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Improved OSIRIS NO_2 retrieval algorithm: Description and validation

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Abstract

A new retrieval algorithm for OSIRIS (Optical Spectrograph and Infrared Imager System) nitrogen dioxide (NO_2) profiles is described and validated. The algorithm relies on spectral fitting to obtain line-of-sight (LOS) column densities of NO_2 followed by inversion using an algebraic reconstruction technique and the SaskTran spherical radiative transfer model to obtain vertical profiles of local number density. The validation covers different latitudes (tropical to polar), years (2002-2012), all seasons (winter, spring, summer, and autumn), different concentrations of nitrogen dioxide (from deNOxified polar vortex to polar summer), a large range of solar zenith angles (68.6 to 90.5°) and altitudes between 10.5 and 39 km, thereby covering the full retrieval range of a typical OSIRIS NO_2 profile. The use of a larger spectral fitting window than used in previous retrievals reduces retrieval uncertainties and the scatter in the retrieved profiles due to noisy radiances. Improvements are also demonstrated through the

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validation in terms of bias reduction at 15-17 km relative to the OSIRIS operational v3.0 algorithm. By accounting for the diurnal variation along the LOS in the two-dimensional radiative transfer model, the scatter of the differences relative to the correlative balloon NO_2 profile data is reduced.

1. Introduction

Nitrogen oxides, such as NO and NO_2 are the reactive nitrogen-containing species in the middle atmosphere and are produced mainly from the breakdown of nitrous oxide in the stratosphere. Oxides of nitrogen dominate ozone loss in the middle stratosphere, whereas in the lower stratosphere, they react with oxides of chlorine and bromine, such as ClO and BrO, to reduce the halogen-catalyzed destruction of ozone.

The partitioning between NO and NO_2 depends on several factors such as the local ozone concentration and the photolysis frequency of NO_2. Reactive nitrogen is chemically converted at night to N_2O_5 and, upon hydrolysis, can be further sequestered into unreactive 'reservoir' species such as HNO_3. NO_2 increases steadily during daylight hours due to the UV photolysis of N_2O_5 (e.g. Wetzel et al., 2012).

The photochemistry of NO_2, which is particularly rapid near the day-night terminator, leads to spatial gradients within the field of view, particularly for limb sounders such as OSIRIS (Optical Spectrograph and Infrared Imager System) (Llewellyn et al., 2004), or for solar occultation instruments operating in either the UV-visible or mid-infrared (e.g., Kerzenmacher et al., 2008).

The OSIRIS operational NO_2 retrieval algorithm was developed and validated by Haley and Brohede (2007) and the current version is 3.0. The work of Kerzenmacher et al. (2008) is the only other publication comparing version 3.0 OSIRIS NO_2 data to correlative profile measurements. Earlier versions (e.g., 2.x, Haley et al., 2004) were more thoroughly validated, for example by Brohede et al. (2007). The pseudo-spherical forward model used in the operational OSIRIS NO_2 retrieval algorithm is less accurate than the SaskTran spherical radiative transfer model (RTM, Bourassa et al., 2008, Zawada et al., 2015), currently used as a forward model in the operational retrieval algorithm for OSIRIS ozone and aerosol extinction data products. Recently, Bourassa et al. (2011) developed an alternative NO_2 algorithm which relied on 4 wavelengths covering a single NO_2 absorption band. This was later modified to 13 wavelengths

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covering three adjacent NO_2 bands (438-450 nm) and used to process the entire OSIRIS data record and is referred to here as the 'fast' OSIRIS NO_2 product. While the spectral information content is reduced relative to the operational OSIRIS algorithm and the algorithm described below (see Table 1), the 'fast' algorithm has two key common elements to the one described herein:

1) The forward model is the successive-orders-of-scattering version of SaskTran.
2) MART (Multiplicative Algebraic Reconstruction Technique) (Degenstein et al., 2003) is used for inversion.

In this work, we provide a detailed description of the new retrieval algorithm whose heritage is the 'fast' algorithm (Bourassa et al., 2011) as well as the algorithm developed in a series of papers (Sioris et al., 2003; Sioris et al., 2004; Sioris et al., 2007). The current algorithm was developed to demonstrate that improved accuracy is possible through the combination of a better forward model, better forward model inputs, and additional, longer wavelengths, with a particular focus on the lower stratosphere (and upper troposphere).

We then compare NO_2 profiles retrieved from OSIRIS observations to balloon-borne NO_2 profile measurements during the decade (2002-2012) when several balloon-borne limb measurements were performed. Balloon profiles are chosen for the validation for many reasons, of which the most important is the expected accuracy of this data. The accuracy is due to two main factors: very high signal-to-noise afforded by the luxury of long exposure times (which can be traded for higher vertical and/or spectral resolution) and superior altitude determination, which for balloon-borne limb geometry is due to the sensor being an order of magnitude closer to the tangent point than for satellite limb sounders, thereby reducing the impact of imperfect viewing angle knowledge. Profile measurements from balloons are preferable to those from satellite for the purpose of validation because of their high vertical resolution, generally matching or exceeding the ~2 km vertical resolution of OSIRIS NO_2 (e.g. Sioris et al., 2003) (see below). Balloon measurements exploit a greater diversity of methods as in-situ techniques are possible in addition to remote sensing. Furthermore, one balloon-borne remote sensing technique relies on occultation during balloon ascent/descent, which is not possible for satellite instruments, and provides very accurate altitude registration, offers potentially finer vertical resolution than limb

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occultation for instruments observing the full solar disk (see Sect 2.3) and smaller errors due to the neglect of diurnal NO_2 gradients.

2. Method

2.1 Algorithm settings

The algorithm is a classic 2-step approach of spectral fitting using absorption cross-sections to determine slant column densities (SCDs) and vertical fitting to invert the SCDs. This approach is used by many groups including some of the balloon remote sensing teams providing data used in this study. The reference spectrum is the co-addition of spectra at tangent heights (THs) in the 50-70 km range (Sioris et al., 2003). Spectral fitting refers to a multiple linear regression including the following basis functions: a fourth order closure polynomial which is justified based on an adjusted-R^2 test, and temperature-dependent NO_2 (Vandaele et al., 1998) and O_3 (Serdyuchenkov et al., 2014) absolute absorption cross sections interpolated to the temperature (T) of the tangent layer using the European Centre for Medium-Range Weather Forecasting (ECMWF) analysis and convolved with a Gaussian to OSIRIS spectral resolution. Water vapour absorption is neglected despite maximal absorptions of >0.1% in the fitting window (434.8-476.7 nm) in the upper troposphere as it is not spectrally correlated with NO_2 absorption over this window and would greatly increase the forward modelling computational burden. The spectral fitting is exactly the same for observed and simulated normalized radiances. For example, the actual OSIRIS wavelengths and tangent heights are inputs into the simulation and any spectral pixels which are rejected due to radiation hits or detector saturation at the Level 1 processing stage (i.e. observed radiances) are also omitted from the fit of the SaskTran-simulated radiances. The longest wavelength in the fitting window is extended to 476.7 nm, raising the number of spectral pixels to 107, thereby increasing the spectrally-integrated signal-to-noise ratio and the penetration of the lower atmosphere relative to both existing OSIRIS NO_2 algorithms mentioned above. Both of these benefits of an extended fitting window had been demonstrated for SCIAMACHY limb scattering (Sioris et al., 2004) but OSIRIS has a glass filter that prevents the detection of higher orders of light reflected off the grating that was positioned such that the 477-530 nm region is not usable (Warshaw et al., 1996). Thus the 434.8-476.7 nm window is used here and spectral fitting residuals are shown in Fig. 1. Using a discontinuous fitting window that included wavelengths greater than 530 nm is not beneficial. The NO_2 SCD uncertainties are

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improved relative to those obtained by Sioris et al. (2003) who used a 434.8-449.0 nm fitting window and the 'tilt' pseudo-absorber. The improved NO_2 number density precision is illustrated below. The 'tilt' basis function is now excluded from the spectral fitting. We also tested an alternative approach of fitting an NO_2 spectral weighting function to the normalized radiances, as is used to fit the ozone absorption signal in nadir reflectance spectra (Coldewey-Egbers et al., 2005) and the spectral fits did not improve significantly.

