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An improved retrieval of tropospheric NO_2 from space over polluted regions using an Earth radiance reference

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Abstract. A novel tropospheric NO_2 DOAS retrieval algorithm optimised for a nadir-viewing satellite instrument imaging polluted areas is proposed in this work. Current satellite DOAS retrievals have relied on using a solar reference spectrum to derive a total slant column, then using either model assimilation or spatial filtering to derive the tropospheric component. In the ERrs-DOAS (Earth radiance reference sector DOAS) algorithm, tropospheric NO_2 slant columns are derived using spectra averaged from measurements over unpolluted regions, thus removing the need for post-hoc separation techniques, though some residual stratospheric biases may still remain. To validate the ERrs-DOAS algorithm, DOAS retrievals were performed on modelled spectra created by the radiative transfer model SCIATRAN, as well as L1B Earth radiance data measured by the NASA/KNMI Ozone Monitoring Instrument (OMI). It was found that retrievals using an Earth radiance reference produce spatial distributions of tropospheric NO_2 over eastern China during June 2005 that highly correlate with those derived using existing retrieval algorithms. Comparisons with slant columns retrieved by the operational NO_2 retrieval algorithm for OMI (OMNO2A) show that the ERrs-DOAS algorithm greatly reduces the presence of artificial across-track biases (stripes) caused by calibration errors, as well as the removal of path length enhancement in off-nadir pixels. Analysis of Pacific SCDs suggests that the algorithm also produces a 27 % reduction in retrieval uncertainty, though this may be partially due to biases introduced by differences in the retrieval algorithm settings. The ERrs-DOAS technique also reveals absorption features over the Sahara and similar regions characteristic of sand and liquid H_2O absorption, as first discovered in the analysis of GOME-2 NO_2 retrievals.

1 Background

Anthropogenic emissions of nitrogen dioxide (NO_2) have been associated with poor health in urban areas; both as a direct contributor to respiratory conditions and as a source of secondary pollutants such as nitric acid (WHO, 2003). Additionally, tropospheric NO_2 through photolysis contributes to tropospheric ozone (O_3) production (Chameides et al., 1992). A significant proportion of NO_2 also exists in the stratosphere, where it is active in processes involved in the creation and destruction of O_3 (Crutzen, 1979).

Since the launch of the GOME instrument in 1996 (Burrows et al., 1999) satellite instruments have been employed to retrieve global tropospheric NO_2 concentrations from Earth radiance spectra. The NO_2 vertical column densities (VCDs) derived from these measurements have been used for a range of applications (Monks and Beirle, 2011), such as determining pollution trends over megacities (e.g. Konovalov et al., 2010; Hilboll et al., 2013), shipping emissions (e.g. Vinken et al., 2014), and to validate air quality models (e.g. Huijnen et al., 2010). Validation of tropospheric NO_2 VCDs from these retrievals are primarily performed through intercomparison campaigns with ground-based or airborne instruments during satellite overpasses. During an overpass the satellite-derived tropospheric NO_2 VCDs are compared with those derived by the ground-based instruments in the ground pixel. Measurements of the ambient NO_2 and aerosol profile are also used to validate the a priori information used in

the satellite VCD calculation (e.g. Hains et al., 2010). However, biases arising from factors such as ground pixel coverage need to be accounted for in order to accurately quantify the precision of the retrieval.

A significant issue in retrieving tropospheric NO_2 from space is that of separating the tropospheric NO_2 VCD from the background stratospheric contribution, which can be a significant source of error (Boersma et al., 2004). In order to remove the presence of stratospheric NO_2 previous retrieval algorithms have relied on either spatial filtering of averaged data (e.g. Bucsela et al., 2006), or on model assimilation (e.g. Boersma et al., 2007).

In the case of some push-broom instruments (e.g. OMI, Levelt et al., 2006) the retrieved slant columns also exhibit non-physical "stripes", which result from across-track biases caused by slight differences in wavelength calibration between adjacent viewing angles. These biases need to be removed by spatial filtering over several adjacent swaths (Boersma et al., 2011; Bucsela et al., 2013).

An implicit part of the DOAS retrievals from these UV/VIS instruments is that the reference spectrum is normally a solar irradiance spectrum, used as a measure of the incoming radiation before attenuation by the atmosphere. One possible alternative would be to use Earth radiance spectra recorded over an unpolluted region as a reference. This type of technique has previously been employed in several DOAS retrievals of trace gases such as IO (Schönhardt et al., 2008) and HCHO (De Smedt et al., 2008). In both cases averaged Earth radiance spectra over the remote Pacific were used, as the background concentration of these gases are expected to be relatively low in that region. Using an Earth radiance reference spectrum is advantageous, in that it also reduces residual instrument noise occurring from differences between spectra measured during the instrument's solar and terrestrial viewing modes. In addition, the technique may help to mitigate the impact the Ring effect (Chance and Spurr, 1997) has on the retrieval, as the radiance spectra have already been subject to some Ring absorption (Schönhardt et al., 2008). However, this effect would be dependent on the magnitude of Raman absorption attenuating the spectra measured over the reference and observed regions, and would be the subject of further study beyond the scope of this work.

The objective of this work is to determine the efficacy of directly retrieving the tropospheric NO_2 slant column density using an unpolluted Earth radiance measured over an unpolluted reference sector (the "ERrs-DOAS" technique) with a reduced need for model assimilation or spatial filtering, and to evaluate any practical benefits that arise from doing so.

1.1 Differential Optical Absorption Spectroscopy (DOAS)

In general, UV/VIS NO_2 retrieval algorithms for spectra from grating spectrometers (e.g. Richter and Burrows, 2002; Sierk et al., 2006; Bucsela et al., 2006) have used the DOAS technique (Platt and Stutz, 2008) to retrieve the slant column densities (SCDs). In the absence of multiple scattering these can be considered to be the integrated trace gas density along the instrument's geometrical line of sight. The technique is based on the principle that a wavelength-dependent absorption signal can be split into two components: the low-frequency, broadband component (representative of features such as aerosol scattering and surface albedo) that can be approximated by a low-order polynomial, and a high-frequency component that is sensitive to trace gas concentrations. In principle the DOAS fit is a least squares fit of the logarithm of the reflectance spectrum (the ratio of the incident and attenuated spectra) over a given wavelength range, using a modified form of the Beer–Lambert law:

$$\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = -\sum_i \sigma_i(\lambda) N_{s,i} + P(\lambda). \quad (1)$$

In Eq. (1) the reference and object spectra are represented by I_0 and I respectively, while $N_{s,i}$ represents the SCD of trace gas i. For satellite retrievals of NO_2 I would be the measured Earth radiance spectra, while solar irradiance spectra measured separately by the instrument would be used as I_0. In this case the retrieved SCD would be the total slant column density along the line of sight.

Limitations in the instrument design may result in the measured spectra having improper spectral calibration, which can adversely affect the quality of the fitted SCD. To remedy this, additional terms representing a necessary shift and stretch in the wavelength grid can also be included in Eq. (1). The resulting solution would then be found through nonlinear least squares fitting of Eq. (1) (Platt and Stutz, 2008).

σ_i represents the absorption cross-section of the ith trace gas considered in this fit, while P represents the low-order polynomial used to account for the broadband structure in the spectra. Ideally, the trace gas absorption cross-sections and wavelength ranges considered in the fit should be such that the cross-sections are orthogonal to each other to give the best result, though in practice this often does not occur, and can be a large source of error in the fit.

In DOAS retrievals of NO_2 from instruments measuring in the UV/Vis range a fitting window is usually selected in the 400–500 nm range. Often used is the 425–450 nm window, which minimises contamination from other species while taking advantage of the distinct NO_2 spectral features present in this region (Sierk et al., 2006; Valks et al., 2011). For OMI measurements a wider fit window of 405–465 nm is used to improve the signal-to-noise and therewith improve the fit (Bucsela et al., 2006; van Geffen et al., 2014). For GOME-2 spectra the use of the window 425–497 nm has been tested successfully (Richter et al., 2011).

In addition to NO_2, trace gas absorption cross-sections such as O_3, H_2O and the O_2–O_2 collision complex within the UV/Vis range have also been included in the fit to account for other sources of absorption in the spectra. Furthermore, a synthetic cross-section to account for absorption caused

by rotational Raman scattering (the Ring effect; Chance and Spurr, 1997) is also included in the fit.

SCDs retrieved by DOAS still need to be weighted in order to account for enhancement owing to factors such as optical path length, scattering from clouds/aerosols, and surface albedo. To that end, the SCDs are divided by an air mass factor (AMF) to convert them into VCDs (e.g. Boersma et al., 2004). The AMFs are in turn created by inputting forward model parameters describing local conditions such as surface albedo, trace gas profile information and cloud cover into a radiative transport model (RTM). Quantifying the uncertainty in the forward model parameters is important for determining the final retrieval error of the derived VCDs (Boersma et al., 2004).

