique. They are depicted in red in Fig. 4 and show lower tropospheric ozone columns for the ground based DOAS data compared to the results of either GOME (40%) or ozone sonde measurements (33%) on these two days. The differences between the sonde data and the remotely sensed satellite data are within a range of 4% (1.2 DU). Taking into account the error bars of both the O₃-sondes and satellite

based data, during this episode the two instruments agreed within their error limits (see Fig. 4).

The reason for the differences in the values between ground based, satellite, and ozone sonde measurements is likely a combination of limitations arising from the DOAS ground based measurements. One of the main error sources is poorly known type and amount of aerosol. Following from the high amount of aerosol over the Indian Ocean, the use of the dual-axis-DOAS instrument, in contrast to the MAX (multi axis)-DOAS instruments (Wittrock et al., 2004), as used presently, can introduce large errors. The calculation of the tropospheric AMFs taking into account only two different observing modes (zenith-sky and off-axis) consequently leads to an overall uncertainty of the analysis with estimated errors on the order of 10 DU, a value usually expected for this type of study. Thus, within the combined error limits, the ground based measurements agree with the GOME results.

3.3 Tropospheric column amounts of NO₂

In this study, in addition to the analysis of tropospheric O₃, the influence of tropospheric pollution with respect to NO₂ was determined. Using the high temporal resolution of ground based data, a localised tropospheric NO₂ plume could be observed on 15 March 1999; on most of the days the tropospheric NO₂ amounts did not significantly rise above the detection limit. An increase of the slant column of NO₂ due to polluted air masses was observed in the off-axis mode first. The same polluted air mass was later transported through the zenith-sky telescope's field of view, and the slant columns of the zenith-sky measurements increased as well. After the air mass has passed the telescope, the slant columns of both observing modes were then decreasing back to the stratospheric background value. Based on the measurements of both observing modes, the increase and the following decrease of the NO₂ slant columns can be determined as a function of time (see Fig. 5a). Using the wind speed in off axis direction ($v_w = 5 \text{ m s}^{-1}$), as measured at KCO), the elevation angle of the off axis viewing mode ($\alpha = 2^\circ$), the assumed vertical height of the plume ($h = s \times \tan(\alpha) = 262 \text{ m}$) with $s = 7500 \text{ m}$ (the horizontal distance of the plume from the measuring point), its horizontal extension in the viewing direction ($l = (\text{time of decrease of SC of both viewing modes} - \text{time of the first increase of SC of zenith data}) \times v = 900 \text{ m}$) and its horizontal distance from the measuring point at a defined time (see Fig. 2) the tropospheric NO₂ amount during a short pollution event can be obtained.

Dual-axis-DOAS reveals for the 15 March 1999 a maximum concentration of $1.2 \times 10^{11} \text{ molecules cm}^{-3}$ (5 ppb) of NO₂ based on the model assumption for a well mixed air mass over the Maldives (see Fig. 5b). On this day the observed total vertical column amount from ground based measurements was $1.8 \times 10^{15} \text{ molecules cm}^{-2}$ (a.m. value, see Fig. 3b). This means using the maximum concentra-

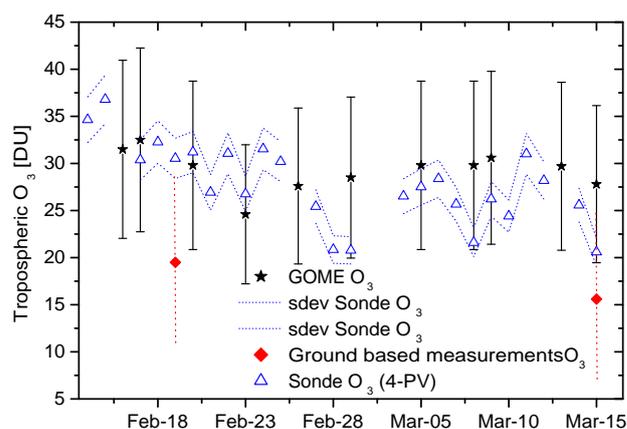


Fig. 4. Tropospheric columns of O₃ measured by the ground based DOAS system compared with the O₃-sondes and with GOME data for the time period of 14 February to 16 March 1999 during the INDOEX campaign.