The retrieval upper altitude limit is defined by the lowest tangent height in a limb scan for which the NO_2 SCD error is <100% for all tangent heights below. This can be as high as 49 km, but is typically ~40 km and typically a few kilometres higher than the upper altitude of the 'fast' NO_2 product. The lower limit of the retrieval is often determined by cloud tops as Odin generally scans the limb into the upper troposphere. Cloud-contaminated observations are excluded as they can lead to biases and difficulty in retrieval convergence. Cloud top detection is particularly important for MART since spectra from successive tangent heights immediately below a given altitude are used in a weighted fashion to retrieve the NO_2 number density at that altitude. We assume, for OSIRIS geometry (scattering angles of 90±30°), that an observed scene near a cloud top sampled by the ~1 km tall instantaneous-field-of-view has larger limb radiance at ~810 nm than if it were cloud-free. A scene is deemed to be cloudy if the ~810 nm radiance scale height is < 2.4139. This threshold is lowered from an overly stringent value of 3.84 (Sioris et al., 2007). The new threshold is chosen to allow NO_2 retrievals (and validation) to extend below 2-3 month old volcanic aerosol layers due to Sarychev Peak and Nabro, two of the eruptions during the OSIRIS mission which led to the largest stratospheric aerosol optical depth.

Algebraic reconstruction techniques (Fesen and Hays, 1982) have been used to recover the vertical and along-track distribution of atmospheric constituents for over four decades (Thomas and Donahue, 1972). Chahine's (1968) relaxation method, used by Sioris et al. (2007) for the retrieval of OSIRIS NO_2 vertical profiles, is a variant of MART in which only the tangent layer is used to retrieve the local number density and is also tested (see Sect. 4). The MART retrieval in this work uses a 0.6:0.3:0.1 weighting following the OSIRIS aerosol extinction retrieval (see Eq. 8 of Bourassa et al., 2007). Exactly 15 retrieval iterations are used, which appears to be adequate for most cases and, with MART, does not lead to overfitting. Five orders of scattering are used (Sioris et al., 2004). The retrieval uses a 1 km altitude grid, although the NO_2 vertical

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resolution remains ~2 km, a consequence of the ~2 km vertical sampling provided by Odin. Above the retrieval range, NO_2 profiles are scaled every iteration using a Chahine-like update based on the highest tangent height within the retrieval range. Below the retrieval range, the NO_2 profile is assumed to have a constant number density down to the ground, equal to the number density at the lowest retrieved altitude. The air number density profile is from ECMWF.

The retrieval uses OSIRIS-retrieved ozone and aerosol extinction profiles (version 5.07, v5.07 hereafter) and the 675 nm scene albedo (Bourassa et al., 2007) to provide more realistic forward model inputs into SaskTran.

The NO_2 retrieval uncertainty is obtained by perturbation as described by Sioris et al. (2010), with the NO_2 SCD standard errors and an altitude-independent number density perturbation serving as inputs. The 1D profile retrieval including the error calculation takes ~5 minutes on a desktop computer with eight 3.4 GHz processors.

2.2. Modelling diurnal gradients within SaskTran

Zawada et al. (2015) describe the high spatial resolution capability which is required for modelling (horizontal) diurnal gradients of NO_2 within SaskTran. SaskTran is capable of modelling radiation fields with the atmosphere varying along the line-of-sight (LOS), and also along the incoming solar beam (referred to as ‘2D mode’ and ‘3D mode’, respectively, hereafter). The 1D forward model and associated retrieval (Table 1) completely neglects diurnal gradients in NO_2. In 2D mode, the atmosphere consists of sectors along the LOS but the diurnal variation of NO_2 along the incoming solar beam is not considered. In 3D mode, the atmosphere essentially consists of stacked triangular prisms of increasing horizontal extent with increasing distance from the tangent point as illustrated by Zawada et al. (2015) and diurnal gradients are simulated for any light path from its point of entry into the atmosphere to its exit.

To provide realistic diurnal gradients in the atmosphere of the forward model, SaskTran has been linked to the PRATMO stratospheric gas-phase photochemical box model (McLinden et al., 2000). PRATMO is configured to converge to 0.5% between the start and end of each one day run. The atmosphere is aerosol-free for photolysis frequency calculations. The latitudinal and vertical resolutions are 5° and ~2 km, respectively. The default number of time steps per day is 35. More details are available in McLinden et al. (2006) and references therein.

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2.3 Validation approach and datasets

Even though the OSIRIS 2D and 3D profiles are retrieved accounting for the diurnal gradients expected for the OSIRIS viewing geometry, photochemical modelling is also required to scale all of the OSIRIS NO_2 profiles to the local time of the balloon measurement. The PRATMO box model is also used for this purpose.

Balloon correlative data are used from the following instruments:

Differential Optical Absorption Spectroscopy (DOAS, Butz et al., 2006; Kreycy et al., 2013, and references therein), miniDOAS (Weidner et al., 2005), Limb Profile Monitor of the Atmosphere (LPMA, Butz et al., 2006), Spectromètre Infra-Rouge d'Absorption par Lasers Embarqués (SPIRALE, Kerzenmacher et al., 2008; Moreau et al., 2005), Système d'Analyse par Observation Zénithale (SAOZ, Pommereau and Piquard, 1994; Wetzel et al., 2007), SAOZ-BrO (Pundt et al., 2002), mini-SAOZ (Vicomte and Pommereau, 2011), MkIV (Toon et al., 2002), and Spectroscopie d'Absorption Lunaire pour l'Observation des Minoritaires Ozone et NO_x – Nacelle 2 (SALOMON-N2) operating in solar occultation mode (Jégou et al., 2013). Table 2 provides information on these correlative datasets. The five balloon-borne instruments not previously used in OSIRIS NO_2 validation are LPMA, miniDOAS, SPIRALE, SALOMON-N_2 and MkIV. DOAS and SAOZ had been used previously (Brohede et al., 2007; Haley et al., 2004; Sioris et al., 2003). SPIRALE, LPMA, and SALOMON-N2 data were obtained from the CNES/CNRS-INSU Ether web site (http://www.pole-ether.fr).

Coincidence criteria are within 1000 km (Brohede et al., 2007) and on the same calendar day (using UT time). Only daytime correlative measurements are considered. The closest spatial coincidence is used if located within a 1000 km range. Comparisons between OSIRIS NO_2 and balloon correlative data are performed only down to the lower altitude limit of each profile retrieved with the v3.0 algorithm in an effort to keep the number of balloon-coincident altitudes the same between that algorithm and the algorithm debuting here. The upper limit for validation is determined in all cases by the balloon float altitude.

