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Atmospheric Chemistry and Physics Discussions

Interactive comment on "NO_2 climatology in the northern subtropical region: diurnal, seasonal and interannual variability" *by* M. Gil et al.

M. Gil et al.

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Response to Anonymous Referee #1

First we would like to thank the reviewer for the very detailed positive review of our manuscript and his/her constructive remarks.

The shortcoming mentioned in the general paragraph will be treated when they appear in the following specific comments.

Specific comments Abstract, line 7: suggest replacing "source" by "sources" -> Corrected

Abstract, lines 13-15: suggest mentioning what years this study concerns. -> Corrected

Abstract, line 18-19: I suggest specifying what "significantly" is in quantitative terms. -> OK. We will rewrite the abstract to give the % values. In the text we do give values (e.g. maximum underestimates of 25% at sunrise and 12% at sunset). We will summarise these.

P15069, line 4: contribution of what? -> NOx was missing at the beginning of the sentence. It is included now.

P15069, line 5: suggest replacing "mid" by "middle" -> Corrected

P15069, line 16: I think "and" should be removed before "with a" -> Corrected

P15069, lines 16-18: I think it would be more clear if the authors would mention the modelled trend instead of making a relative statement against the observed trend. -> The purpose of the sentence is to reinforce the statement made in these analyses that NO2 increases at a larger rate than N2O. We understand that it is not clear enough and has been rewritten: "Struthers et al. (2004) extended the Liley et al. work by comparing Lauder and Arrival Height (Antarctica, 78 deg.S) data with a three-dimensional coupled chemistry-climate model (CCM). They found again a greater rate of increase of NO2 compared with N2O both in measurements and model."

P15069, line 27: suggest mentioning NDACC web link here. -> OK

P15070, line 3: recommend spelling out the abbreviation before using "SAOZ" and providing SAOZ web link, same for "BREDOM" -> OK

P15070, lines 9-11: This statement is true if only one sensor is used. A combination of two satellite instruments with different local overpass times, for instance SCIAMACHY and OMI, allows for a comparison of NO2 columns if both instruments observe the location under cloud-free conditions on the same day. In fact, a paper on this subject has recently been accepted for publication in the Journal of Geophysical Research (Boersma, K. F., D. J. Jacob, H. J. Eskes, R. W. Pinder, J. Wang, and R. J. van der A (2007), Intercomparison of SCIAMACHY and OMI tropospheric NO2 columns: observ-

ACPD
7, S8739–S8749, 2008

ing the diurnal evolution of chemistry and emissions from space, J. Geophys. Res., doi:10.1029/2007JD008816, in press.). -> We agree with the reviewer that the difference in local overpass time of the various LEO satellite instruments has the potential to study the diurnal evolution of NO2. The paper of Boersma et al. nicely demonstrates this for tropospheric NO2, where both absolute columns and diurnal changes are expected to be large. The problem with this approach for stratospheric NO2 is the high degree of consistency in absolute values which is needed to resolve the small diurnal changes in stratospheric NO2 expected over most locations, and as can be seen in the figures of Boersma et al., on the level of 5E14 molec cm-2, systematic differences between NO2 retrieved from i.e. OMI and SCIAMACHY exist. At high latitudes, LEO instruments with large swath have several overpasses per day providing consistent sampling of the diurnal variation in the stratosphere, and it has been suggested to use that for better validation of the satellite products and studies of stratospheric NO2 chemistry.

P15070, line 25: recommend mentioning what the "recorded period" actually is. -> Included

P15071, lines 3-9: this formulation is awkward. What is "the equivalent path for a given wavelength"? Do the authors mean the equivalent photon path? Please formulate more clearly. Also the sentence "At twilight ... tropospheric one" has not been written clearly. Stratospheric contribution of what? What is a slant, tropospheric path? This should be rewritten, and I strongly recommend providing references to earlier work that did a good job describing zenith-sky DOAS observations. -> The sentence has been reformulated. We hope it is clear now. The relevant reference is added.