tion of $1.2 \times 10^{11} \text{ molecules cm}^{-3}$, a tropospheric vertical column amount for NO₂ of $7.1 \times 10^{15} \text{ molecules cm}^{-2}$ was determined. Therefore, on this day an increase by a factor of 4 occurred over Kaashidhoo during this brief pollution event (see Fig. 5b) for the total column amount of NO₂.

Comparing this result with the tropospheric amount of NO₂ measured with GOME for the same day, a difference of $6.1 \times 10^{15} \text{ molecules cm}^{-2}$ can be observed (see Fig. 5b). This case study shows that a local increase of tropospheric NO₂ up to $7.1 \times 10^{15} \text{ molecules cm}^{-2}$ could be observed with ground based DOAS measurements in the afternoon whereas GOME measured $1 \times 10^{15} \text{ molecules cm}^{-2}$ at 10:30 over this region. The difference between the two results is best explained by the strongly localised nature of the enhancement observed, both in space and time. For the large GOME pixel size, such a local event does not lead to a significant enhancement in tropospheric column. The different vertical sensitivity of the two measurement setups might also contribute, but given the good visibility on that day, the dilution effect alone can explain the results. Locally observed high values for tropospheric NO₂ can be caused by different sources like combustion processes of anthropogenic or natural origin, such as biomass burning, and lightning discharge (Wayne, 1991). In this particular case, the increase of NO₂ was probably caused by nitrogen oxide (NO_x = NO + NO₂) emissions from ships (Lawrence et al., 1999), (Kasibhatla et al., 2000), (Richter et al., 2004), (Wittrock et al., 2004). From GOME measurements the mean background tropospheric amount of NO₂ was determined to be $4 \times 10^{14} \text{ molecules cm}^{-2}$, while the mean total column amount of NO₂ during the INDOEX campaign was $1.7 \times 10^{15} \text{ molecules cm}^{-2}$ (both values for the above mentioned region of 300 km around KCO). That means an average tropospheric fraction of 24% under clean air background conditions was observed.

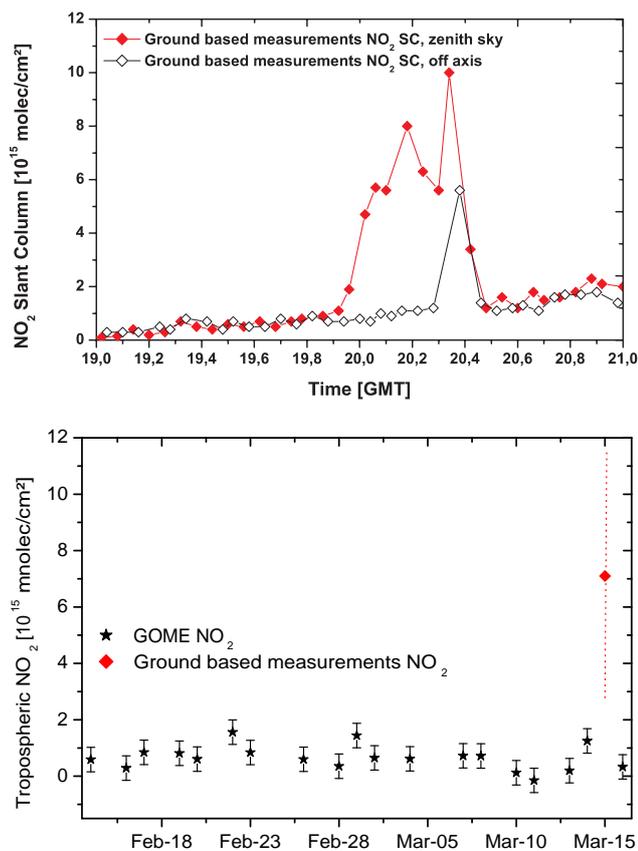


Fig. 5. Tropospheric slant columns of NO₂ (a) measured by ground based (GB) DOAS system (off-axis and zenith-sky-data) for March 15, 1999. Tropospheric columns of NO₂ (b) measured by ground based DOAS system and compared with tropospheric excess columns of GOME (GOME is only measuring at 10:30 a.m. and therefore not able to observe an enhancement of localised NO₂ in the afternoon) for the time period of February 14 to March 16 1999 during the INDOEX campaign.