The best opportunities for validation of a deNOxified profile come on March 4th and 16th, 2003 in Kiruna, Sweden when the NO_2 number density measured by LPMA and SAOZ, respectively, did not exceed 10^9 molec/cm^3 at any altitude. These peak number densities are the lowest in the

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validation dataset. Note that OSIRIS does not measure in the northern polar region until late February due to a lack of sunlight at ~6 AM/PM. NO_2 profiles at southern high-latitudes have not been measured by balloon-borne instruments during the OSIRIS mission.

Averaging kernels are not taken into account since the vertical resolution is similar between the NO_2 profiles from most of the selected validation instruments and from the three OSIRIS algorithms, namely the operational v3.0, 'fast', and the algorithm described herein. Results from the current algorithm will be treated separately for each of the forward model modes (1D, 2D, and 3D) described in section 2.2.

In section 3, the 1D profiles used in the validation are those processed by a network of computers (using a solar zenith angle cutoff of SZA<90°). The entire OSIRIS data record has now been processed and is currently available at ftp://odin-osiris.usask.ca/Level2/NO2/ following registration. One time-saving approximation is used to process the entire record: multiple scattering (MS) is only calculated at 21 wavelengths corresponding to the peaks and troughs of the NO_2 absorption cross-section across the spectral fitting window rather than the entire set of 107 wavelengths. The single-scattering radiances at the remaining 86 wavelengths are scaled by the ratio of radiances between multiple scattering and single scattering simulations at these 21 wavelengths, linearly interpolated to the remaining wavelengths. The radiance error due to the MS approximation is typically <0.05% at all wavelengths and all tangent heights used in the NO_2 retrieval.

3 Results

One difference in the method described above (Sect. 2) compared to previous OSIRIS NO_2 algorithms (Haley and Brohede, 2007; Bourassa et al., 2011) is the use of spectral information from longer wavelengths. Two sources of random error in retrieved NO_2 are shot noise, a consequence of the finite number of electrons generated by the detector by impingent limb-scattered photons, as well as radiation hits by energetic particles (e.g. protons) that are not filtered in the Level 1 data. The extended fitting window tends to reduce the susceptibility of the retrieved NO_2 to these noise sources. Using the 1D inversion approach described above, the 33 OSIRIS limb scans used in validation are processed with the extended fitting window and the

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one used in the operational algorithm (Haley and Brohede, 2007). The standard deviation in retrieved NO_2 number density for each set (i.e. fitting window) is calculated over the common altitude range for each of the 33 scans. Natural variability of NO_2 is identical since the same limb scans and altitude ranges are used, so any difference in the standard deviation is due solely to the different spectral fitting windows. Figure 2 shows the slight reduction in NO_2 variability at all altitudes with the extended fitting window. Note that the NO_2 profiles retrieved from the two fitting windows do not have a significant bias (± 1 standard error) between themselves, which points to the self-consistency of NO_2 spectral cross-section between the two windows.

Other benefits of the extended fitting window are that the NO_2 retrieval uncertainty is improved and the upper altitude limit of the retrieval moves slightly higher, as shown for a sample case in Fig. 2. For this tropical case, only at the NO_2 number density minimum at 15.5 km is the current retrieval unable to measure NO_2 with uncertainty of <100%, whereas with the fitting window of the operational algorithm, the measurements are below the lower detection limit between 11.5 and 17.5 km and at 7.5 km (Fig. 2). The significant upper tropospheric NO_2 enhancement at ~10 km is also observed by the mini-SAOZ (not shown).

Figure 3 shows that the 1D retrieval overestimates NO_2 by 29% relative to the 3D one at 17.5 km. This overestimate is due to the larger NO_2 concentrations that are present on the far side of the limb (yet neglected by a 1D model) for a SZA (86.6°) that is small enough to allow significant far side contribution to the radiance. The increasing NO_2 gradient toward the far side of the limb occurs because of the decreasing photolysis frequency of NO_2 with increasing SZA. The 2D retrieval underestimates slightly since the slightly lower NO_2 concentrations along the incoming solar beam are not included in that model version. The 3D retrieval clearly reduces the bias versus SAOZ relative to the 1D case at altitudes below 18 km where the relative diurnal gradients are expected to be largest. This improved precision is demonstrated below for a large ensemble of profiles by contrasting the correlation of the 1D and 2D retrievals and the standard error of the biases relative to coincident balloon data.

In order to compare the various OSIRIS NO_2 products to the balloon correlative data, all profiles are linearly interpolated onto a 1 km grid (12.0 to 39.0 km) commonly used in the balloon data. The 'fast' product tends to be limited in its vertical range at both extremes of the profile, not only relative to the other OSIRIS NO_2 products but also relative to the coincident balloon profiles and

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also the 'fast' retrieval is not available for some coincidences (Fig. 4). The sample size is ≥20 between 13 and 31 km for all OSIRIS NO_2 products and the validation discussion focusses mostly on this altitude range.

The v3.0 operational OSIRIS NO_2 has proven to be of high quality in the 15 to 42 km range from previous satellite intercomparisons (e.g. Haley and Brohede, 2007) and the same can also be inferred for the upper troposphere from the ability to detect small lightning-generated NO_2 enhancements with the expected latitudinal and longitudinal distribution (e.g. Sioris et al., 2007). Thus, in Fig. 5, we examine the standard error of the coincident profiles for OSIRIS and balloon data to compare the variability of each dataset, similar to Kerzenmacher et al. (2008). The upper altitude limit of the data obtained from balloons launched by CNES (Centre National d'Etudes Spatiales) is 31±2 km (Table 2). This excludes MkIV and SAOZ-BrO. From 31 down to 28 km, the balloon-borne NO_2 profiles show more scatter than any of the OSIRIS data products. This is likely due to the need to assume the NO_2 vertical distribution above float altitude for the remote sensors which is particularly problematic in the tropics where the NO_2 profile typically peaks at a higher altitude than for the extratropics. A second factor is the smaller absorption signal for the remotely-sensing balloon instruments due to the short path lengths when observing altitudes near float. Below 16 km, the balloon data clearly exhibits less scatter than OSIRIS, thereby quantitatively supporting the choice of balloon validation data for reasons discussed in Sect. 1. Kerzenmacher et al. (2008) show that this is not true for NO_2 at ~15 km measured by the (Atmospheric Chemistry Experiment) ACE satellite instruments versus OSIRIS v3.0 NO_2. Between the three OSIRIS products, 'fast' exhibits the largest scatter at all altitudes, whereas the 2D algorithm described here offers noticeably less scatter between 15 and 20 km as compared to the v3.0 product. The 3D algorithm takes 1.5 hours to retrieve a profile on the computer specified above and thus the entire set of balloon-coincident OSIRIS limb scans was not processed. The 2D algorithm takes half of the processing time of the 3D algorithm.

