Algorithm Description

Tropospheric vertical column densities of NO_2 from SCIAMACHY

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Algorithm Description

1 Retrieval of total slant column densities of NO_2 with DOAS

NO_2 Slant Column Densities (SCDs) *S*, i.e. concentrations integrated along the effective light path, are derived from SCIAMACHY (Bovensmann et al., 1999) nadir spectra using Differential Optical Absorption Spectroscopy DOAS (Platt and Stutz, 2008). We consider SCIAMACHY spectra corrected for memory effect, leakage, pixel-to-pixel gain, etalon, wavelength calibration, and straylight. Cross-sections of O_3, NO_2, O_4, H_2O and CHOCHO are fitted simultaneously in the spectral range 430.8-459.5 nm. In addition, two Ring spectra, accounting for inelastic scattering in the atmosphere (rotational Raman) as well as in liquid water (vibrational Raman), an absorption cross-section of liquid water, and a polynomial of degree 5 are included in the fitting procedure. A daily solar measurement (A_0) is used as Fraunhofer reference spectrum, which can be adjusted by a spectral shift by the fit algorithm. Table 1 lists the fitted cross sections and other data plus the respective references.

Table 1: Absorption cross sections and additional data used for the DOAS fit

	T	Reference	Remarks
O_3	223 K	Bogumil et al., 2003	SCIAMACHY pre-launch measurement
NO_2	220 K	Vandaele et al., 1998	
O_2-O_2	296 K	Greenblatt et al., 1990	
H_2O	300 K	Rothman et al., 1992	HITRAN
CHOCHO	296 K	Volkamer et al., 2005	
Ring			Calculated by WinDOAS
„Waterring"			Calculated from vibrational Raman (T. Kurosu, pers. comm.) and solar reference
Liquid water absorption		Pope and Fry, 1997	
Polynomial			Degree 5
Solar Reference			A0 (daily, no radiometric calibration)

This NO_2 DOAS retrieval setup is different from previous versions (Beirle, 2004) in so far that liquid water absorption and vibrational Raman scattering on liquid water molecules, which have been shown to affect spectra in the UV/vis (Vasilkov et al., 2002; Vountas et al., 2007), is now accounted for. This modification improves the spectral fits over oligotrophic oceanic regions, where NO_2 SCDs of the previous fit version show a systematic negative bias. The remaining (but significantly smaller) systematic spatial patterns over oligotrophic oceanic regions are subject to further investigations. These effects are related to tropospheric NO_2 in so far that large parts of the reference region in the Pacific chosen for the stratospheric correction (Section 2) cover oligotrophic regions.

In the DOAS set-up, a single NO_2 cross-section for a temperature of 220 K is included. The temperature dependency of NO_2 cross-section (Boersma et al., 2004) is simply corrected by applying a factor of 1.2 in the tropospheric product (see Section 3).

Only measurements from the descending part of the orbit with solar zenith angles (SZA) below 80° are considered.

2 Stratospheric correction

NO_2 is present both in stratosphere and troposphere. Thus, the stratospheric fraction has to be removed from the total atmospheric column density. For this purpose, we estimate the latitudinal dependency of stratospheric column densities in a reference-sector over the Pacific (Beirle, 2004). In addition, a correction of the longitudinal dependency is applied based on integrated stratospheric profiles derived from SCIAMACHY limb measurements. The details of this stratospheric correction procedure can be found in Beirle et al., 2010.

The basic steps and assumptions are

- total SCDs are converted in "total Vertical Column Densities" (VCDs) *V*, i.e. vertically integrated concentrations, by a stratospheric Air-Mass Factor *A*:

$$V' = S / A \quad (1)$$

  The prime indicates that *V'* can not be interpreted quantitatively as total VCD, since the tropospheric fraction of the total SCD was converted (inappropriately) with a stratospheric AMF.

- the latitudinal and temporal dependency of V_{Strat} is estimated from the mean of *V'* over a Reference Sector in the Pacific in 1° latitude bins on daily basis. This is similar to earlier versions of our SCIAMACHY retrieval (Beirle, 2004).