1.2 The Ozone Monitoring Instrument (OMI)

Launched in 2004 onboard the NASA AURA satellite, the Ozone Monitoring Instrument (OMI, Levelt et al., 2006) produces tropospheric NO_2 VCDs at a near-urban spatial resolution (nadir pixel size: $13 \times 24\,km^2$, though in its spatial zoom modes this can be reduced to $13 \times 12\,km^2$ or even $13 \times 3\,km^2$, as discussed in Valin et al., 2011). As a push-broom spectrometer, OMI has a swath width of 2600 km which is divided into 60 across-track pixels. Each pixel corresponds to a separate viewing angle. OMI follows a sun-synchronous orbit, with a local overpass time of approximately 13:45. The instrument's visible channel has a 350–500 nm spectral range, with an average spectral resolution of 0.63 nm.

The process of deriving tropospheric NO_2 VCDs from the Level 1B Earth radiance data (OML1BRVG product, see Sect. 2) via DOAS is briefly described in this section. In the operational OMI DOAS slant column retrieval algorithm OMNO2A (Bucsela et al., 2006; van Geffen et al., 2014), the Earth radiance reflectance spectra are fitted using a 405–465 nm fitting window. The reflectance spectra are fitted with absorption cross-sections for NO_2, O_3 and H_2O, as well as a fifth-order polynomial to account for broadband variations (see Table 1).

In the OMNO2A algorithm the Ring effect is treated differently compared with traditional DOAS retrievals. In this case the Ring effect is treated as a source of photons, rather than a pseudo-absorber. Because of this, the algorithm performs a nonlinear least squares fit using the following equation:

$$\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = P(\lambda)\exp\left[\left(-\sum_i \sigma_i N_{s,i}\right)\right] \times \left(1 + \frac{C_{RING} I_{RING}(\lambda)}{I_0(\lambda)}\right). \quad (2)$$

In Eq. (2) P represents a fifth-order polynomial, while the I_{RING} term is the Ring radiance spectrum, I_0 is the measured solar irradiance spectrum, and C_{RING} is the Ring absorption coefficient determined by the fit.

There are currently two operational algorithms that process the SCDs retrieved by OMNO2A into tropospheric NO_2 VCDs; brief descriptions of each are given below.

1.2.1 Standard Product (OMNO2, v 2.1, NASA)

After an initial geometric AMF is applied to the SCD, the stratospheric NO_2 VCD is estimated by first masking polluted regions and then interpolating from known unpolluted regions to compute the smoothly varying stratospheric background. After subtracting this component a tropospheric AMF is calculated using profile data from the Global Monitoring Initiative (GMI) Chemical Transport Model (CTM), along with scattering weights derived from the TOMS radiative transfer model (TOMRAD) and terrain albedo derived from OMI reflectance data (Kleipool et al., 2008). AMFs are weighted for cloud cover using cloud fraction data from the OMI O_2–O_2 cloud algorithm (OMCLDO2, Acarreta et al., 2004). See Bucsela et al. (2013, 2006) and Celarier et al. (2013) for more details.

1.2.2 Derivation of OMI Tropospheric NO_2 Product (DOMINO, v 2.0, KNMI)

In the DOMINO algorithm the stratospheric SCD is derived by assimilating the retrieved SCD in the TM4 global CTM (Boersma et al., 2007). As in the Standard Product, the resulting tropospheric VCD is calculated using an AMF using similar data sets for terrain albedo, and cloud fractions, while the NO_2 profiles and scattering weights are derived from TM4 model runs and the DAK radiative transfer (RTM) model. The assimilated stratospheric NO_2 SCD has been validated by comparing assimilated data with independent ground-based measurements (Dirksen et al., 2011). See Boersma et al. (2007, 2011) for more details.

1.2.3 Across-track variability ("striping")

It has been previously noted that NO_2 VCDs retrieved by OMI show systematic enhancements over specific viewing angles ("stripes"). These stripes do not correspond to any known geophysical behaviour, and were found to be a result of a combination of solar diffusor features and noise in solar irradiance measurements (Veihelmann and Kleipool, 2006). These features result in slight differences in wavelength calibration between the 60 across-track viewing angles, which in turn result in unknown offsets in the DOAS fits dependent on the viewing zenith angle (VZA). Therefore, these features need to be empirically corrected after the retrieval. In order to suppress these stripes the daily solar irradiance spectra used in the DOAS fit was instead replaced with a composite of all solar irradiance measurements during 2005. Additionally, current retrievals attempt to filter these defects by compar-

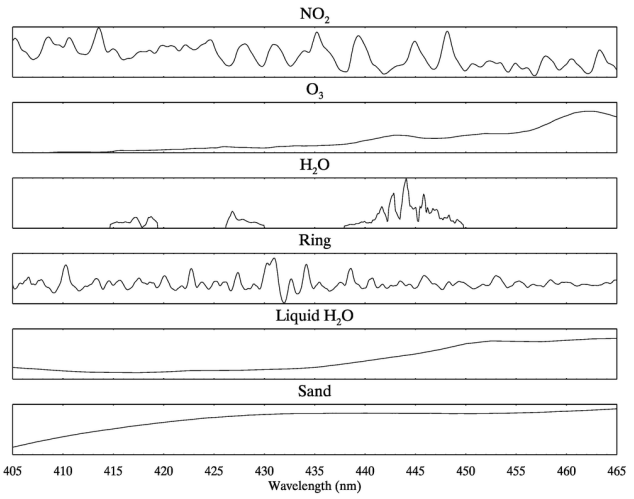

Figure 1. The absorption cross-sections used in this work (see Table 1).

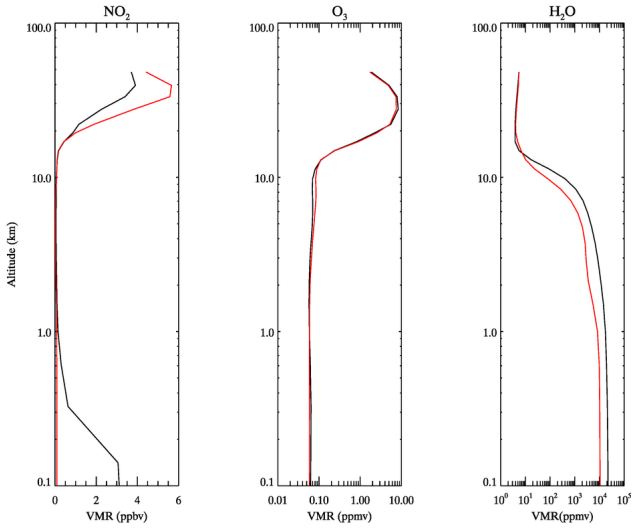

Figure 2. Atmospheric volume mixing ratio (VMR) profiles used in the modelled spectra retrieval for the polluted China (black) and the clean Pacific (red) scenarios. The profiles were taken from Veefkind (2009).

ing the background NO_2 field over several adjacent orbits (Boersma et al., 2011; Celarier et al., 2008).

2 Method

The QDOAS software package (v 2.1, http://uv-vis.aeronomie.be/software/QDOAS/, last access: 1 October 2013; Fayt et al., 2013) was employed to perform the DOAS fits in this investigation. This software package has typically been used in the past to process spectral data from ground-based and airborne observations (e.g. Vlemmix et al., 2011; Popp et al., 2012), as well as in retrievals using satellite data (e.g. Hewson et al., 2013). A summary of all absorption cross-sections used in this paper is included in Table 1 and Fig. 1.

As with the OMNO2A algorithm, the fitting window for all DOAS fits in this work is expanded to 405–465 nm in order to minimise the effect of instrument noise on the retrieval (Boersma et al., 2007). All DOAS retrievals for this work were performed using optical density fitting, in which Eq. (1) was solved using a nonlinear least squares fit. In all fits a second-order stretch function was applied to the spectra, along with a linear wavelength shift. No further wavelength calibration was applied to the reference spectra outside of the linear offset determined by the OMNO2A algorithm (see Sect. 2.2).

2.1 Retrieval using modelled spectra

The goal of this first effort was to demonstrate the theoretical possibility of using an Earth radiance reference in the DOAS fit and show in the absence of noise, aerosol and trace gas contamination that the Earth radiance-retrieved SCD is the difference in NO_2 between the reference and observed region. In order to demonstrate the validity of using Earth radiance reference spectra to retrieve tropospheric NO_2, the SCIATRAN RTM (v 3.1.27, Rozanov et al., 2005) was used to simulate spectra that may typically be observed over the Pacific and China. Vertical profile data for temperature, NO_2, O_3 and H_2O in these scenarios was provided by the CAMELOT data set (Veefkind, 2009) and are summarised in Fig. 2. The Pacific is relatively free of tropospheric NO_2, which theoretically makes it possible for spectra taken over this region to be used as an estimation of the local stratospheric field over a given location.