To determine if OSIRIS NO_2 is biased relative to the balloon data, we studied medians and means of individual profile differences over all coincidences (as a function of altitude). These results are shown in Figs. 6-7. It is clear that all of the OSIRIS NO_2 algorithms have a statistically significant bias near the NO_2 peak (typically ~30 km). This overestimate near the peak is similar to the overestimate by OSIRIS v3.0 relative to ACE Fourier Transform

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Spectrometer and MAESTRO (Measurements of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation) which coincided with the NO_2 peak altitude. Local biases were +17% and 14%, respectively (Kerzenmacher et al., 2008). Haley and Brohede (2007) found no such overestimate at the peak versus SAGE (Stratospheric Aerosol and Gas Experiment) III and POAM (Polar Ozone and Aerosol Measurement) III, but a similar positive bias near ~28 km versus HALOE (Halogen Occultation Experiment). The 'fast' product has the largest overestimate at the peak of ~16% with a sharp gradient in its bias, swinging to a statistically significant ~18% underestimate at 18 km. The retrieved profiles using the 2D retrieval described above have a similar bias profile shape with 'fast' (Figs. 6-7) but of smaller amplitude, with a ~+10% typical bias at the number density peak for the 2D retrieval and a ~10% negative bias at 18 km which is statistically insignificant in terms of the median (Fig. 6). The bias of the v3.0 product is similar to the alternative OSIRIS NO_2 products above 20 km, but between 15 and 17 km, there is a significant positive bias using both central tendency statistics (Figs. 6-7). In contrast to 'fast' and v3.0 products, there are no altitudes in the lower stratosphere (below 24 km) with statistically significant average and median biases for the 1D and 2D products. This conclusion is not sensitive to the use of the multiple scattering approximation used for the 1D product (see Sect. 2) (not shown).

While Figs. 6-7 address the systematic errors of the various OSIRIS products, it is also important to consider the precision of these data since a product whose biases in individual profiles average to zero could still fail to adequately capture the variability. This is potentially a greater concern for the v3.0 product since it relies slightly on a priori NO_2 and vertically smooths the retrieved NO_2 when measurement precision is lacking. However, Haley and Brohede (2007) and Haley et al. (2004) show that these are very minor concerns as the measurement response and vertical resolution do not deteriorate significantly down to an altitude of 12 km. Figure 8 shows that the v3.0 product captures the variability of the balloon measurements down to ~22 km as well as the 2D and 1D products and better than 'fast' NO_2, but then has larger scatter below 20 km than the 2D and 'fast'. The 'fast' retrieval benefits from more accurate forward modelling than the v3.0 algorithm. The reduced scatter in the lower stratosphere is unlikely to be a difference between inversion approaches (MART versus the optimal estimation approach used in the v3.0 algorithm) as discussed above. The 2D retrieval also may have an edge over the v3.0 algorithm by virtue of using SaskTran as its forward model. There is also the specific benefit of its forward model

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accounting for diurnal gradients in NO_2. This can be seen clearly between 13 and 16 km where the 2D retrieval is more precise than the 1D retrieval owing to this built-in photochemical modelling capability. This confirms the better precision of the 2D retrieval suggested by Fig. 3, and is only expected for large SZAs (McLinden et al., 2006). Note that errors due to the neglect of diurnally varying chemical gradients can alternate in sign depending on the viewing geometry (McLinden et al., 2006; Brohede et al., 2007).

Correlation can be used as an alternative statistic to verify whether an OSIRIS product captures the variability observed by coincident balloon data. It is different from the standard error statistic used in Fig. 8 since multiplicative or additive biases do not affect the correlation but do affect the standard error of the individual biases. The correlation is calculated over the 46 coincident balloon profiles at each available altitude (Fig. 4). Figure 9 shows a general decrease in correlation between OSIRIS and coincident balloon data with decreasing altitude. There is higher correlation with balloon NO_2 data for the 2D retrieval over the 1D retrieval at the lowest altitudes, consistent with Fig. 3. The correlation of the v3.0 product is comparable with the 1D and 2D product down to the lowest validated altitudes, whereas the 'fast' product has generally lower correlations above 22 km than the OSIRIS NO_2 products relying on spectral fitting.

Finally, since the coverage of balloon is limited to latitudes north of -22°S, Fig. 10 is included to illustrate the climatological (2001-2015) vertical and meridional distribution of stratospheric NO_2 volume mixing ratio in the southern hemisphere during austral spring. For each NO_2 vertical profile, the conversion to mixing ratio uses the local air density profile from the ECMWF analysis.

4 Discussion

Next, we review and discuss the sensitivity of the retrieval to forward model parameters. There is a slight sensitivity of the retrieved NO_2 to changes in aerosol extinction. Previous sensitivity studies (Sioris et al., 2003; Haley et al., 2004) are consistent with the current findings. The scene albedo in the visible can vary from <0.03 for calm ocean to almost unity for fresh snow, although the NO_2 retrieval is, by design, insensitive to surface albedo by virtue of the high-TH normalization of the radiance spectra (Sioris et al., 2003). Use of the retrieved scene albedo (instead of the default value of 0.3) and of the v5.07 aerosol extinction profile further reduce these sensitivities. Finally, use of OSIRIS-observed (v5.07) ozone instead of the default ozone

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climatology in SaskTran (McPeters et al., 2007) is expected to have a minor impact on retrieved NO_2 via errors in modelling the atmospheric extinction based on Sioris et al. (2007).

With a method that involves simulating spectra at high tangent heights for the purpose of normalizing radiances simulated for tangent heights within the retrieval range, the forward model must accurately compute the radiance over a large range of tangent heights. The NO_2 retrieval error due to the pseudo-spherical approximation is expected to have its largest impact at low altitudes, because of the vertical gradient in pseudo-spherical RTM errors (Griffioen and Oikarinen, 2000). At the top of the retrieval range (40 km), errors cancel with the high altitude reference.

While not included in Figs. 5-9, Chahine's relaxation method tends to produce sharper extrema in the retrieved NO_2 profile than MART that tend to be slightly displaced vertically from those in the balloon data. This may stem from the coincidence criterion of 1000 km in distance, but may also relate to the ~2 km vertical sampling of OSIRIS and the 1 km altitude grid used for the retrieval. If the vertical grid of the retrieval is finer than the vertical sampling, a vertically narrow layer at 19 km, for example, would be retrieved as peaking at 18 km when the available radiance spectra are measured at THs of 18 and 20 km. The comparison of MART and Chahine inversion approaches is worth revisiting with the 1 km vertical sampling offered by the Ozone Mapping Profiler Suite (Jaross et al., 2014).

In order to rigorously validate this new retrieval algorithm in the upper troposphere, tropospheric chemistry must be added to the photochemical model used to scale the OSIRIS observations to balloon local time. The reaction of NO_2 with the hydroxyl radical to form HNO_3 drives the diurnal variation of tropospheric NO_2 more than N_2O_5 photolysis (Boersma et al., 2009). Accurate knowledge of the seasonal variation of the OH concentration is required for modelling the diurnal variation of upper tropospheric NO_2.

5 Conclusions

Profiles of NO_2 retrieved from OSIRIS have been improved in terms of reduced bias and scatter versus the current v3.0 operational algorithm in the lower stratosphere (e.g. 15 km) as determined using highly accurate balloon measurements as truth. The bias is within ~±10% between 14 and 37 km.

The benefits of spectral fitting and extending the fitting window to longer wavelengths are evident at the highest altitudes where the photoelectron shot noise tends to be large relative to the NO_2 absorption signal, but also at the lowest altitudes where the retrieved profile shape is largely driven by small differences in NO_2 SCDs obtained from spectra at adjacent tangent heights. Algorithms that exploit the richness of the NO_2 absorption spectrum are shown to better capture the mid-stratospheric variability of this key constituent. The use of a fully spherical forward model is an important advantage, particularly at lower altitudes since, while the pseudo-spherical RTM errors are largest at the top of the retrieval range, the largest NO_2 retrieval errors due to the use of a pseudo-spherical RTM occur at low altitudes because a high tangent height reference is used in the retrieval.