3.4 Tropospheric column amounts of BrO

Tropospheric BrO has been positively detected over long periods of the year especially in polar spring in both hemispheres. These events have already been studied and compared with model output, balloon-borne observations and ground based measurements in previous publications (Wagner and Platt, 1998), (Richter et al., 1998), (Wagner et al., 2001), (Rooszendael et al., 2002). They are attributed to boundary layer effects, in which photochemically produced active bromine can temporarily accumulate to high abundances in a shallow surface layer, consuming ozone while not being sequestered in chemically more stable bromine species. The source of BrO has not been identified beyond doubt but active bromine species are presumed to be released either from sea salt, especially in the form of frost-flowers, or from biogenic organo-bromine species. In addition to the large values observed in polar spring, enhanced

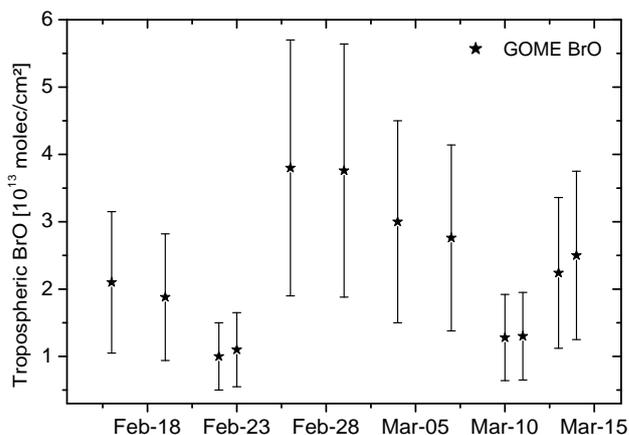


Fig. 6. Free tropospheric columns of BrO calculated from GOME data for the time period of February to March 1999 during the INDOEX campaign using the difference between “low cloud” and “high cloud” observations.

BrO is also observed globally in GOME data (Hegels et al., 1998), (Richter et al., 2002). This has tentatively been attributed to a significant background concentration of BrO in the free troposphere of several ppt, and direct evidence for BrO in the free troposphere was found by (Fitzenberger et al., 2000). Here, this assumption has been tested in the tropics by analysing ground-based DOAS measurements and satellite-based GOME data during the INDOEX campaign in the wavelength region 344–359 nm where BrO shows strong absorption features. Since several power failures have had an impact on the stability of the ground based instrument, only a detection limit of 3×10^{14} molecules cm^{-2} , was achieved for BrO from our ground based dual-axis-DOAS measurements. Using the difference of the slant columns of BrO retrieved at low (at 900–1013 mbar) and high cloud (at 0–600 mbar) situations during the INDOEX campaign an upper limit for the free tropospheric column of BrO of 3.8×10^{13} molecules cm^{-2} from GOME (see Fig. 6) can be determined. Assuming a 4 km atmospheric layer at 1000 hPa, 4 ppt of BrO can be calculated for this time period. The value calculated in this study for the amount of tropospheric BrO during the campaign is representative for background conditions as estimated in other studies (Richter et al., 2002), (Wagner et al., 2001), (Pundt et al., 2002), (Fitzenberger et al., 2000) (Dickerson et al., 1999), (Rooszendael et al., 2002).