An Earth radiance spectrum from the Pacific and polluted Chinese scenarios was modelled, with absorption due to O_2-O_2 provided by a profile created by SCIATRAN from the pressure profile. Absorption from the Ring effect was calculated by SCIATRAN using the algorithm developed by Vountas et al. (1998). While no aerosol information was included, the solar zenith angle in either scenario was varied between 0–80° in order to demonstrate the retrieval's accuracy at different diurnal ranges. DOAS fits were carried out on all spectra, using a solar irradiance spectrum as a reference. For Chinese scenarios, the Pacific Earth radiance spectrum was used as a reference as well. The results of this study are discussed in Sect. 3.1.

2.2 Retrieval using OMI L1B spectral data

In order to test the validity of the ERrs-DOAS technique using operational satellite spectra, data from the OML1BRVG (collection 3, Van den Oord et al., 2006; Dobber et al., 2008a) product were used to provide the calibrated, wavelength-corrected spectra for both the reference and ob-

ject spectra in the DOAS retrieval in this work. Data regarding the ground pixel quality (e.g. cloud cover, surface albedo) were provided by the DOMINO (v. 2.0) product. Tropospheric SCDs retrieved by DOMINO were used to compare with the retrieved NO_2, though these had to be reconstructed using the "TroposphericVerticalColumn" and "AirMassFactorTropospheric" fields in the DOMINO data product. Similarly, the tropospheric SCDs retrieved by OMNO2 were derived from the "ColumnAmountNO2Trop" and "AmfTrop" fields in the OMNO2 data product, while the OMNO2A total SCDs were taken from the "SlantColumnAmountNO2" field. For most of this work only data collected before 2008 were considered, as this was largely before the emergence of the "row anomaly" artefacts that have affected OMI data coverage since 2007 (Braak, 2010). All cross-sections used were convolved with the OMI slit function prior to the DOAS fit (Dobber et al., 2005).

Prior to the DOAS fit, the reference spectrum is interpolated onto the same wavelength grid as the observed Earth radiance spectrum using the same interpolation technique as used in Bucsela et al. (2006). The interpolated reference spectrum $I_{0,\lambda(\mathrm{ES})}$ is calculated using the following equation:

$$I_{0,\lambda(\mathrm{ES})} = I_{0,\lambda(\mathrm{REF})} \frac{F_{\lambda(\mathrm{REF})}}{F_{\lambda(\mathrm{ES})}}. \quad (3)$$

First, a high-resolution oversampled solar atlas that is convolved to the OMI instrument line shape (Dobber et al., 2008b) is interpolated onto both the reference and radiance spectra wavelength grids ($F_{\lambda(\mathrm{REF})}$ and $F_{\lambda(\mathrm{ES})}$ respectively) using cubic spline interpolation. The ratio of these interpolated spectra is then multiplied by the intensity of the solar irradiance, which therefore gives the desired interpolation.

A wavelength correction is applied to the Earth radiance spectra before the DOAS fit, in order to correct for shifts caused by cloudy scenes (Voors et al., 2006). The correction is performed as a single offset, calculated from comparing the 408–423 nm spectral window to the high resolution solar atlas (van Geffen et al., 2014). The offsets applied for each OMI ground pixel can be found in the "WavelengthRegistrationCheck" field in the OMNO2 product. Additionally, spectral pixels flagged as being affected by instrumental defects such as random telegraph signals or dark current behaviour were removed prior to the DOAS fit (Van den Oord et al., 2006). In QDOAS this removal can be performed by specifying gaps in the spectral window which are then ignored in the analysis.

3 Results

3.1 ERrs-DOAS retrievals of modelled polluted Chinese spectra

The results from the ERrs-DOAS fits of modelled CAMELOT spectra (see Sect. 2.1) are discussed herein. As shown in Fig. 3, for all solar zenith angles considered the SCD retrieved by DOAS fitting spectra from the Chinese scenario using a Pacific Earth radiance reference was near-identical to the difference in the modelled total SCD between the two scenarios. From Fig. 2 it appears that the difference in SCD is largely due to differences in tropospheric NO_2, though the difference in stratospheric NO_2 between the two scenarios would also greatly contribute to the retrieved SCD. Ideally, the reference spectra should be collected from a region where the stratospheric NO_2 is similar to the target region to minimise this bias.

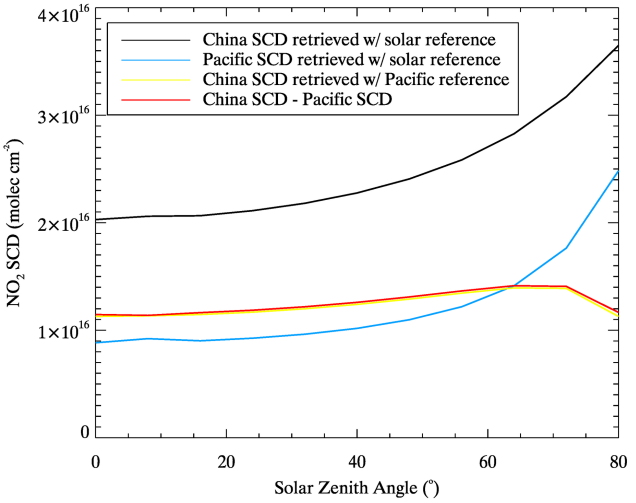

Figure 3. The retrieved NO_2 SCDs from DOAS fitting spectra modelled using SCIATRAN based on the Pacific and Chinese CAMELOT scenarios (Fig. 2) using a range of solar zenith angles (SZA). The red curve indicates the difference between the total SCD of the Pacific and Chinese scenarios directly modelled by SCIATRAN, while the other curves show the SCDs retrieved by using a solar or Earth radiance reference spectrum in the DOAS fit.

3.2 Residual bias in QDOAS retrieval estimation using OMI spectra

Prior to comparing tropospheric SCDs in satellite data, it is essential to determine any inherent biases present in the retrieval algorithm, as QDOAS performs DOAS fits differently to OMNO2A. QDOAS performs a nonlinear DOAS fit by solving a variant of Eq. (1), in which the Ring is treated as a pseudo-absorber like other trace gases, and no treatment of elastic scattering is considered. To determine the magnitude of possible biases resulting from these differing assumptions a comparison exercise was established. As with the OMNO2A retrieval, a composite set of solar irradiance reference spectra derived from OMI irradiance data (OML1BIRR, collection 3, Van den Oord et al., 2006) taken during 2005 were used in this initial test. These were used to retrieve total NO_2 SCDs in cloud-free regions (i.e. pixel cloud fraction $< 25\,\%$) over the whole globe during June 2005, using the

Table 1. The absorption cross-sections used in the DOAS fits for this work. N/A: not applicable.

Species	Reference (SCIATRAN, Sect. 2.1)	Reference (OMI, OMNO2A)	Reference (OMI, Earth radiance reference, Sect. 3.3)
NO_2 (220 K)	Vandaele et al. (1998)	Vandaele et al. (1998)	Vandaele et al. (1998)
O_3	Bogumil et al. (1999)	Bass and Johnsten (1975)	Bass and Johnsten (1975)
H_2O	Rothman et al. (2009)	Rothman et al. (2005)	Rothman et al. (2005)
Ring	Vountas et al. (1998)	Chance and Spurr (1997)	Chance and Spurr (1997)
Polynomial	3rd order	5th order	3rd order
H_2O (liquid)	N/A	N/A	Pope and Fry (1997)
Sand	N/A	N/A	Richter et al. (2011)

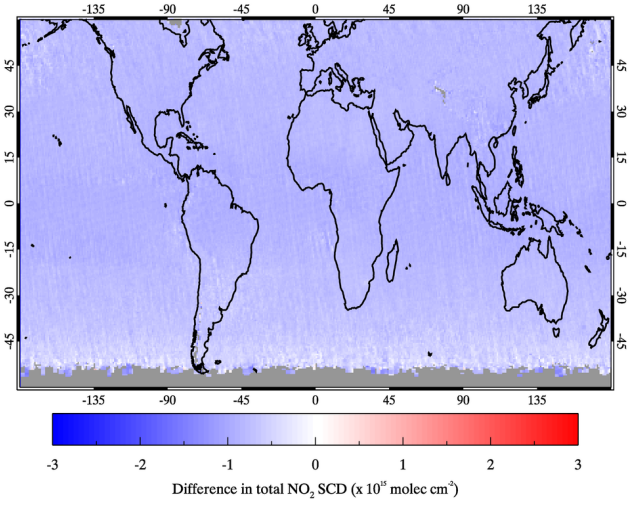

Figure 4. Average total NO_2 SCD bias between the QDOAS-based solar reference retrieval and the OMNO2A algorithm for cloud-free (cloud fraction < 25 %) scenes during June 2005.