A model capable of modelling diurnal gradients in NO_2 also helps to improve the precision of the retrieved number density profile, particularly at the lowest altitudes where the horizontal gradients in NO_2 are sharpest and where the radiance is predominantly from the near side of the limb.

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Table 1. Main features of OSIRIS NO_2 algorithms compared in this work.

	v3.0 operational	*'fast'*	*1D, 2D, 3D*
Wavelength range (nm)	435-451	438-450	435-477
Number of spectral pixels	41	13	107
RT model	LIMBTRAN	SaskTran (1D)	SaskTran (1D, 2D, 3D)
Inversion scheme	Optimal estimation	MART (0.5: 0.3: 0.2)	MART (0.6: 0.3: 0.1)
Cloud detection	Yes	No	Yes
NO_2 absorption cross-sections	220 K (Vandaele et al., 1998)	(Burrows et al., 1998)	220, 298 K (Vandaele et al., 1998)
Interpolation of fitted cross-section to effective *T*	No	yes, using local ECMWF temperature at each TH	yes, using local ECMWF temperature at each TH

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Table 2. Summary of validation data based on OSIRIS coincidences. The minimum relative uncertainty is reported on the native vertical grid. Vertical resolution is quoted or calculated for an altitude of 16 km. The vertical resolution is provided by Butz (2006) for LPMA and DOAS, Weidner et al. (2005) for mini-DOAS, available at http://mark4sun.jpl.nasa.gov/m4data.html for MkIV, and calculated for limb occultation for the SAOZ-type instruments, including SALOMON-N2 (Jégou et al., 2013) assuming vertical resolution equal to the vertical extent of the solar disk at the tangent point. Uncertainties are for a 1 km vertical grid, except for SPIRALE (0.005 km) and mini-DOAS (2 km).

Instrument	Number of coincidences	Relative uncertainty (%)	Vertical Resolution (km)	Average lower altitude (km)	Average upper altitude (km)
MkIV	6	2	~2	9	38
SPIRALE	4	<1	0.005	16	33
SALOMON-N2	1	15	2	15	33
DOAS asc	3	5	1.5	9	29
DOAS limb	4	<1	1.5	13	32
mini-DOAS	2	4	2	8	29
LPMA asc	1	10	6	10	33
LPMA limb	4	10	5	15	31
Mini-SAOZ	1	4	2	15	29
SAOZ-BrO asc	1	2	1	3	36
SAOZ-BrO SS	1	4	2	22	37
SAOZ asc/desc	9	<1	1	6	29
SAOZ limb	9	<1	2	11	29

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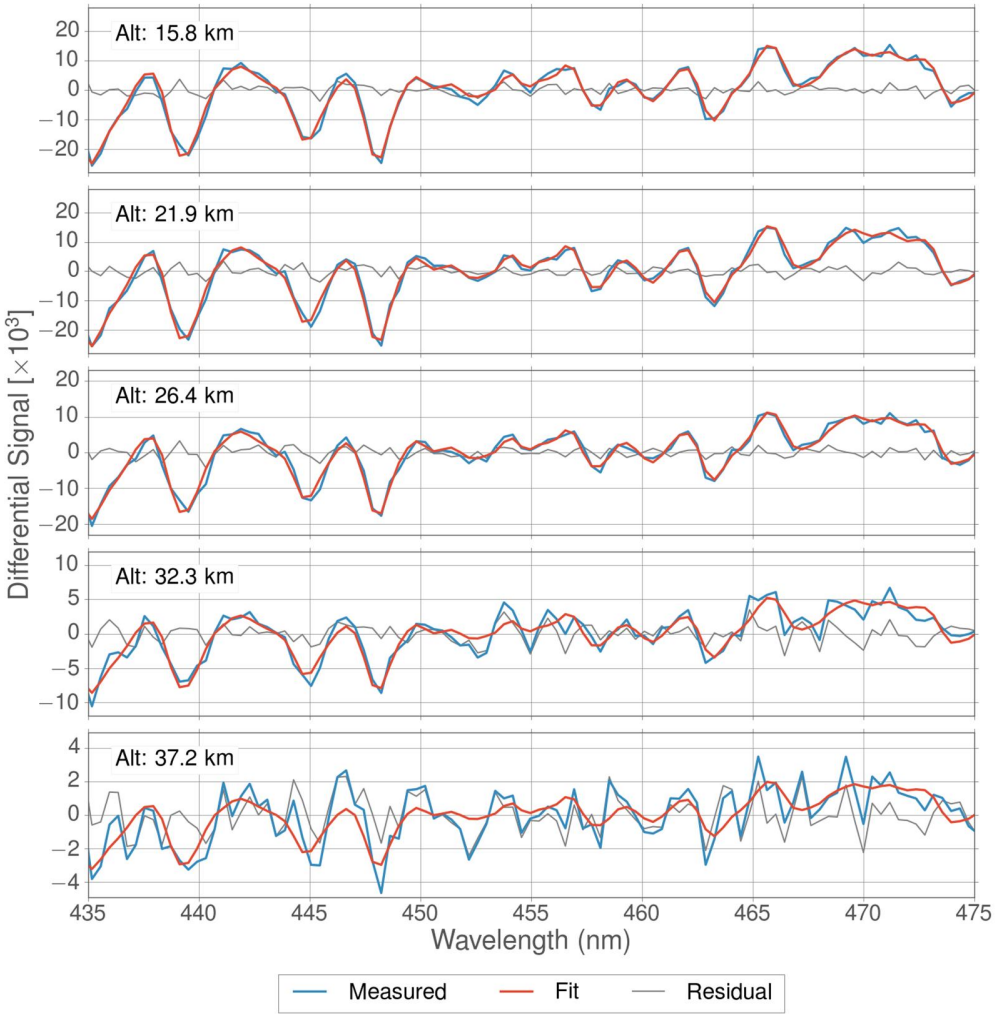

Figure 1. Measured and fitted differential optical depth (DOD) as a function of tangent height ('Alt') in the spectral window used for NO_2 retrieval. The residual is calculated as measured DOD – fitted DOD.

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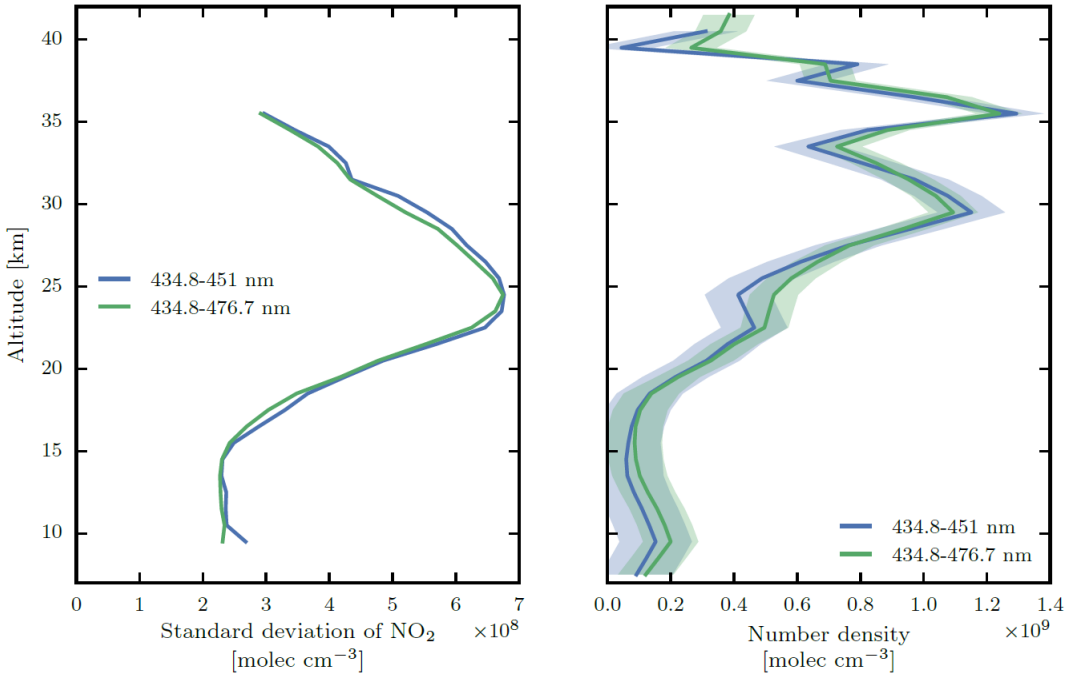