4 Conclusions

During the INDOEX campaign in February and March 1999 on Kaashidhoo, ground based dual-axis DOAS measurements (zenith and off-axis-measurements) were performed in the equatorial region. This method provides information on total column as well as on tropospheric column amounts of O₃ and NO₂ and can distinguish between background

and polluted atmospheric situations. In addition, an upper limit of 3.8×10^{13} molecules cm⁻² for the free tropospheric amount of BrO could be given by comparing measurements of GOME under high and low cloud situations. This abundance confirms previous studies. The comparison between ground based dual-axis DOAS, GOME (both detecting O₃, NO₂, BrO), and O₃-sonde data demonstrates that all measurement systems agreed within their error limits. The relatively large errors in the ground based data are related to the assumed homogeneity of the tropical air masses encountered. Differences between ground based and satellite measurements can result from the temporal variability of the atmosphere when measurements are not exactly coincident in time, and from the limited spatial resolution of GOME compared to ground based measurements. The dual-axis-DOAS-technique and in addition the calculation of the different AMFs allowed to calculate around 19 DU for tropospheric O₃ (two case studies on 19 of February and 14 of March 1999) and 263 DU for the total amount of O₃. The results were compared to satellite based GOME-data and O₃-sondes launched over Kaashidhoo. Differences of up to 40% for the GOME (24.6–32.5 DU) data and of 33% for the O₃-sonde measurements (20.6–36.8 DU) with respect to ground based results in the tropospheric part for both case studies were obtained; a discrepancy of 3% for ground based and GOME data was observed for the vertical columns for the time period of the INDOEX campaign. Pollution events such as on 15 March 1999 could be detected by applying both, the zenith-sky and the off-axis mode of the ground based measurements of NO₂. This demonstrates the ability of this measurement method to differentiate between local tropospheric emissions of, e.g., NO and stratospheric NO₂ columns. A simple model based on a homogenous air mass with enhanced NO₂-loading passing the two different observing modes yields an increase of up to 5–10 ppb in this case study. GOME satellite data from the same day show no significant increase in NO₂, highlighting the strengths and weaknesses of the two different observing systems. While GOME has excellent spatial coverage but limited spatial and temporal resolution and therefore limited sensitivity for the detection of localized events, the ground based measurements with the dual-axis-technique can observe local pollution events on a short time scale at one location. Furthermore, the above mentioned results for tropospheric BrO were made possible by the high spectral resolution and the comparably low detection limit of GOME for BrO in the tropical free troposphere. In the future additional campaigns should be carried out and also long term studies to confirm and extend the data set and our understanding of tropical pollution events.

Acknowledgements. Parts of this work have been funded by the University of Bremen, Germany, the DLR/DARA, the European Community, and the European Space Agency (ESA). We would like to thank H. Altmeyer who carried out with M. Bruns the measurements at KCO. We would like to thank R. B. A. Koelemeijer for providing the FRESKO data. We would like to thank

the International sharing steering Group of the INDOEX campaign for great assistance, without which this work would not have been possible. We thank especially the organizers of the INDOEX campaign P. Crutzen and V. Ramanathan, J. Lobert and the whole KCO team during the IFP 1999. We thank in particular R. Dickerson for great help during the campaign. We also appreciate the warm hospitality of the Maldivians on the island Kaashidhoo, Republic of Maldives. Discussions with R. v. Kuhlmann, M. G. Lawrence and A. M. Thompson were very helpful.