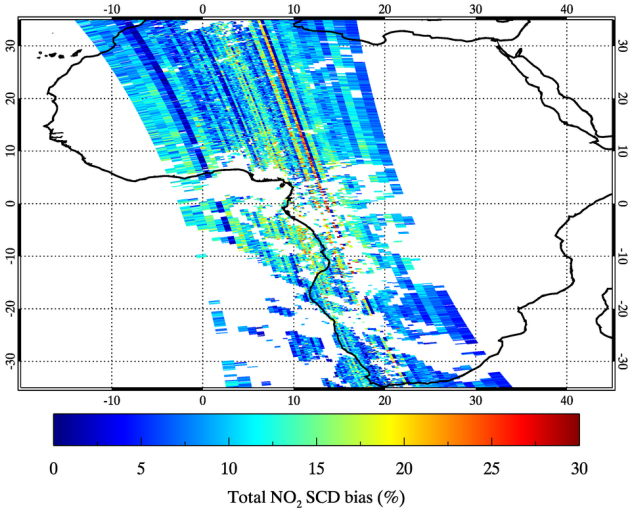

Figure 5. The normalised magnitude of the bias between the total NO_2 SCD retrieved using the OMNO2A algorithm and the QDOAS-based solar reference retrieval. Cloud-free pixels (cloud fraction < 25 %) were compared. The Earth radiance L1B data was taken from orbit no. 06644. (OML1BRVG).

retrieval parameters shown in Table 1, as care was taken to ensure that the cross-sections, interpolation method and retrieval settings employed were a close approximation to those used in the current OMNO2A retrieval (v2006; van Geffen et al., 2014). The resulting SCDs and uncertainties were then compared with those retrieved by OMNO2A, as shown in Fig. 4.

The results show an almost constant negative SCD bias between the QDOAS-based retrieval and OMNO2A over all regions (average SCD bias $\sim -1.0 \times 10^{15}$ molec cm^{-2}). There appear to be no geospatial features other than a slightly stronger bias over mountainous regions, potentially due to possible retrieval sensitivity to surface albedo. The lack of spatial features suggests that this bias is the result of some flaw in the retrieval algorithm, rather than any unforeseen geophysical process. A similar bias has previously been reported in other comparisons between OMNO2A and QDOAS-based retrievals, which appears to be resolved in part through better wavelength and slit function calibration (van Geffen et al., 2014).

Additionally, the bias also exhibits a strong across-track variation, as shown in Fig. 5. The reason for this effect is currently unknown. One possible cause could be how QDOAS treats spectral pixels flagged for removal due to random telegraph signals or dark current behaviour (Van den Oord et al., 2006); the number of pixels that need to be removed from the DOAS fit for this reason varies between across-track pixels, which may add to the bias caused by the retrieval algorithm differences.

As a result, comparisons between the retrievals covered in this paper with existing retrievals were conducted using only ground pixels in which the QDOAS-based retrieval using solar reference spectra produced total SCDs that were within 5 % of the total SCDs produced by OMNO2A. It was assumed that ERrs-DOAS retrievals of NO_2 over such pixels using the QDOAS software would be representative of what would be retrieved if the ERrs-DOAS fits were performed us-

ing the OMNO2A algorithm, as they would be relatively free from this bias.

3.3 DOAS retrieval using Earth radiance reference spectra

The cross-sections used in this study are identical to those used in the OMNO2A retrieval (see Table 1). Following preliminary testing over the Sahara desert (see Sect. 3.3.2), cross-sections for sand and liquid H_2O were also included in the ERrs-DOAS fit.

For the first phase of this study Earth radiance spectra recorded during June 2005 were considered. Daily Earth radiance data from a Pacific reference sector (125–180° W, 60° S–60° N) over this month were binned into a set of 60 reference spectra for each OMI viewing angle, as the stratospheric NO_2 present in the observed spectrum will be highly dependent on the scattering path length, and so the viewing geometry. Consequently, all DOAS retrievals were performed using reference spectra measured at the same viewing angle as the observed radiance spectra. To account for latitudinal gradient in stratospheric NO_2 and SZA the spectra were also binned into 1° latitude bins, such that DOAS retrievals of Earth radiance spectra observed over the rest of the planet made use of the reference spectra obtained from the closest latitude bin.

Using a latitudinal reference sector also resolves potential biases resulting from changes in SZA between the reference and observed region. Observations made with high SZAs will be more sensitive to the stratosphere due to an increase the mean scattering height (Hendrick et al., 2004; Preston et al., 1997), which may result in unforseen stratospheric contamination in the SCDs retrieved with this method. However, as OMI follows a sun-synchronous orbit, the ground pixel SZA is dependent on latitude and season. As a result, using a daily, latitudinally binned reference spectrum means that the difference in SZA between the reference and observed region will be negligible, so this effect will be negated.

The choice of reference sector and frequency of data collection will result in unknown uncertainties affecting the overall retrieval accuracy. For instance, pollution transport events (e.g. outflow from the mainland) will result in a negative bias exhibited in the retrieved SCDs. The static reference sector used in this work was to maximise the number of usable spectra which could be binned at all latitudes. Similarly, the temporal frequency of the binned reference spectra will also contribute to the retrieval uncertainty (e.g. accounting for seasonal variation in the stratospheric field). An operational algorithm will therefore need to automatically select remote regions which are assumed to be free of such contamination; possible selection methods are discussed in Sect. 4.

It was determined that only spectra that were measured over largely cloud-free scenes (i.e. cloud fraction $< 25\,\%$) would be binned to this data set. Scattering from clouds would lead to inhomogeneous illumination of the OMI entrance slit, which in turn leads to a change in the position and shape of the instrument slit function. The change in the slit function then results in an observed shift in the wavelength mapping of the Fraunhofer lines on the detector (Voors et al., 2006). As the DOAS fit depends on good wavelength calibration, cloudy pixels would need to be avoided to obtain the best possible result in this work. As well as this, using cloudy scenes would otherwise introduce a cloud height dependence on the inherent stratospheric NO_2 retrieved.

As shown in Fig. 6a and b the ERrs-DOAS retrieval shows good agreement with tropospheric SCDs retrieved by DOMINO, particularly showing good spatial similarity with megacities and regions with known anthropogenic activity (e.g. mining), as well as possible biomass burning over central Africa. Overall, the retrieved SCDs highly correlate with those retrieved by the operational DOMINO product ($r^2 = 0.85$), particularly over heavily polluted regions such as China ($r^2 = 0.96$, 0.99 for SCDs $> 1.0 \times 10^{16}$ molec cm^{-2}).

However, the retrieval produces significant, broad negative biases over remote regions such as Tibet, particularly at higher northern latitudes over land. This is potentially due to undersampling of reference spectra in the Pacific reference sector resulting from excessive cloud cover at those latitudes, which would result in a degradation in the quality of the DOAS fit and an underestimation of the local stratospheric field; both factors would result in lower SCDs retrieved.

As well as this, Fig. 6d shows that the stratospheric NO_2 field varies considerably with longitude at the latitudes where this bias appears. This variation is especially pronounced in the Pacific reference sector, which has higher stratospheric SCDs compared with other longitudes. The increased NO_2 absorption present in the reference sector would therefore lead to lower tropospheric SCDs retrieved over other areas.

One particularly significant positive bias appears over the region (70° W–160° E, 16–22° S) and the Southern Atlantic Ocean, in which the retrieval overestimates the magnitude and spatial spread of the tropospheric NO_2 band that is detected in the DOMINO retrieval (Fig. 6b). According to the assimilated stratospheric NO_2 available from DOMINO (Fig. 6d) these regions had considerable longitudinal variation in stratospheric fields compared with the Pacific reference sector, which would result in the Pacific reference sector being an underestimate of the local stratospheric field. Both of these cases show the need to accurately estimate the stratospheric NO_2 field and to have enough cloud-free measurements in the reference sector in order for this type of retrieval to be successful.