Figure 2. (left) Comparison of the standard deviation of the NO_2 number density profiles retrieved with the algorithm described above using the default window (435-477 nm) versus the fitting window used in the OSIRIS v3.0 operational algorithm (Haley and Brohede, 2007), (right) Comparison of a single NO_2 profile retrieved from scan 20 of orbit 60346 with the algorithm described above using the default window (435-477 nm) versus the fitting window used in the OSIRIS v3.0 operational algorithm.

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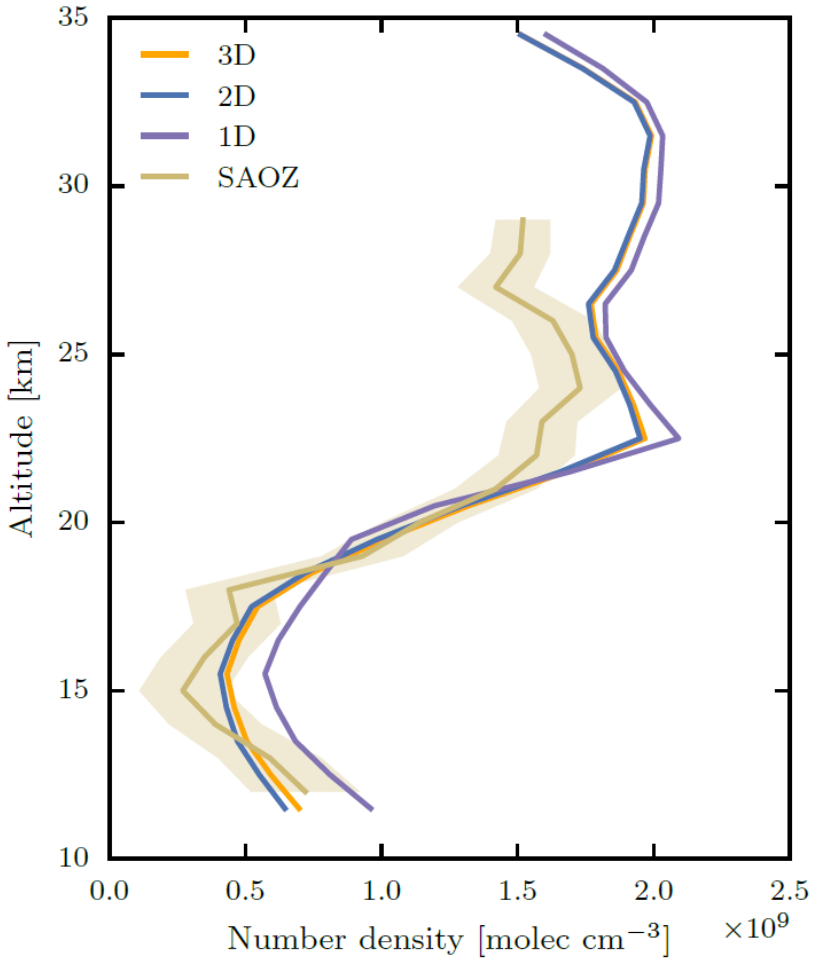

Figure 3. NO_2 profile retrieved from scan 44 of orbit 16011 using the 1D, 2D, and 3D retrievals, all converted to sunset (tangent point SZA=90°), the local time of coincident SAOZ measurements. OSIRIS is on the day side with SZA=86.6° (pm) and an azimuth difference angle of 99° such that the far side of the limb is closer to the terminator.

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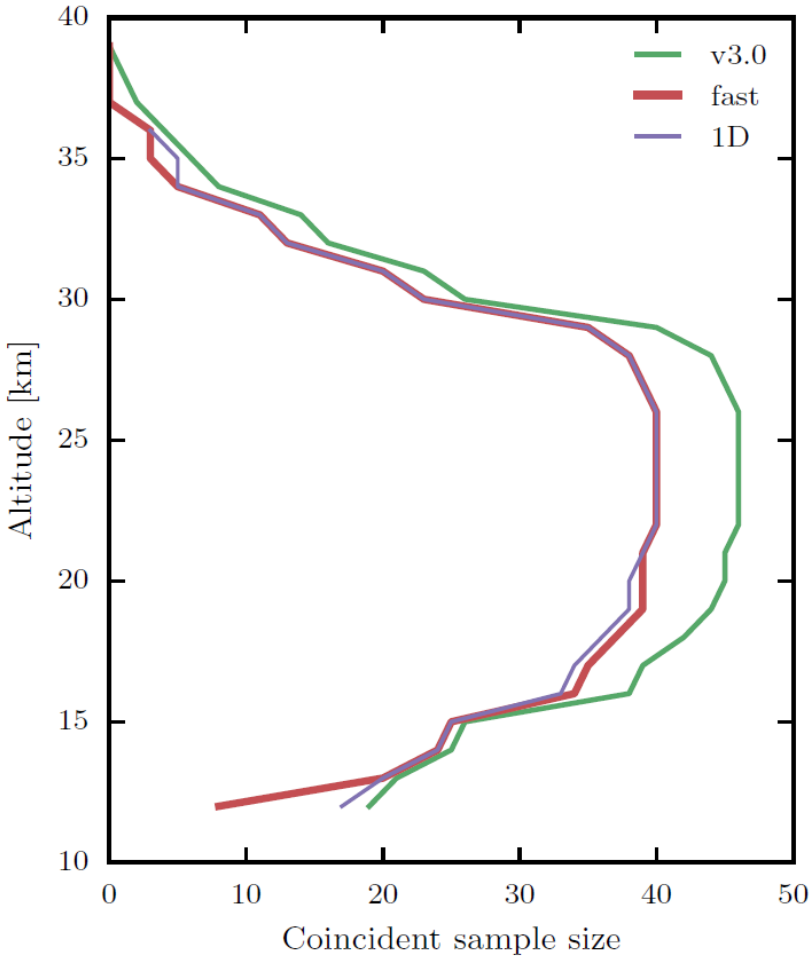

Figure 4. Sample size of coincident balloon data versus altitude and as a function of retrieval algorithm.