- Additionally, the longitudinal dependency of V_{Strat} is determined using the SCIAMACHY NO_2 limb profile product developed at MPI Mainz (Kühl et al., 2008): The limb NO_2 concentration profiles are integrated to stratospheric NO_2 VCDs, which are likewise normalized w.r.t. the pacific reference sector, and the resulting longitudinal variation is applied as correction to V_{Strat}.

  Note that the attempt to estimate the stratospheric VCD of NO_2 directly from the collocated limb-measurements ("limb-nadir-matching") failed due to different latitudinal dependencies of limb and nadir NO_2 VCDs, which are not fully understood so far.

- Tropospheric residue vertical column densities are calculated by

$$V'_{Trop} = V' - V_{Strat} \quad (2)$$

- V'_{Trop} is transferred back to a tropospheric SCD (TSCD) S_{Trop} by multiplication with the stratospheric AMF:

$$S_{Trop} = V'_{Trop} * A_{Strat} \quad (3)$$

- S_{Trop} is finally transferred in a tropospheric VCD (TVCD) with a tropospheric AMF (next section).

Our stratospheric estimation scheme is rather simple and robust and is based on measurements and mostly free of model assumptions. It successfully removes artefacts which arise from a simple reference sector method at high latitudes around the polar vortex.

One has to keep in mind that any reference sector method approach assumes a "clean" region with negligible tropospheric NO_2. I.e., the resulting TSCDs are too low by the actual tropospheric SCD over the Pacific (about $0.5*10^{15}$ molec/cm^2) (Martin et al., 2002).

3 Tropospheric Air-Mass Factors and Vertical Column Densities

For the conversion of tropospheric SCDs S_{Trop} into tropospheric VCDs T, appropriate tropospheric AMFs A_{Trop} are required:

$$T := \frac{S_{\mathrm{Trop}}}{A_{\mathrm{Trop}}} \tag{4}$$

A_{Trop} corrects for the height-dependent sensitivity of the satellite observations for tropospheric NO_2. It can be expressed as the sum of box-AMFs a_i, i.e. local AMFs for vertical layer i, multiplied with the (relative) vertical NO_2 profile p_i.

$$A_{\mathrm{trop}} = \sum_i a_i * p_i \quad , \tag{5}$$

where p_i is the fraction of the column density in layer i with respect to the total column density, and the sum of p_i is 1.

While stratospheric AMFs depend mainly on viewing geometry, tropospheric (box-) AMFs have a strong dependency on ground albedo, aerosols, and particularly on clouds. We created a look-up table (LUT) of box AMFs a_i in dependency of the SZA, ground albedo, and ground elevation, for both, cloud free and fully cloudy conditions with varying cloud top height (CTH). Cloud geometrical thickness is fixed to 1 km. A universal aerosol is assumed within the boundary layer (1 km high) with an extinction of 0.5/km, a single scattering albedo of 0.9, and a Henyey-Greenstein asymmetry parameter of 0.68. The LUT is calculated using the Monte-Carlo radiative transfer model (RTM) McArtim (Deutschmann et al., 2011).

For each individual satellite pixel, the appropriate box-AMFs a_i are derived in two steps, assuming that the ground pixel can be devided into a clouded and a cloud-free part. First, box-AMFs are calculated for both cloud-free as well as clouded conditions by interpolating the LUT for the respective SZA and ground elevation (GTOPO) (so far, a globally constant ground albedo of 5% is applied. This will be modified in the next version). For the interpolation of a_i under clouded conditions, the CTH is taken from FRESCO (Wang et al., 2008) which is also derived from analysis of SCIAMACHY spectra. Note that for our radiative transfer setup, the absolute CTH has to be transformed to a relative CTH above ground. In a second step, the clouded and cloud-free box-AMFs are averaged, weighted by the respective reflectivity of the clouded and the cloudfree part of the pixel, using the cloud fraction derived from FRESCO.

Note that the clouded box-AMFs are undefined for CTH above ground below 1 km, since the geometrical thickness of the cloud was set to 1 km in the RTM. In the case of a low cloud fraction, such low CTH might indicate fog or aerosols. Thus, for the calculation of a_i in these cases, only the cloudfree box-AMFs are used. These cases should be interpreted with care.