P15071, line 12-15: it should be made clear that ratioing with a high sun spectrum instead of an extraterrestrial spectrum introduces a bias in the retrieved NO2. This is now fumbled away in lines 13-15 that state that the NO2 SCD (the concept of the SCD should be introduced here) is "in fact" the DSCD. In fact, the NO2 SCD is the DSCD + an unknown bias! The authors acknowledge this later, at P15072, line 1, but it should

ACPD

7, S8739–S8749, 2008

be made clear here already. -> We agree that the sentence was not clear enough. The concept of the SDC is now introduced when defining the equivalent photon path (EPP) and also the need to estimate the unknown NO2 in the reference spectrum

P15071, eq. (4): I think I see what the authors want to do here, but the formulation needs to be improved. The authors want to find those parameters a, b, c, d, and Ni, that minimize the residuals between the observed (ratioed) spectra, and the modelled spectra. By differentiation with respect to the unknowns Ni and setting to zero, they will only find solutions for Ni, not for a-d. So where do the coefficients a-d come from? -> These are the non-linear components in the equation. Parameters a and b are obtained in addition to the Ni parameters by successive iterations until the residuals are minimum. The parameters c and d are obtained by matching the reference spectrum with a well aligned solar spectrum with the help of the Fraunhofer lines. We have rewritten the equation and the text in a more or less similar way as Vandaele et al 2005 and made a reference to this paper.

Furthermore the plus sign on the right hand side should be a minus sign or Lambert-Beer would not hold. -> The problem was an "equal" sign appearing for some reason in between the two terms.

The double use of brackets is awkward -why not using the proper symbol for minimization, i.e. the norm-symbol? -> OK

Furthermore the summation should be over i absorbers/scatterers. -> Only absorbers. Scatterers change slowly with wavelength and are removed by the use of a polynomial.

Finally I suggest using a proper symbol for multiplication instead of a low dot. -> OK

I think it would be appropriate if the authors mention here which spectral fitting window and what set of reference spectra they use. -> In this section we present the generalities of the technique. Spectral ranges of the instruments are shown in the "Data and setting" section.

ACPD

7, S8739–S8749, 2008

What are typical values for shift and squeeze that they get? -> With the instrumental thermal control, shift remains within +- 0.2 pixels which is 0.024 or 0.048 nm, depending on the instrument, and within +- 1 pixel in stretch (all measurement spectral range). A correction of these missalingnments improves the fit. Typical values of shift and stretch are included in the table I.

What is the theoretical precision of the NO2 slant column (random error)? -> This is presented in line 3 and 4 of page 15076. We understand that the differential optical density can be meaningless and we have converted it into molec/cm2.

P15072, lines 4-5: I don't understand what O3 has to do with the reference spectrum bias correction. -> In order to introduce the concept of modified-Langley plot we have started by the classical Langley plot. O3 is one of the typical molecules in which the reference content can be estimated precisely. However, to avoid confusion we have deleted in page 15072 "as for O3" in line 5 and "the gas under consideration" line 8

P15072, lines 23-25: Interesting approach. Have the authors done more than just one calculation of the reference content? It would be reassuring if the authors had done so, and that the newer reference estimates would not differ too much from the original Langley plot result. -> Due to the NO2 column change with the solar zenith angle the classical Langley method does not work well and therefore is not useful to compare with. All references used during the measurement period are taken at 50 deg. sza am. The estimated amounts at Izaña are of 4-5 x 1015 molec/cm2 being the overall uncertainty of about 20% of this amount. The following sentence has been added in section 3.3: "Uncertainty in the amount of the reference content from modified-Langley plots estimated as the standard deviation of the intercept for a cluster of days accounts for another 2%"

Equation (6) should have a proper multiplication sign instead of a low dot. -> OK

What is the typical reference content.Does the number make sense? -> Answered just above

ACPD

7, S8739–S8749, 2008

P15073, line 8: "constraint" should be "constrained" -> Corrected

P15073, lines 10-12: the fact that the station is under tropospheric conditions most of the time does not in itself prevent pollution from the coastal towns. I guess that the authors want to state that pollution from these towns has little chance of being sampled at Izana. -> We thank the referee to note that part of the sentence was missing. We have added the following sentence after "coastal towns": "to reach the station except in punctual occasions associated to the passing of low pressure systems"

P15073, line 12: typo twilight. Corrected

P15073, lines 25-26: I suggest the authors provide a number here on the signal-tonoise ratio that they typically obtain. -> The residuals from the molecules retrieval analysis are not dominated by the detector STN ratio, which is very high (>10000 in Artist, 4000 in RASAS and EVA), but by improper elimination of Fraunhofer lines, changes in cross-sections shape with temperature, inaccurate treatment of Ring effect, absorbents not contemplated in the analysis, etc. We find more useful to the reader to include the typical evaluation error in molec/cm2 when discussing figure 1 (page 15076, lines 3-4).