Edited by: N. Mihalopoulos

References

- Burrows, J. P., Dehn, A., Deters, B., Himmelmann, S., Richter, A., Voigt, S., and Orphal, J.: Atmospheric remote-sensing reference data from GOME: Part 1, Temperature-dependant absorption cross-sections of NO₂, *J. Quant. Spectrosc. Radiat. Transfer*, 60, 1025–1031, 1998.
- Burrows, J. P., M. Weber, M. Buchwitz, V. V. Rozanov, A. Ladstätter-Weißmayer, A. Richter, R. de Beek, R. Hoogen, K. Bramstedt, K.-U. Eichmann, M. Eisinger and D. Perner, The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results, *J. Atm. Sciences*, 56, p. 151–175, 1999.
- Chipperfield, M. P.: Multiannual simulations with a three-dimensional chemical transport model, *J. Geophys. Res.*, 104, 1781–1805, 1999.
- Coldeyew-Egbers, M., Weber, M., Lamsal, L. N., de Beek, R., Buchwitz, M., and Burrows, J. P.: Total ozone retrieval from GOME UV spectral data using the weighting function DOAS approach, *Atmos. Chem. Phys.*, 5, 5015–5025, 2005, <http://www.atmos-chem-phys.net/5/5015/2005/>.
- Dickerson, R. R., Rhoads, K. P., Carsey, T. P., Oltmans, S. J., Burrow, J. P., and Crutzen, P. J.: Ozone in the remote marine boundary layer: A possible role for halogens, *J. Geophys. Res.*, 104, 21 385–21 395, 1999.
- Fitzenberger, R., Bösch, H., Camy-Peyret, C., Chipperfield, M. P., Harder, H., Platt, U., Sinnhuber, B. M., Wagner, T., and Pfeilsticker, K.: First Profile Measurements of Tropospheric BrO, *Geophys. Res. Lett.*, 27, 2921–2925, 2000.
- Grainger, J. F. and Ring, J.: Anomalous Fraunhofer line profiles, *Nature*, 193, 762, 1962.
- Greenblatt, G. D., Orlando, J. J., Burkholder, J. B., and Ravishankara, A. R. Absorption measurements of oxygen between 330 and 1140 nm, *J. Geophys. Res.*, 95, 18 577–18 582, 1990.
- Heckel, A., Richter, A., Tarsu, T., Wittrock, F., Hak, C., Pundt, I., Junkermann, W., and Burrows, J. P.: MAX-DOAS measurements of formaldehyde in the Po-Valley, *Atmos. Chem. Phys.*, 5, 909–918, 2005, <http://www.atmos-chem-phys.net/5/909/2005/>.
- Hegels, E., Crutzen, P. J., Klüpfel, T., Perner, D., and Burrows, J. P.: Global distribution of atmospheric bromine-monoxide from GOME on earth observing satellite ERS-2, *Geophys. Res. Lett.*, 25, 3127–3130, 1998.
- Hoeningner G., von Friedeburg, C., and Platt, U.: Multi axis differential optical absorption spectroscopy (MAX-DOAS), *Atmos. Chem. Phys.*, 4, 231–254, 2004, <http://www.atmos-chem-phys.net/4/231/2004/>.