The vertical profile of box-AMFs (equivalent to averaging kernels) is stored and provided in addition to the TVCD product to enable a-postiori modifications.

For the calculation of A_{trop} (eq. 5), a simple, globally constant, relative vertical profile of NO_2 is assumed, which consists of a 1 km high boundary layer, containing 80% of the tropospheric column (constant concentrations), and a free troposphere from 1-15 km, containing the remaining 20% (constant mixing ratio). This setup was chosen in order to provide a dataset which, as far as possible, a) is free from model input, and b) results in reasonable NO_2 TVCDs over source regions.

Finally, as noted in section 1, the TVCDs are scaled up by a factor of 1.2 to correct for the temperature dependency of the NO_2 cross section (Boersma et al., 2004). A more appropriate temperature correction might be applied in future versions, using temporally and spatially resolved atmospheric temperature data.

One has to be aware that the final TVCDs are not appropriate if the simple profile assumptions are wrong. This is in particular the case over remote regions, where the upper troposphere contains far more than 20% of the tropospheric column. Consequently, A_{Trop} is generally underestimated, and T is generally overestimated, over clean regions. However, if information on the NO_2 profile is available, T can be corrected a-posteriori using the provided box-AMFs.

The most convenient approach for this procedure would be to

a) interpolate the relative a-posteriori NO_2 profile to the altitude grid used for the box-AMFs,

b) calculate the a-posteriori AMF via eq. 5,

c) determine a modified a-posteriori TVCD via

$$T^{post} := T^{prior} \cdot \frac{A^{prior}}{A^{post}} \tag{6}$$

Alternatively, A^{post} could be directly applied to S_{Trop}. In this case, the additional temperature correction (*1.2) has to be applied in addition.

4 Uncertainties

DOAS / Slant column densities

Total SCDs of NO_2 are derived by DOAS. Random noise can be estimated from the standard deviation of SCDs over unpolluted regions, which is about <0.5*10^{15} molec/cm^2.
Since earthshine and solar reference spectra are measured with different optical setups, artificial spectral structures caused by the optical system can lead to additive offsets in total SCDs (Richter and Wagner, 2001). However, such additive offsets have only minor impact on TSCDs, as they are to large part eliminated intrinsically by the referene sector method.
Systematic errors may be caused by spectral structures not (appropriately) accounted for in the fit setup. This was observed over oligotrophic oceanic regions, where SCDs have been systematically low, but improved systematically when liquid water absorption and vibrational Raman has been included in the fit. Remaining systematic structures over oligotrophic regions are less than 0.5*10^{15} molec/cm^2 (in terms of TSCDs).

Stratospheric correction

Estimating the stratospheric VCD in a Pacific reference sector generally works well for low- and midlatitudes, but can results in systematic biases in TSCDs of the order of some 10^{15} molec/cm^2 at higher latitudes, especially in wintertime as a consequence of asymmetric polar vortices. These artefacts are largely improved if SCIAMACHY limb measurements are used in addition for the estimation of the longitudinal dependency of stratospheric VCDs (Beirle et al., 2010).
For monthly means, the remaining uncertainty of TSCDs due to the stratospheric estimation is about 1*10^{15} molec/cm^2 on individual days, and <0.5*10^{15} molec/cm^2 for monthly means.

The integrated limb profiles used for the longitudinal correction are smoothed over time and space (see Beirle et al., 2010). For each latitudinal bin, the standard deviation of the difference of original and smoothed limb VCDs is calculated and stored (δT_{RLC} in Beirle et al., 2010). δT_{RLC} might be used to identify and flag events with poor stratospheric correction.

Tropospheric AMFs

Tropospheric AMFs are strongly dependent on a-priori data such as ground albedo, aerosol and cloud properties, and the NO_2 profile. Consequently, A_{Trop} dominates the uncertainty of TVCDs over polluted regions (~30%, Boersma et al., 2010).
Generally, the uncertainty of A_{Trop} is increasing with the cloud fraction. Thus, quantitative interpretation of TVCDs should focus on cloud free observations.
In the current dataset, a rather simple, globally constant (relative) tropospheric profile was assumed. As noted above, this causes systematic biases, i.e. too high TVCDs over clean regions, and generally too low TVCDs over highly polluted regions. This has to be considered for quantitative interpretations of our dataset. In future versions, an additional TVCD using model profiles will be included (see section 6).