P15074, I recommend that the authors also give a typical signal-to-noise for the advanced visible spectrograph. Also, on this page and later, the abbreviations EVA, RASA, and ARTIST have not been properly introduced. Now the reader has to guess whether EVA is the first of the two instruments contributing to the data record, RASAS the advanced visible spectrograph and so on. I suggest including a table with a brief overview of the three instruments and techniques here, including operational time period, S/N ratios, fitting windows, resolutions etc. would help here. -> A table has been included summarising all characteristics that play a role in the molecules retrieval. The signal to noise has also been added.

P15075, last line: "van Roozendael" should be "Van Roozendael" -> Corrected

P15076, first line: what is a "pseudo-cross-section?" -> Something was clearly miss-

ACPD

7, S8739–S8749, 2008

ing. We have now included the following entence "Finally, the inverse of the reference spectrum was ncluded as a pseudo cross-section"

P15076, lines 19-20: I wonder why the authors do not mention that uncertainties in all cross-section spectra contribute to the error budget. Have they established that? -> We have made sensitivity tests by changing O3 cross sections sets and shifting slightly with negligible results. This effect is certainly of significance in BrO retrieval but not in NO2.

P15076, line 26: I recommend removing "a" in "on a realistic NO2 profiles." -> OK

P15076, line 27: I suggest the authors clarify what a "single AMF-set" is. The way I read it, it seems an AMF computation with one fixed AFGL-profile, and dependencies solely on viewing geometry. The 5% error would then be from not accounting for NO2 profile variability and another 4-5% error from non-sphericity in the radiative transfer model? If so, I suggest the authors clarify this. -> We understand that the sentence is not clear. It is rewritten as: "For practical reasons a single AMF-set has been used for all the year round. AMF has been computed for the AFGL profiles for the tropical scenario by the INTA fully spherical single-scattering radiative transfer code. The model was run for sunrise and sunset during the solstices to estimate the error introduced by this approximation"

P15075, line 9: suggest replacing "temperature is larger" by "temperature is higher." -> OK

P15077, eq. (7): I suggest the authors provide a reference here. -> To our knowledge this has only been published for the O3 community. We reformulate the sentence as: "The NO2 effective temperature at a given sza can be defined as the mean temperature of the atmosphere weighted by the NO2 concentration at each layer contributing to the total observed rays in the same way as the O3 effective temperature (Bernhard et al., 2005)":

ACPD

7, S8739–S8749, 2008

P15077, lines15-22: Interesting discussion, and the results make sense. However, the cited "uncertainty" is rather a systematic effect (the sign change is likely to occur with season), and should be treated accordingly, or the authors should convice the readers that the effect is truly random. -> An accurate correction requires de daily knowledge of the NO2 and T profiles. Alternatively data can be seasonally corrected as the referee points out. However at this moment no correction has been applied due to uncertainties in the actual vertical distribution of the NO2. We will, therefore, rewrite the sentence as "About +- 2% error can be produced due to changes in the NO2 effective temperature at twilight during the year, not corrected in the presented data".

P15078, line 7: I suggest the authors explain what PDA stands for. -> It is now described when appearing by first time. The name of the instruments are included for more clarification.

P15078, section 3.4: The authors present a very impressive result here with little difference between retrievals from two independent measurements. From here on, the authors could use aprox. 0.2 x 1015 molec.cm-2 as an upper limit for the random error component on their retrievals. Is this number consistent with the uncertainty they get from the DOAS fit? -> Random errors from individual measurements are now included in section 3.2. What has been correlated in figure 4 is the twilight mean NO2 VCD value.