3.3.1 Effect of cloud screening on retrieval performance

The 25 % cloud fraction threshold for the reference spectra binning in this work was chosen as a compromise between ensuring maximum data availability over the Pacific and minimising cloud contamination. However, cloud cover at this

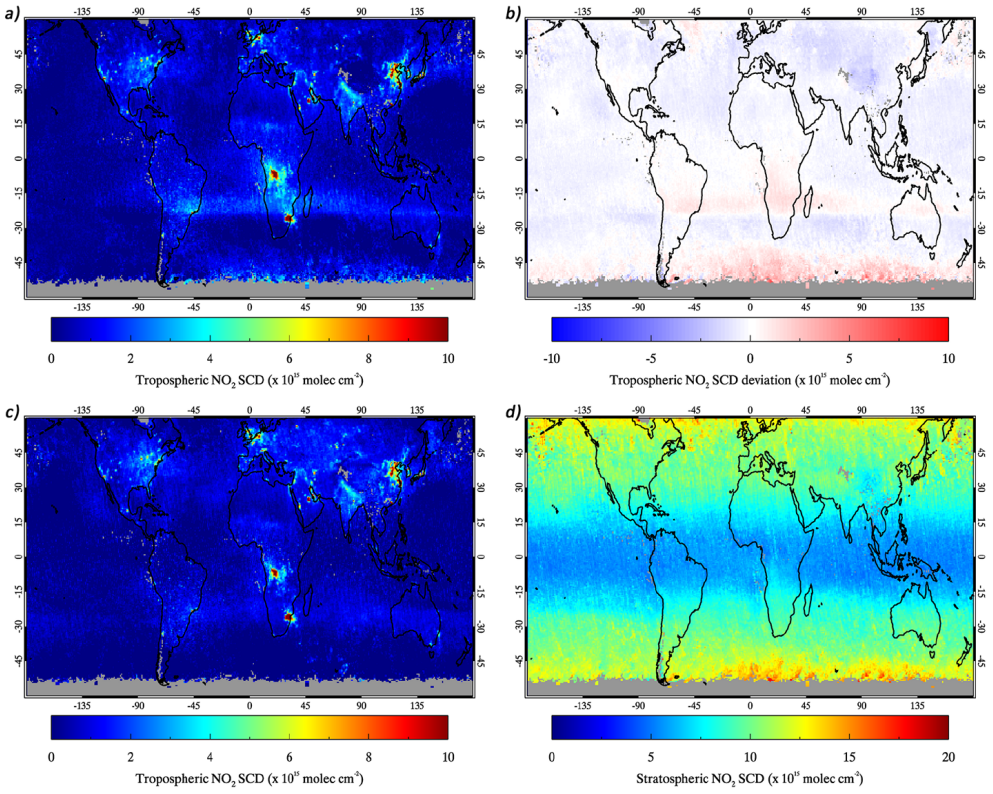

Figure 6. Comparison of average tropospheric NO_2 SCD retrieved during June 2005 using the ERrs-DOAS technique with DOMINO. **(a)** Average tropospheric NO_2 SCD retrieved using an Earth radiance reference. **(b)** Average bias between Earth radiance retrieval and DOMINO tropospheric SCD. **(c)** Average tropospheric NO_2 SCD retrieved by DOMINO. **(d)** Average stratospheric NO_2 SCD retrieved by DOMINO.

threshold may still be a significant contaminant, and so may still affect the ERrs-DOAS retrieval accuracy.

To investigate the effect of a more restrictive reference sector cloud threshold, a comparison exercise was performed. SCDs retrieved using the ERrs-DOAS algorithm over China (15–55° N, 100–135° E) were compared with those retrieved when the reference sector cloud threshold was set to 10 %. It was found that reducing the cloud threshold resulted in a mean rms rise of 6.9 %, and a mean SCD rise of 4.0 %. However, no significant spatial variation in the tropospheric field was observed by this change, which suggests that no further information over polluted regions is gained by choosing a smaller cloud threshold.

3.3.2 Existence of sand and liquid H_2O absorption features

Preliminary DOAS fits using only the existing OMNO2A cross-sections and fifth-order polynomial (see column 2 of Table 1) revealed that using an Earth radiance reference produces anomalously high root mean square (rms) error values over regions such as the Sahara and Namibian deserts, as well as the Atlantic and Pacific oceans. The fine structure present in the residual spectra retrieved over these regions suggested that another absorber unaccounted for by the DOAS fit may be present over these regions. The spatial ranges of these anomalous regions appear to be similar to those encountered by Richter et al. (2011) when investigating improvements to the GOME-2 tropospheric NO_2 retrieval.

The ERrs-DOAS retrieval adds a liquid H_2O and sand (empirically measured using GOME-2 spectra, Richter et al., 2011) absorption cross-section to the DOAS fit and reduces the polynomial order from 5 to 3. It was found that this change in retrieval settings reduced the rms over deserts and oceans to background values. Figure 1 shows that these absorption cross-sections are sufficiently different from purely polynomial functions, and so may not be accounted for by the polynomial term used in the fit.

To illustrate this effect tropospheric NO_2 SCDs were retrieved from OMI spectra recorded over the Sahara desert during June 2005 using an Earth radiance reference with these added cross-sections. The rms of the ERrs-DOAS fits were compared with those resulting from DOAS fits with an Earth radiance reference, but using only the same cross-sections and fifth-order polynomial used in OMNO2A (see Table 1). As shown in Fig. 7, the addition of the sand and liquid H_2O cross-sections and reduction in polynomial order resulted in a reduction in rms over the whole region. Overall,

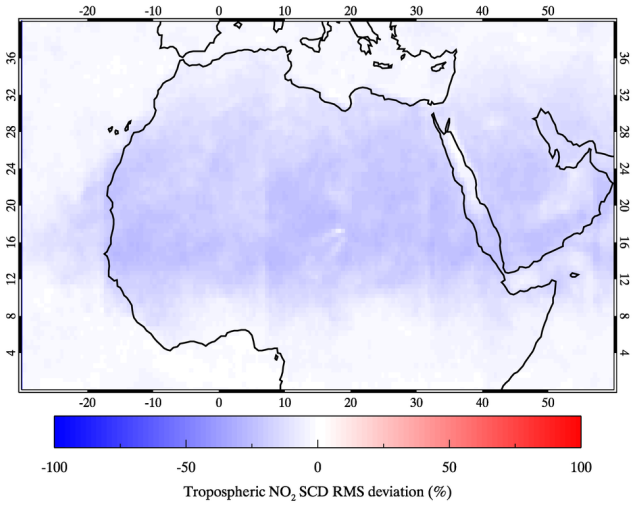

Figure 7. The change in rms resulting from adding the sand and liquid H_2O absorption cross-sections to the Earth radiance reference DOAS fit. DOAS fits for OMI spectra measured over the Sahara desert during June 2005 were performed using a Pacific Earth radiance reference with and without the sand and liquid H_2O absorption cross-section included (see Table 1).

the addition of the liquid H_2O and sand cross-sections and reducing the polynomial order lead to an 11 % decrease in the rms and a corresponding 6.3 % rise in NO_2 SCD over the Sahara.

It is possible that at least part of this rms decrease could be attributed to the change in polynomial order. To determine this, another comparison exercise was performed over the Sahara to determine the impact in reducing the polynomial order from 5 to 3. The ERrs-DOAS retrievals were compared with those made using the same cross-sections, only with the polynomial order set to 5. It was found that only reducing the polynomial order resulted in an rms increase of 6.7 %, and an NO_2 SCD increase of 5 %. No change in the spatial distribution of the sand, liquid H_2O, and NO_2 SCDs were observed because of this change, suggesting that the polynomial order does not affect the retrieval sensitivity to local features.

The mean ERrs-DOAS retrieved liquid H_2O and sand fit coefficients during June 2005 are shown in Fig. 8. These plots show a remarkable spatial similarity with the GOME-2 retrieval results of Richter et al. (2011), which suggests that accounting for this contamination will need to be addressed in future instrument and retrieval designs. Despite this similarity, there are also anomalously high liquid H_2O and sand fit coefficients retrieved over extreme northern latitudes. As with the negative NO_2 bias at these latitudes this could potentially be the result of artefacts introduced by having undersampled reference spectra at the corresponding Pacific reference sectors.

3.4 Urban transect comparison

In order to determine the sensitivity of this retrieval to the relative difference in NO_2 between urban and rural areas a comparison exercise was undertaken between the ERrs-DOAS, OMNO2 and DOMINO retrievals. As shown in Fig. 9, the mean tropospheric NO_2 SCDs retrieved during June 2005 are selected over a latitudinal transect across China, from Hong Kong to Inner Mongolia (20–50° N, 114° E). The average tropospheric SCD retrieved using an Earth radiance reference spectrum during June 2005 is compared with that retrieved by the DOMINO and OMNO2 algorithms.