5 Verification

Our NO_2 TVCD product was compared to TVCDs derived from zenith-sky measurements as well as surface concentrations derived from long-path DOAS measurements over Shanghai (Chen et al., 2009). For cloud free observations (and CTH>1 km), the correlation to zenith-sky TVCDs was found as R=0.86, and an orthogonal linear regression results in a slope of 0.50. If our standard profile was modified such that the BL contains 95% of the total column, the slope becomes 0.56.

The finding that the satellite TVCDs are lower by a factor of 2 is partly due to the spatial averaging over the SCIAMACHY ground pixel (30*60 km²), while the zenith-sky measurements are performed within the city, which is a general difficulty for comparisons of SCIAMACHY TVCDs to local measurements.

Further comparisons with ground based (MAX-DOAS) measurements and models (EMAC, Jöckel et al., 2010) are in progress.

An intercomparison of TVCDs from different retrievals was recently initiated by A. Richter, Uni Bremen.

6 Recommendations, known issues and planned updates

For comparisons of our tropospheric VCDs of NO_2 with other datasets, the simple profile assumptions used for our product have to be taken into account. If the other dataset contains profile information, this has to be used to modify our dataset, using the box-AMFs, for a consistent comparison.

Future versions of our retrieval will contain an additional TVCD product which uses model profile information (EMAC, Jöckel et al., 2010), to allow quantitative comparison to other measurements.

Within the current LUT, ground elevation is considered between 0 and 5 km. For SCIAMACHY observations with ground elevations outside this range, box AMFs are not defined. This leads to data gaps above the Caspic sea (<0 km) and parts of the Himalaya (>5 km). Future versions will solve this issue.

It is also planned to include a more advanced temperature correction and a spatially resolved ground albedo for the calculation of box-AMFs in the next version.

7 Data availability

SCIAMACHY TVCDs of NO_2 are available for 2003-2011 (ascii-format) on request. Please contact

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References

Beirle, S., Kühl, S., Puķīte, J., and Wagner, T.: Retrieval of tropospheric column densities of NO_2 from combined SCIAMACHY nadir/limb measurements, Atmos. Meas. Tech., 3, 283-299, 2010.

Beirle, S., Estimating source strengths and lifetime of Nitrogen Oxides from satellite data. PhD Thesis, University of Heidelberg, 2004. http://archiv.ub.uni-heidelberg.de/volltextserver/volltexte/2005/5225/pdf/diss_komplett.pdf

Boersma, K., Eskes, H. and Brinksma, E.: Error analysis for tropospheric NO_2 retrieval from space, JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES, 109(D4), doi:10.1029/2003JD003962, 2004.

Boersma, K. F., Eskes, H. J., Veefkind, J. P., Brinksma, E. J., van der A, R. J., Sneep, M., van den Oord, G. H. J., Levelt, P. F., Stammes, P., Gleason, J. F. and Bucsela, E. J.: Near-real time retrieval of tropospheric NO_2 from OMI, Atmos. Chem. Phys., 7(8), 2103-2118, 2007.

Bogumil, K., Orphal, J., Homann, T., Voigt, S., Spietz, P., Fleischmann, O. C., Vogel, A., Hartmann, M., Kromminga, H., Bovensmann, H., Frerick, J. et al.: Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote-sensing in the 230-2380 nm region, Journal of Photochemistry and Photobiology A: Chemistry, 157(2-3), 167-184, doi:10.1016/S1010-6030(03)00062-5, 2003.

Bovensmann, H., Burrows, J., Buchwitz, M., Frerick, J., Noel, S., Rozanov, V., Chance, K. and Goede, A.: SCIAMACHY: Mission objectives and measurement modes, JOURNAL OF THE ATMOSPHERIC SCIENCES, 56(2), 127-150, 1999.