- Kasibhatla, P., Levy II, H., Moxim, W. J., Pandis, S. N., Corbett, J. J., Peterson, M. C., Honrath, R. E., Frost, G. J., Knapp, K., Parrish, D. D., and Ryerson, T. B.: Do emissions from ships have a significant impact on concentrations of nitrogen oxides in the marine boundary layer?, *Geophys. Res. Lett.*, 27, 2229–2232, 2000.
- Koelemeijer, R. B. A., Stammes, P., Hovenier, J. W., and de Haan, J. F.: A fast method for retrieval of cloud parameters using oxygen A-band measurements from GOME, *J. Geophys. Res.*, 106, 3475–3490, 2001.
- Komhyr, W. D., Barnes, R. A., Brothers, G. B., Lathrop, J. A., and Opperman, D. P.: Electrochemical concentration cell ozonesonde performance evaluation during STOIC 1989, *J. Geophys. Res.*, 100, 9231–9244, 1995.
- Ladstätter-Weissenmayer, A., Meyer-Arneck, J., Schlemm, A., and Burrows, J. P.: Influence of stratospheric air masses on tropospheric vertical O₃ columns based on GOME (Global Ozone Monitoring Experiment) measurements and backtrajectory calculation over the Pacific, *Atmos. Chem. Phys.*, 4, 903–909, 2004, <http://www.atmos-chem-phys.net/4/903/2004/>.
- Lawrence, M. G. and P. Crutzen.: Impacts of Ongoing ship NO_x Emission on Tropospheric Photochemistry, *Nature*, 402, 167–170, 1999.
- Lelieveld, J. P., Crutzen, J. and Ramanathan, V., et al.: The Indian Ocean Experiment: Widespread Air Pollution from South and Southeast Asia, *Science*, 291, 1031–1036, 2001.
- Leue, C., Wenig, M., Wagner, T., Klimm, O., Platt, U., and Jähne, B.: Quantitative analysis of NO_x emissions from GOME satellite image sequences, *J. Geophys. Res.*, 106, p. 5493–5505, 2001.
- Lobert, J. M. and Harris, J. M.: Trace gases and air mass origin at Kaashidhoo, Indian Ocean, *J. Geophys. Res.*, 107, D19, 8013, doi:10.1029/2001JD000731, 2002.
- Martin, R. V., Chance, K., Jacob, D. J., Kurosu, T. P., Spurr, R. J. D., Bucselo, E., Gleason, J. F., Palmer, P. I., Bey, I., Fiore, A. M., Li, Q., Yantosca, R. M., and Koelmeijer, R. B. A.: An improved retrieval of tropospheric nitrogen dioxide from GOME, *J. Geophys. Res.*, 107(20), doi:10.1029/2001JD001027, 2002.
- Platt, U.: Differential optical absorption spectroscopy (DOAS), in: *Air Monitoring by Spectroscopic Techniques*, Chem. Anal. Ser., edited by: Sigrist, M. W., John Wiley, New York, 127, 27–84, 1994.
- Pundt, I., Pommereau, J.-P., Chipperfield, M. P., Van Roozendaal, M., and Goutail, F.: Climatology of the stratospheric BrO vertical distribution by balloon-borne UV-visible spectrometry, *J. Geophys. Res.*, 107, D24, doi: 10.1029/2002JD002230, 2002.
- Ramanathan, V., Crutzen, P. J., Lelieveld, J., Althausen, D., Anderson, J., Andreae, M. O., Cantrell, W., Cass, G., Chung, C. E., Clarke, A. D., Collins, W. D., Coakley, J. A., and Dulac, F.: The Indian Ocean Experiment: An integrated assessment of the climate forcing and effects of the great Indo-Asian haze, *J. Geophys. Res.* 106, (D22), 28 371–28 398, 2001.
- Richter, A., Wittrock, F., Eisinger, M., and Burrows, J. P.: GOME observations of tropospheric BrO in Northern Hemispheric spring and summer 1997, *Geophys. Res. Lett.*, 25, pp. 2683–2686, 1998.
- Richter A. and Burrows, J. P.: Retrieval of tropospheric NO₂ from GOME measurements, *Adv. Space Res.*, 29, 11, 1673–1683, 2002.
- Richter, A., Wittrock, F., Ladstätter-Weissenmayer, A., and Burrows, J. P.: GOME measurements of stratospheric and tropospheric BrO, *Adv. Space Res.* 29, 1667–1672, 2002a.
- Richter, A., Eyring, V., Burrows, J. P., Bovensmann, H., Lauer, A., Sierk, B., and Crutzen, P. J.: Satellite Measurements of NO₂ from International Shipping Emissions, *Geophys. Res. Lett.*, 31, L23110, doi:10.1029/2004GL020822, 2004.