The Earth radiance reference retrieval demonstrates sensitivity to NO_2 enhancement over urban areas, as the latitudinal variation is very similar to that exhibited by the DOMINO and OMNO2 transects. Over the Pearl River Delta (23° N) the SCDs retrieved by all three algorithms appear to be nearly identical, while enhancement over other urban areas is also detected by the Earth radiance retrieval and shows good agreement with the other algorithms. However, further along the transect there is a consistent negative offset associated with the Earth radiance retrieval, particularly over Inner Mongolia (45–50° N), though this bias appears to be largely within the mean uncertainty of the DOAS fit as reported by QDOAS. The residual bias is likely the result of longitudinal differences in stratospheric NO_2 over the Pacific reference sector and China, which could not be accounted for when collecting reference spectra. Residual biases arising from differences between the OMNO2A and QDOAS algorithms would also contribute to the discrepancy. Despite the presence of such biases, the sensitivity to tropospheric NO_2 variability demonstrates that this technique could be used to retrieve spatially resolved tropospheric NO_2 over urban areas.

3.5 Retrieval using local reference sector over South Africa

A significant issue when using reference spectra from a single location is that differences in the local tropospheric and stratospheric NO_2 field can lead to substantial biases in estimating tropospheric NO_2 over other longitudes. One possible solution is to use reference spectra from an area closer to the region of interest in order to provide a better representation of the local stratospheric field. Such regions may also be comparatively cloud-free, which would lead to better sampling of reference spectra. To determine the validity of this technique a comparison exercise is set up over a region covering South Africa. This region is particularly interesting as South Africa has the largest industrialised economy in Africa, with major cities and anthropogenic activities such as mining and agriculture primarily centred around Bushveld and Highveld. Because of this, these regions are considered to be air quality hotspots, and have been the subject of several studies to determine the impact emissions from these regions have on

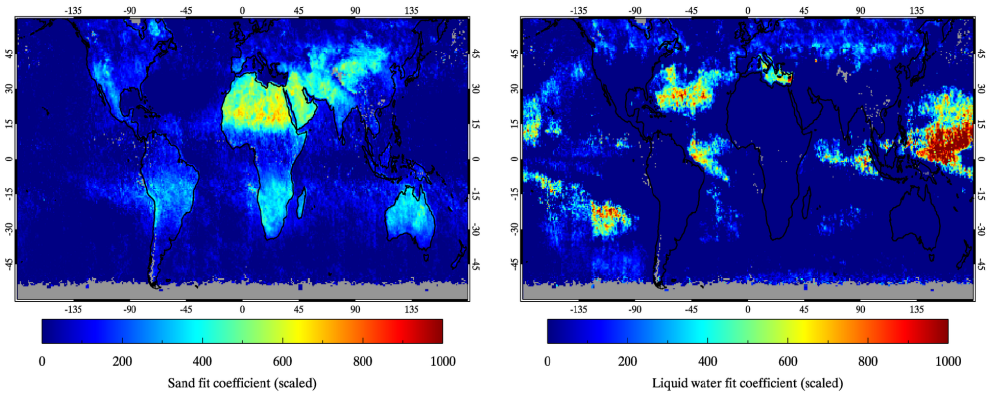

Figure 8. Average tropospheric sand (left) and liquid H_2O (right) fit coefficient retrieved using Earth radiance reference DOAS during June 2005. Note that only positive SCDs have been plotted, and have been scaled to arbitrary values.

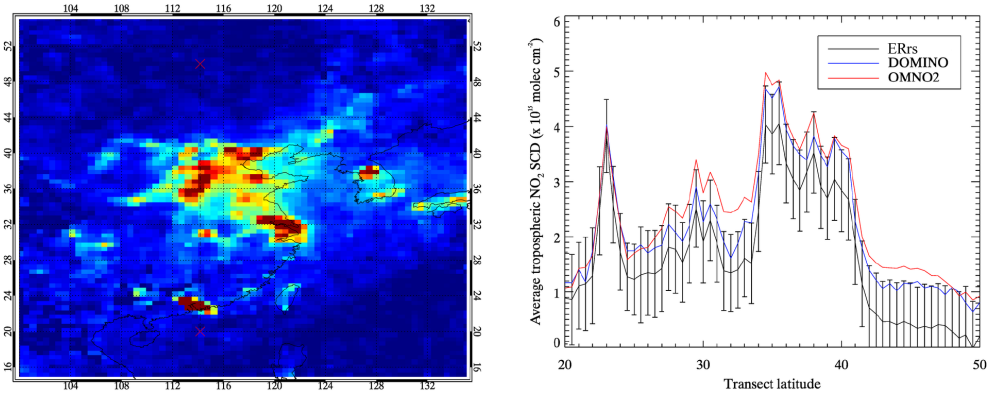

Figure 9. The mean tropospheric NO_2 SCD retrieved over the transect (20–50° N, 114° E) during June 2005. The mean tropospheric SCD retrieved by DOMINO (left, also showing the transect coordinates) was compared with that retrieved using the OMNO2 algorithm and the Earth radiance reference method (right). The error bars are the mean uncertainty of the SCDs retrieved using an Earth radiance reference, as calculated by QDOAS (Fayt et al., 2013).

ambient air quality (e.g. Josipovic et al., 2010; Lourens et al., 2011; Venter et al., 2012). The region is an ideal candidate for determining the impact of this technique on retrieval accuracy, as it is distant from other NO_2 sources which allows for both point sources and pollution transport to be clearly visible.

For this study Earth radiance spectra measured during June 2005 are analysed over the region (20–40° S, 50° W–80° E). Here, the Earth radiance reference spectra are instead collected from the South Atlantic (20–40° S, 0° W–30° E) for use in the DOAS fit. The reference region was chosen as it was close to the region of interest, while still being distant enough to avoid tropospheric contamination from pollution transport. Figure 10 shows a comparison between tropospheric SCDs retrieved using this reference sector, the Pacific reference sector and the DOMINO product. Using a nearby reference sector improves correlation with the DOMINO results, while removing the longitudinal bias present beyond $\sim$ 23° S.

3.6 Improvement in striping reduction

In order to determine the impact the ERrs-DOAS technique has on removing across-track striping, all retrievals in a single OMI swath from a region in the Pacific deemed to be distant from tropospheric pollution sources and the reference sector (30° S–5° N, 90–130° W) are analysed. All SCDs retrieved using the multiple Earth radiance reference algorithms over this region for each viewing angle are averaged to form a single data set. The mean is then subtracted in order to determine the across-track variability between pixels. This is then repeated with corresponding data from DOMINO and OMNO2.

As shown in Fig. 11, the reduction in across-track variability when using multiple Earth radiance reference spectra is greater than the existing destriping algorithms used by OMNO2 and DOMINO, suggesting that this technique could be used to account for biases resulting from instrument design without post hoc filtering. The flat curve of the ERrs-DOAS data also shows that using an Earth radiance reference

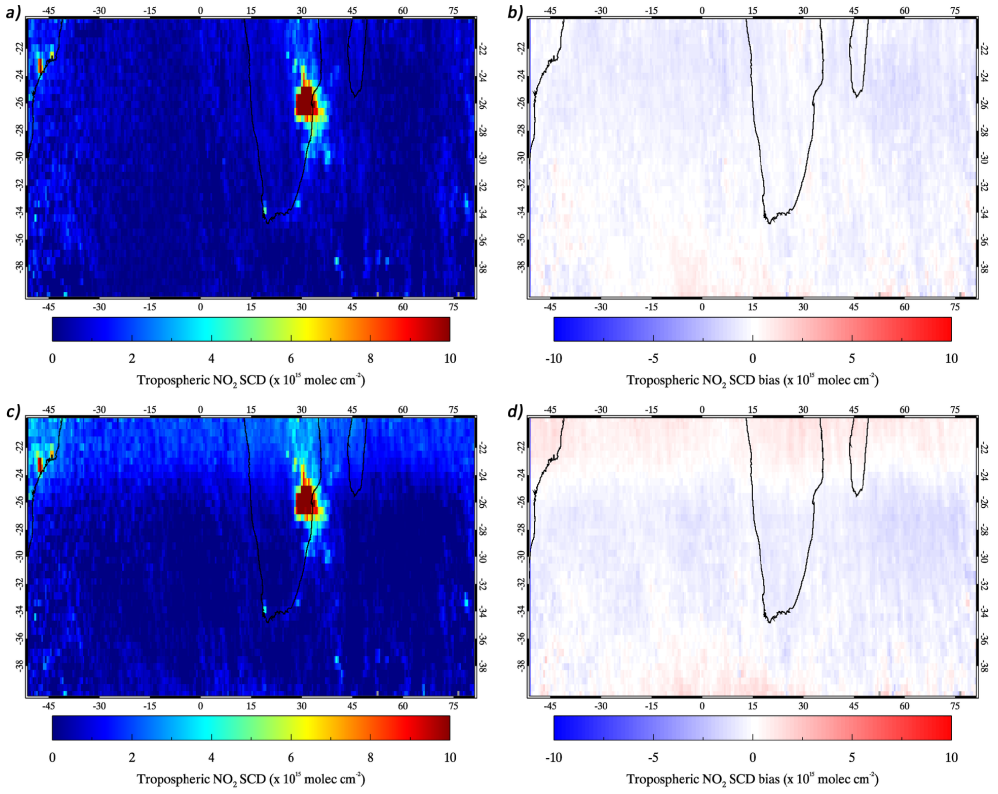

Figure 10. Comparison of tropospheric NO_2 SCDs retrieved over South Africa (20–40° S, 50° W–80° E) using Pacific and South Atlantic reference spectra with DOMINO. **(a)** Average tropospheric NO_2 SCD retrieved using a S. Atlantic Earth radiance reference. **(b)** Average bias between S. Atlantic Earth radiance retrieval and DOMINO tropospheric SCD. **(c)** Average tropospheric NO_2 SCD retrieved using a Pacific Earth radiance reference spectrum. **(d)** Average bias between Pacific Earth radiance retrieval and DOMINO tropospheric SCD.