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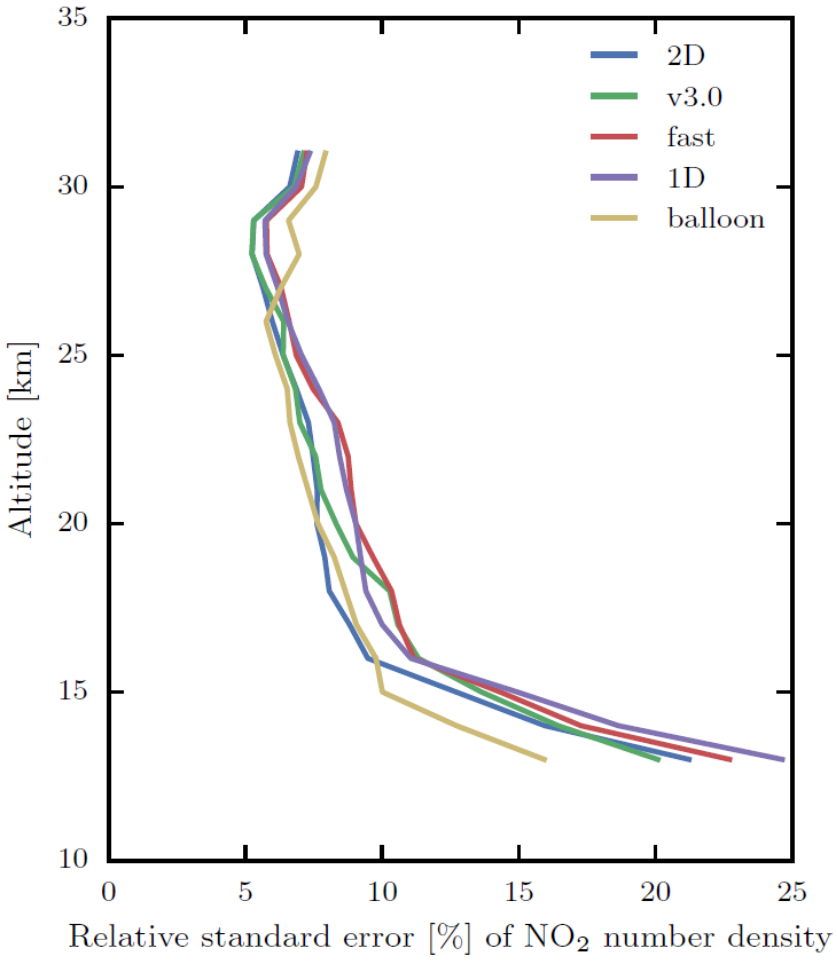

Figure 5. Relative standard error of coincident NO_2 profiles. Note that OSIRIS profiles have been scaled to various local times of the balloon measurements which adds random error to the OSIRIS profiles due to random variations between the photochemical model atmosphere and true atmosphere.

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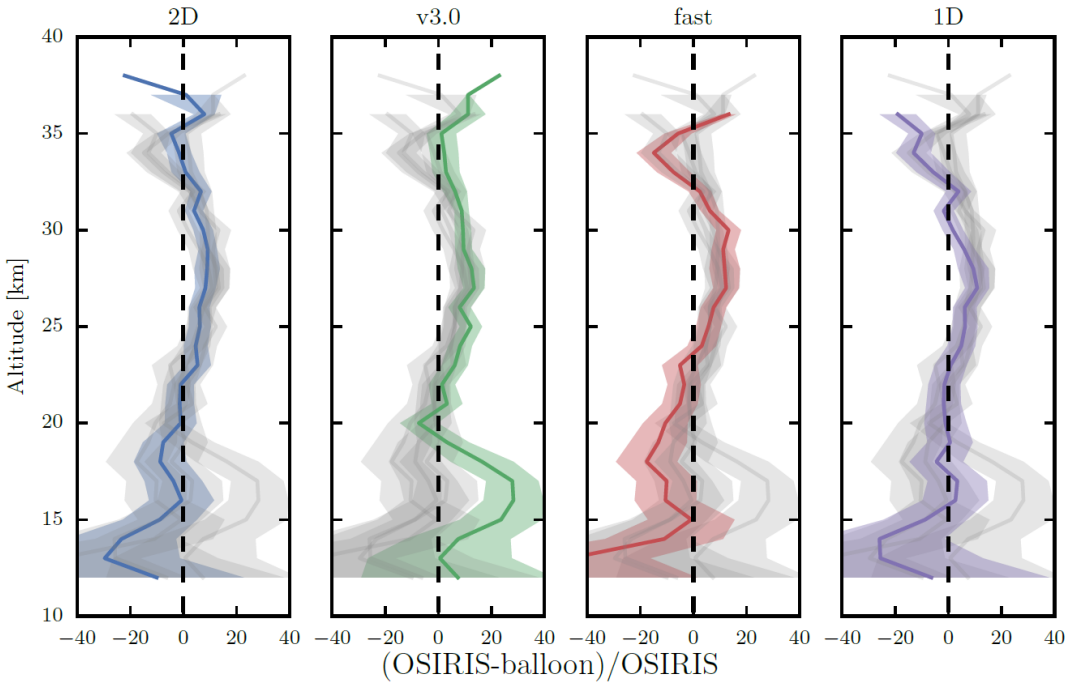

Figure 6. Median of individual biases versus balloon data. The error bar shows ±1 standard error of the median NO_2 bias profile. The median and standard error of the individual biases are converted to relative quantities by dividing by the corresponding median OSIRIS NO_2 profile (scaled to balloon local time). The relative median bias profiles for the other three algorithms are shown in gray for comparison.

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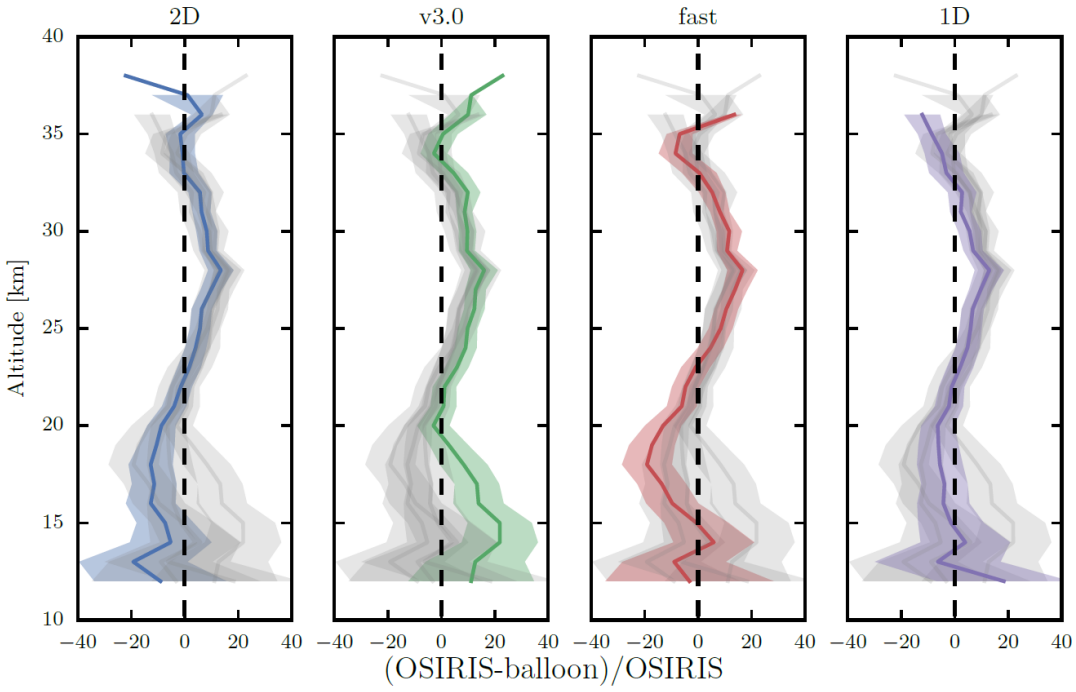

Figure 7. same as Fig. 6, but the bias is an average over individual differences between OSIRIS and balloon correlative data. The average and standard error of the individual biases are converted to relative quantities by dividing by the corresponding average OSIRIS NO_2 profile (scaled to balloon local time).