- Van Roozendaal, M., Wagner, T., Richter, A., Pundt, I., Arlander, D. W., Burrows, J. P., Chipperfield, M., Fayt, C., Johnston, P. V., Lambert, J.-C., Kreher, K., Pfeilsticker, K., and Platt, U., Pommereau, J.-P., Sinnhuber, B.-M., Toernkvist, K. K., and Wittrock, F.: Intercomparison of BrO Measurements from ERS-2 GOME, ground-based and Balloon Platforms, *Adv. Space Res.*, 29(11), 1661–1666, 2002.
- Van Roozendaal, M., Fayt, C., Post, P., Hermans, C., and Lambert, J.-C.: Retrieval of BrO and NO₂ from UV-Visible Observations, in: *Sounding the troposphere from space: a new era for atmospheric chemistry*, Springer-Verlag, ISBN 3-540-40873-8, edited by: Borell, P., Borell, P. M., Burrows, J. P., Platt, U., 2003.
- Rothman, L. S., Gamache, R. R., Tipping, R. H., Rinsland, C. P., Smith, M. A. H., Benner, C. D., Devi, V. M., Flaud, J. M., Camy-Peyret, C., Perrin, A., Goldman, A., Massie, S. T., and Brown, L. R.: The HITRAN molecular database editions 1991 and 1992, *J. Quant. Spectrosc. Radiat. Transfer*, 48, 469–507, 1992.
- Roazanov, V., Diebel, D., Spurr, R. J., and Burrows, J. P.: GOME-TRAN: A radiative transfer model for the satellite project GOME – the plane parallel version, *J. Geophys. Res.*, 102, 16 683–16 695, 1997.
- Sander, S. P., Friedl, R. R., Golden, D. M., et al.: Chemical kinetics and photochemical data for use in atmospheric studies, *JPL Publ. Jet Propul. Lab., Pasadena, Calif.* 0225, 335 pp., 2002.
- Sinnhuber, B.-M., Roazanov, A., Sheode, N., Afe, O. T., Richter, A., Sinnhuber, M., Wittrock, F., Burrows, J. P., Stiller, G. P., von Clarmann, T., and A. Linden: Global observations of stratospheric bromine monoxide from SCIAMACHY, *Geophys. Res. Lett.*, 32, L20810, doi:10.1029/2005GL023839, 2005.
- Solomon, S. A. L., Schmeltekopf, and Sanders, W. R.: On the interpretation of zenith sky absorption measurements, *J. Geophys. Res.*, 92, p. 8311–8319, 1987.
- Thompson, A. M., Witte, J. C., McPeters, R. D., Oltmans, S. J., Schmidlin, F. J., Logan, J. A., Fujiwara, M., Kirchhoff, V. W. J. H., Posny, F., Coetzee, G. J. R., Hoegger, B., Kawakami, S., Ogawa, T., Johnson, B. J., Vmel, H., and Labow, G.: Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2000 tropical ozone climatology. 1. Comparison with Total Ozone Mapping Spectrometer (TOMS) and ground-based measurements, *J. Geophys. Res.*, 108, art. no. 8238, doi:10.1029/2002JD002241, 2003.
- Vountas, M., Roazanov, V. V., and Burrows, J. P.: Ring Effect: Impact of Rotational Raman Scattering on Radiative Transfer in Earth's Atmosphere, *J. Quant. Spectrosc. Radiat. Transfer*, 60, 943–961, 1998.
- Wagner, T. and U. Platt: Satellite mapping of enhanced BrO concentrations in the troposphere, *Nature*, 395, 486–490, 1998.
- Wagner, T., Leue, C., Wenig, M., Pfeilsticker, K., and Platt, U.: Spatial and temporal distribution of enhanced boundary layer BrO concentrations measured by the GOME instrument aboard ERS-2, *J. Geophys. Res.*, 106, 24 225–24 236, 2001.
- Wayne, R. P.: *Chemistry of Atmospheres*, p. 565–566, 3rd Edition, Oxford 2000.

Weber, M., Lamsal, L. N., Coldewey-Egbers, M., Bramstedt, K., and Burrows, J. P.: Pole-to-pole validation of GOME WFDOAS total ozone with groundbased data, *Atmos. Chem. Phys.*, 5, 1341–1355, 2005,
<http://www.atmos-chem-phys.net/5/1341/2005/>.

Wittrock, F., Oetjen, H., Richter, A., Fietkau, S., Medeke, T., Rozanov, A., and Burrows, J. P.: MAX-DOAS measurements of atmospheric trace gases in Ny-Alesund, *Atmos. Chem. Phys.*, 4, 955–966, 2004,
<http://www.atmos-chem-phys.net/4/955/2004/>.