Chen, D., Zhou, B., Beirle, S., Chen, L. M. and Wagner, T.: Tropospheric NO_2 column densities deduced from zenith-sky DOAS measurements in Shanghai, China, and their application to satellite validation, Atmos. Chem. Phys., 9(11), 3641-3662, 2009.

Deutschmann, T., et al., The Monte Carlo Atmospheric Radiative Transfer Model McArtim, accepted for publication in Journal of Quantitative Spectroscopy and Radiative Transfer, 2011.

Greenblatt, G., Orlando, J., Burkholder, J. And Ravishankara, A.: Absorption-Measurements Of Oxygen Between 330nm And 1140nm, Journal Of Geophysical Research-Atmospheres, 95(D11), 18577-18582, 1990.

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S. and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), Geosci. Model Dev. Discuss., 3(3), 1423-1501, doi:10.5194/gmdd-3-1423-2010, 2010.

Kühl, S., Pukite, J., Deutschmann, T., Platt, U. and Wagner, T.: SCIAMACHY limb measurements of NO_2, BrO and OClO. Retrieval of vertical profiles: Algorithm, first results, sensitivity and comparison studies, ADVANCES IN SPACE RESEARCH, 42(10), 1747-1764, doi:10.1016/j.asr.2007.10.022, 2008.

Martin, R., Chance, K., Jacob, D., Kurosu, T., Spurr, R., Bucsela, E., Gleason, J., Palmer, P., Bey, I., Fiore, A., Li, Q. et al.: An improved retrieval of tropospheric nitrogen dioxide from GOME, JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES, 107(D20), doi:10.1029/2001JD001027, 2002.

Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy, Springer-Verlag Berlin Heidelberg., 2008.

Pope, R. and Fry, E.: Absorption spectrum (380-700 nm) of pure water .2. Integrating cavity measurements, APPLIED OPTICS, 36(33), 8710-8723, 1997.

Richter, A., and T. Wagner, Diffuser plate spectral structures and their influence on GOME slant columns, paper presented to the GOME Science Advisory Group, Bremen, Germany, http://www.iup.uni-bremen.de/gome/data/diffuser_gome.pdf, 2001.

Rothman, L., Gamache, R., Tipping, R., Rinsland, C., Smith, M., Benner, D., Devi, V., Flaud, J., Camy-Peyret, C., Perrin, A., Goldman, A. et al.: The HITRAN molecular database: Editions of 1991 and 1992, Journal of Quantitative Spectroscopy and Radiative Transfer, 48(5-6), 469-507, doi:10.1016/0022-4073(92)90115-K, 1992.

Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., Mérienne, M. F., Jenouvrier, A. and Coquart, B.: Measurements of the NO_2 absorption cross-section from 42 000 cm-1 to 10 000 cm-1 (238-1000 nm) at 220 K and 294 K, Journal of Quantitative Spectroscopy and Radiative Transfer, 59(3-5), 171-184, doi:10.1016/S0022-4073(97)00168-4, 1998.

Vasilkov, A., Joiner, J., Gleason, J. and Bhartia, P.: Ocean Raman scattering in satellite backscatter UV measurements, GEOPHYSICAL RESEARCH LETTERS, 29(17), doi:10.1029/2002GL014955, 2002.

Volkamer, R., Spietz, P., Burrows, J. and Platt, U.: High-resolution absorption cross-section of glyoxal in the UV-vis and IR spectral ranges, JOURNAL OF PHOTOCHEMISTRY AND PHOTOBIOLOGY A-CHEMISTRY, 172(1), 35-46, 2005.

Vountas, M., Dinter, T., Bracher, A., Burrows, J. and Sierk, B.: Spectral studies of ocean water with space-borne sensor SCIAMACHY using Differential Optical Absorption Spectroscopy (DOGS) (vol 3, pg 429, 2007), OCEAN SCIENCE, 3(4), 483-483, 2007.

Wang, P., Stammes, P., van der A, R., Pinardi, G. and van Roozendael, M.: FRESCO+: an improved O2 A-band cloud retrieval algorithm for tropospheric trace gas retrievals, Atmos. Chem. Phys., 8(21), 6565-6576, 2008.