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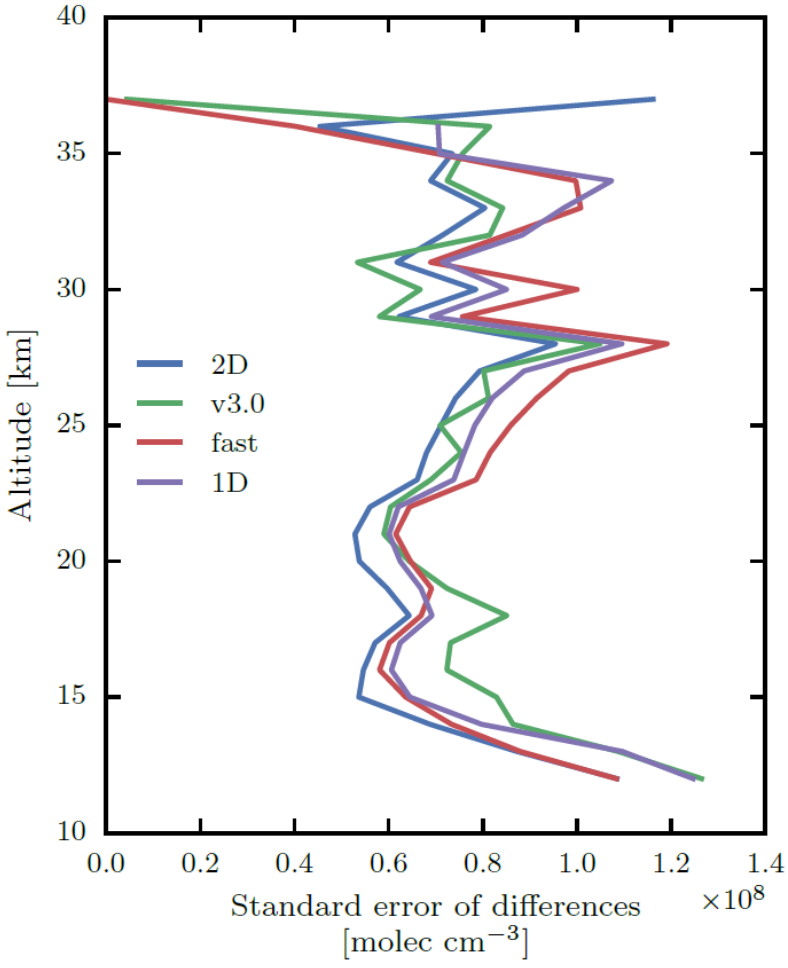

Figure 8. Standard error of the individual biases relative to balloon correlative data for different OSIRIS NO_2 products. The curves here correspond to the half-widths of the error bars in Figs. 6-7.

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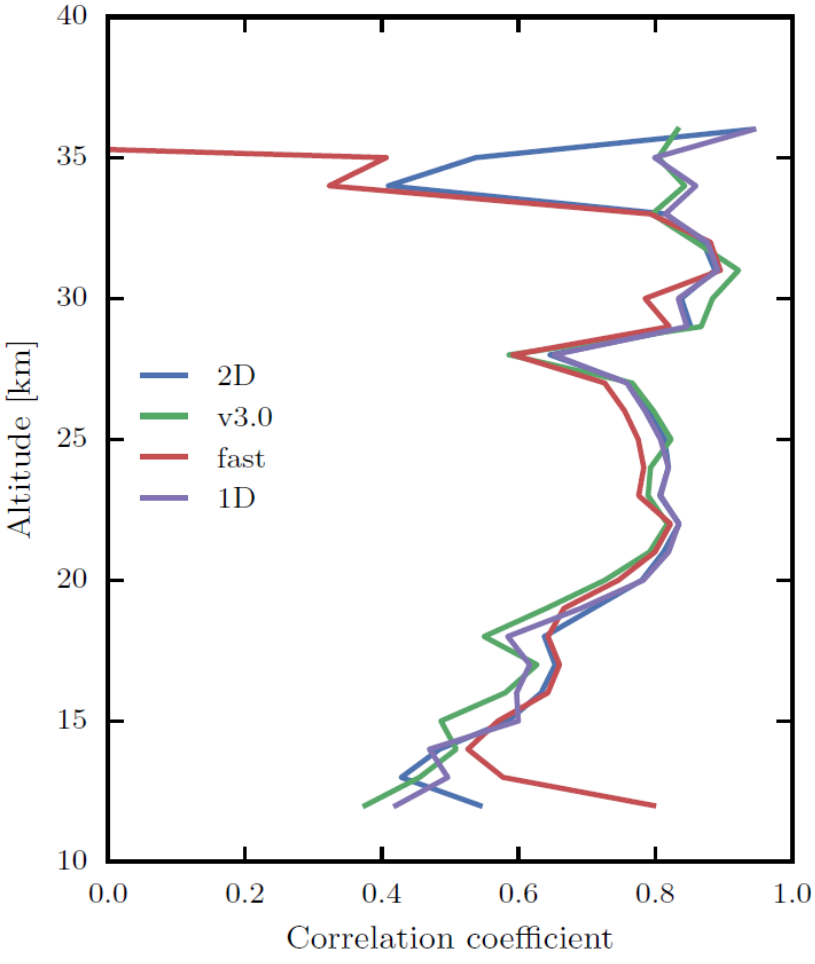

Figure 9. Correlation between various OSIRIS NO_2 products and the balloon validation dataset.

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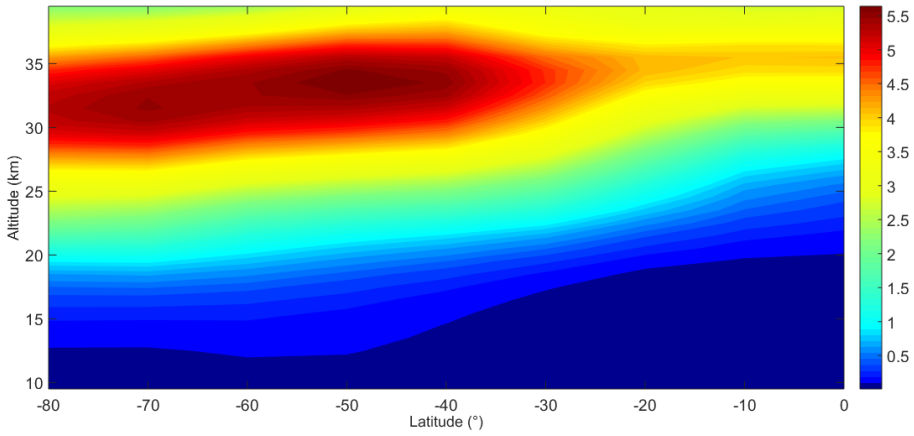

Figure 10. Climatological map of zonal mean NO_2 volume mixing ratio (ppb) with 10° latitudinal binning and 1 km vertical binning centered at altitudes between 9.5 and 39.5 km for November (2001-2014).