removes the geometric enhancement of the SCD introduced by off-nadir viewing geometry which is still present in the other curves. The latitudinal reference sector and viewing angle binning ensures that the reference and observed spectra have been measured in similar viewing geometries. Therefore, the enhancement due to path length difference should be nearly identical and so is inherently removed from the retrieved SCD. Traditionally, this enhancement is removed as part of the AMF computation, so VCD estimation based on the ERrs-DOAS technique may require AMFs to only be computed assuming nadir viewing conditions because of this effect.

3.7 SCD uncertainty estimation

In order to determine the effect of random noise on the retrievals a statistical approach similar to those conducted by Richter et al. (2011) and Valks et al. (2011) is adopted. An area over the Pacific that was assumed to be relatively unpolluted is chosen (100–120° W, 10° N–10° S) and the tropospheric NO_2 retrieved during June 2005 is analysed. It is assumed that the stratospheric NO_2 over this region and timescale is both temporally and spatially invariant, so that the spread in these measurements would primarily originate

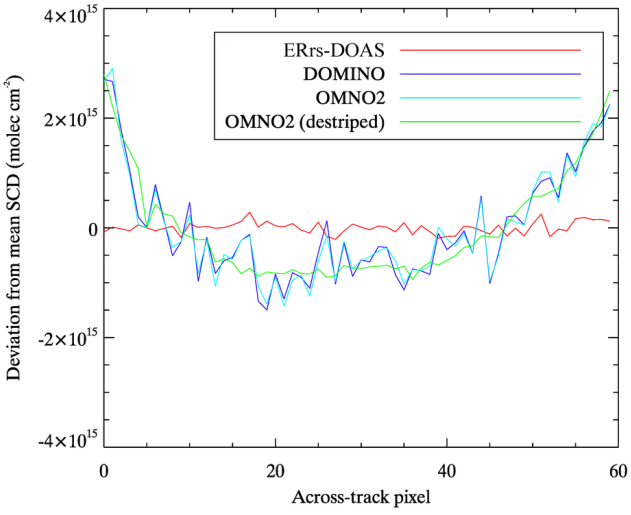

Figure 11. Deviations from the across-track mean NO_2 SCD retrieved by the Earth radiance reference algorithm and the OMNO2 and DOMINO algorithms. The Earth radiance L1B and OMNO2/DOMINO L2 data were taken from orbit no. 04741.

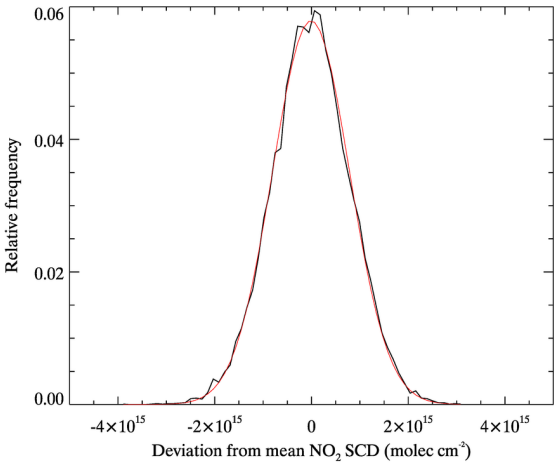

Figure 12. The distribution of the deviations of OMI NO_2 SCDs from the box-mean ($2° \times 2°$) values in the equatorial Pacific region (100–120° W, 10° N–10° S) for June 2005. The SCDs were derived by DOAS fitting OMI spectra using an Earth radiance reference. The red line shows the fitted Gaussian function.

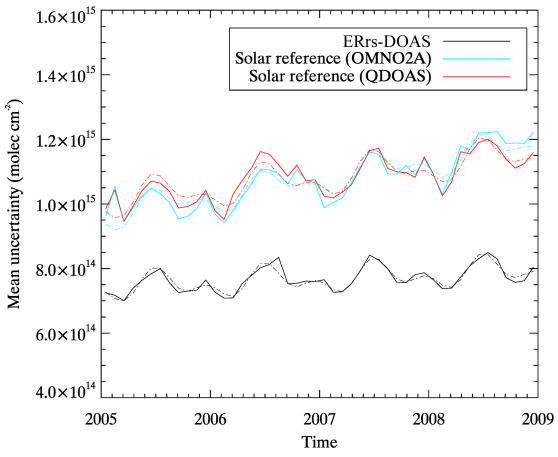

Figure 13. Time series of the monthly mean OMI NO_2 uncertainty between 2005 and 2008 calculated using the box-mean technique in Fig. 12. The dotted line represents the linear trend and seasonal cycle fitted using regression.

from the inherent accuracy of the retrieval. To measure this spread the SCDs retrieved over this region using the Earth radiance reference, and OMNO2A algorithms are scaled with a geometric AMF, in order to account for variability introduced by the changing SZA and viewing geometry over this area and period. The resulting VCDs are then binned to $2° \times 2°$ boxes, from which the deviation from the mean for each SCD is recorded. These deviations are subsequently binned to a histogram to determine the spread of the measurements. It was found that these histograms could be modelled as Gaussian functions, so the retrieval error can represented by the standard deviation, σ, of the distribution.

The OMNO2A SCDs has a σ of 1.1×10^{15} molec cm^{-2}. This value is similar to that derived from the total SCDs retrieved by emulating the OMNO2A algorithm using QDOAS. The Earth radiance retrieval, however, produces a σ of 8.0×10^{14} molec cm^{-2}, which corresponds to a $\sim 27\,\%$ reduction in random error using this retrieval. While this may be indicative of improved retrieval sensitivity this reduction is also the result of additional factors, such as the addition of the sand and liquid H_2O cross-sections, differences between the QDOAS and OMNO2A treatment of the DOAS fit, and reduction in the across-track striping. Figure 12 shows the distribution and the fitted Gaussian function for the ERrs-DOAS retrievals.

This analysis was carried out over all pixels retrieved over the specified region between 2005–2008, with the resulting time series shown in Fig. 13. Both the Earth radiance and solar retrieval uncertainties appear to be subject to an annual cycle, with peak values occurring around June. From regression analysis it was determined that the best fit of the data was achieved when accounting for this cycle (up to the second harmonic in a Fourier series) in addition to a linear trend. This cycle could potentially be related to the periodicity of the insolation observed over the area during the year, though the physical meaning behind the second harmonic is currently unknown. This model also does not fit the solar retrieval uncertainty trends as well as the Earth radiance retrieval, suggesting that DOAS fits using a solar reference are subject to some other factor, such as changes in the solar irradiance reference spectrum. Such changes over time would not be accounted for, as both the OMNO2A and QDOAS solar retrievals only use the composite irradiance reference spectra measured in 2005 previously described in this work.

In addition to the annual cycle there appears to be a statistically significant positive trend for all three time series, which may be the result of instrument degradation during this time period. The trend for the Earth radiance retrieval uncertainty (1.5×10^{13} molec cm^{-2} month^{-1}) is much lower than that of the solar retrieval uncertainty, (5.8×10^{13} molec cm^{-2} month^{-1}), potentially demonstrating this technique's resilience to spectral degradation.

4 Limitations to operationalisation

Despite the enhanced retrieval accuracy the ERrs-DOAS algorithm can be subject to a number of uncertainties which can limit its operational efficacy. For instance, the selection of the reference sector and binning period can introduce biases from tropospheric pollution which can add a negative bias to the retrieved SCDs. To remedy this the reference sector selection could be improved through a priori information provided by a chemical transport model (CTM), which would identify regions where high pollution would be expected. This approach would be similar to the stratosphere–troposphere separation performed by previous iterations of the OMNO2 retrieval algorithm (Bucsela et al., 2006), in

which the stratospheric VCD was inferred from regions where GEOS-CHEM predicted low annual tropospheric NO_2 columns.

Transient pollution trends that may contaminate the reference spectra will need to be empirically detected. One potential method for doing so would be to preliminarily select a small longitude range in the Pacific as the reference sector and then use the reference spectra to retrieve SCDs over the rest of the Pacific. While decreased in magnitude, contamination from transport events should still be observable. Through iterating the longitudinal range and masking polluted regions, it should be possible to identify the optimum reference sector for a global retrieval.

While binning reference spectra over longer timescales would increase the number of cloud-free measurements available, the temporal resolution of the reference spectra can also influence the retrieval uncertainty. Figure 13 shows a seasonal variation of $\sim 1.0 \times 10^{14}$ molec cm^{-2} in the retrieval uncertainty, which suggests that using an annual reference spectrum would produce a similar bias in the retrieval. This uncertainty would also be exacerbated by seasonal variations in the observed Pacific stratospheric NO_2 column. For shorter timescales, the number of cloud-free scenes available in the reference sector will affect the retrieval quality, which may only be partially mitigated by improving the instrument spatial resolution. For regions such as the Intertropical Convergence Zone (ITCZ) and high latitudes, excessive cloud cover means that a daily reference cannot always be taken. For such regions it may instead be prudent to use a several-day average spectrum to compensate for this effect. Because of these factors it is likely that using daily-to-weekly reference spectra would minimise retrieval uncertainty caused by the temporal frequency of the reference measurements. For a single instrument, a daily reference would be the best possible choice, while using a constellation of instruments would also help to account for the diurnal cycle as well.

While optimised for retrieving trace gas slant columns, the ERrs-DOAS algorithm cannot adequately retrieve other parameters such as cloud pressure and surface albedo, which are essential to retrieving the vertical columns. The cloud fraction is a particularly important parameter, as it is required to identify usable reference spectra to bin, and requires the measurement of the O_2–O_2 total SCD (Acarreta et al., 2004). Similarly, surface albedo retrievals typically require the measurement of the top of atmosphere reflectance (e.g. Kleipool et al., 2008). Such measurements require a solar reference spectrum, and so cannot be made using an instrument optimised for nadir viewing only. The solar reference spectrum is also critical to spectral and wavelength calibration as it is not subject to any atmospheric attenuation. Because of these issues, the ERrs-DOAS technique is unlikely to be applicable for near-real-time retrievals, and would instead be suited to reanalysis of operational satellite data sets.

5 Summary and conclusions

This work has shown that Earth radiance reference spectra from the remote Pacific in a satellite NO_2 DOAS fit can be used to retrieve tropospheric NO_2 SCDs over polluted regions with minimal need for model assimilation or spatial filtering. Figure 3 shows that the NO_2 SCD derived from using an Earth radiance reference is (within retrieval error) equivalent to the difference between the total NO_2 SCD retrieved over the reference region and the region of interest. The NO_2 profile can be partitioned into clearly defined tropospheric and stratospheric components, which makes this technique ideal for tropospheric NO_2 retrieval provided that the stratospheric component is the same over both the reference region and the region of interest. As shown in Fig. 6d the stratospheric field is not longitudinally homogeneous, particularly at extreme latitudes. These variations can result in significant biases in tropospheric NO_2 retrieved with this method compared with the model-assimilated DOMINO SCDs. One possible method in resolving these biases would be to use reference spectra from regions closer to the observation, though this limits the efficacy of this retrieval technique to coastal regions or other areas close to regions where tropospheric contamination could be minimised (e.g. deserts).

Despite the magnitude of the biases compared with DOMINO, the Earth radiance reference retrieval appears to give spatially consistent results. As shown in the urban transect comparison (Fig. 9) the retrieval shows sensitivity to the tropospheric NO_2 enhancement owing to anthropogenic activity, as the average transect for all three retrieval algorithms show good correlation. The bias in the Earth radiance reference retrieval appears as a near-consistent offset, potentially due to differences in the OMNO2A and QDOAS retrieval algorithms. However, the bias also appears to increase over the comparatively unpolluted Inner Mongolia region, which suggests that residual biases owing to the longitudinal variation in stratospheric NO_2 or temperature have a significant impact over remote unpolluted regions.

Using the uncertainty derivation technique defined by Valks et al. (2011) it was found that the ERrs-DOAS fits produced ~ 27 % reduction in retrieval uncertainty, though this may be the result of a number of factors, such as the addition of other cross-sections and differences in the OMNO2A and QDOAS algorithms. Time series analysis shows that the retrieval uncertainty owing to instrument degradation may be much less when using an Earth radiance reference. The retrieval technique also largely resolves the biases resulting from across-track striping with a minimal need for a posteriori corrections.

However, the benefits using the ERrs-DOAS technique have only been defined for cloud-free scenes. In cloudier scenes the photons will be scattered more, which will result in greater retrieval uncertainty. In the case of using Earth radiance reference spectra this issue is exacerbated by the influence cloud top height may have on the assumed strato-

spheric component. The wavelength shifts caused by cloud cover (Voors et al., 2006) are also an issue when selecting Earth radiance spectra, and need to be empirically corrected before binning. Future satellite instruments that would utilise this technique will therefore need to have a robust wavelength calibration. Despite the issues in wavelength calibration, there is some potential in using the cloud layer to determine the free tropospheric amount of NO_2 based on the established cloud-slicing technique used in some cases to retrieve tropospheric O_3 and NO_2 (Choi et al., 2014; Ziemke et al., 2001).

It was noted that the retrieval shows sensitivity to absorption from sand and liquid H_2O, as shown by the spatial distributions retrieved in Fig. 8 and the reduction in rms in Fig. 7 when these absorbers were included in the fit. The spatial similarity of the features retrieved with those found by Richter et al. (2011) suggest that these features are the result of real absorption rather than an instrument-specific defect, and should be included in future retrieval algorithms. Previously Merlaud et al. (2012) discussed potential correlations between O_2–O_2 absorption and sand, as both cross-sections have distinct peaks at ~ 477 nm. Currently the fitting window employed by OMNO2A does not extend to this wavelength, as absorption from O_2–O_2 has no impact on retrieval accuracy (Boersma et al., 2007). This algorithm could potentially utilise a larger fitting window to identify absorption from both species and to retrieve aerosol information based on their absorption.

This work has only covered derivation of the tropospheric SCD, while an operational version of this technique will need to consider an appropriate AMF derivation. In the DOMINO algorithm (Boersma et al., 2011) the tropospheric AMF is calculated after the stratospheric component has been subtracted from the total VCD. In this scenario, however, only a differential SCD has been measured, where the stratospheric column has been implicitly defined, rather than explicitly measured. A similar scenario is found in aircraft DOAS measurements (e.g. Popp et al., 2012), in which the reference spectrum is also taken from measurements over a region that is assumed to be unpolluted. The tropospheric VCD calculation therefore has to estimate the VCD of the reference region, such as using a reference climatology. However, in regions such as the remote Pacific the tropospheric contribution is likely to be negligible, so such a correction would only be required if a reference region close to the observation is chosen.

The retrieval impact on Ring absorption has not been investigated in this work. It is possible that the reduced retrieval uncertainty observed in Sect. 3.7 may be partially the result of Ring structures in the reference and observed spectra cancelling out. However, the magnitude of this effect will be dependent on the degree of Ring absorption in both spectra. While the reference sector binning method used in this work will ensure that the geometric path length is near-identical in both cases, differences in the light paths caused by factors such as cloud cover and aerosol loading will need to be explicitly accounted for. The impact of vibrational Raman scattering on the DOAS fit (VRS, Peters et al., 2014) will also need to be accounted for, as the reference spectra is primarily measured over the Pacific Ocean. Accounting for these effects may further improve the ERrs-DOAS performance.

While unsuitable for operationalisation, the ERrs-DOAS technique detailed in this work could potentially be used to create alternative tropospheric NO_2 data sets over urban regions, and potentially retrieve information about other tropospheric species. The reduced across-track variability (as shown in Fig. 11) and viewing angle dependence allows for clearer mapping of pollution fields. The observed reduction in SCD uncertainty and resilience to instrument degradation also potentially demonstrates a resilience to instrumental defects, which may allow for more accurate retrievals to be made, particularly over longer mission lifetimes. However, further work is required to explore the full benefits of this technique, particularly to resolve the inherent biases introduced by differences between the QDOAS and OMNO2A retrieval software.

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