Because the retrievals are similar for the two instruments (same cross sections, same radiative transfer model, same temperature correction), the two retrievals may be expected to be biased in similar ways. Such a bias, if known, would justify a correction to the data, and I think it is misleading to state that because of "these excellent results, no corrections have been applied to the data subsets". -> The main purpose of the cross-correlation was to verify the homogeneity of the series when moving from photomultiplier instrument to diode array instrument. A normalization correction function would be necessary only if either the slope departs from 1 or intercept is not zero in order to get an homogeneous dataset. According to the shown results no correction was

ACPD

7, S8739–S8749, 2008

required. Obviously this argument was not clearly written. Hopefully now is clearer.

I suggest that the authors remove this sentence and tell the reader that there is a possibility that the data is biased, and I even think they can easily come up with an upper limit for this bias (combining the estimates for cross sections 2%, radiative transfer 6-7%, and temperature 3% should give an idea). -> It has been included in the 3.3 errors section.

P15079, line 15: suggest replacing "tracer" by "tracers". -> OK

P15080. line 10: suggest mentioning for what local time the reference content holds (Figure 5 states 70 pm - should that be 70 degrees pm?). -> Yes. It has been added to the text

P15080, line 14: I suggest explaining what "adapted SLIMCAT box model" means. Is it the bias-correction of +0.3 1015 molec.cm-2? -> We have rewritten the sentence to make it clear: "The diurnal cycle has been simulated for the same day and latitude by the vertically-integrated photochemical box model derived from the SLIMCAT-3D"

P15080, section 5.1: how representative is Figure 5 for other days with little aerosol? -> We have added a sentence to clarify this point. "Other tested days provide similar results although this kind of observations is restricted to winter period when days of extremely low aerosol optical depths (AOD $<$ 0.03 at 500 nm) occur."

P15080, line 24-27: The asymmetry is not due to, but rather described with a secondary wave. I suggest the authors rephrase this. -> Corrected

P15081, lines 7-13: this all sounds plausible, but I think the authors should tell us whether and how JNO2, k1, and/or k2 change with temperature. -> The ratio NO/NO2 changes with temperature through the K1 and K2 reaction constants. We have run the photochemical box model derived from the SLICAT-3D for all upper stratosphere levels (25 to 60 km) for Tenerife latitude and different seasons to obtain subtropical profiles of J, [O] and [O3] as input for the equation (9), then computing it for different temperatures.

ACPD

7, S8739–S8749, 2008

Interactive Comment

Results show the same NO/NO2 change with temperature as in the more simplified version published in ACPD. NO2 increases some 1.5%/K when the air temperature rises, and this increase is almost independent of the level in the stratosphere.

P15082, line 9: I suggest adding that there is a lack of simultaneity between *ground-based and satellite* measurements. -> OK

P15082, lines 13-16: the comparison of GOME to Izana ground-based NO2 column provides interesting information on the details of the diffuser plate correction - I recommend the authors discuss this a little bit more. Judging from Fig. 10, the assumption of constant 2.0 1015 molec.cm-2 over the Pacific region is mostly in error in the later months of the year and not so much in Jan-Feb-Mar. Is this consistent with knowledge about the monthly variability of NO2 columns in the Pacific reference box from SCIAMACHY that does not suffer from such errors? -> As the reviewer correctly points out, the assumptions made in the GOME data analysis can be verified with the SCIAMACHY measurements. Three questions are important here: a) is the absolute value (2E15 molec cm-2) assumed for the correction in agreement with SCIAMACHY data, b) is the assumption of negligible seasonal cycle correct and c) does the value over the Pacific vary from year to year. To evaluate these questions, the time series of (absolute) SCIAMACHY NO2 columns over the Pacific region used for the GOME normalisation was extracted for the years 2004 - 2006. The daily vertical columns vary from 1.3E15 to 1.6E15 molec cm-2 over this period with a high degree of similarity between the years. The latter is probably at least in part the result of the same diffuser plate dependence as in GOME, only at a much reduced level. The absolute values are lower than those used for the GOME correction by 4 - 7E14 molec cm-2 which would reduce the GOME values further and actually increase the discrepancy with the ground-based data. There is no indication for larger fall than spring values which would be needed to reduce the differences seen between ground-based and satellite seasonality. In summary, the SCIAMACHY data provide support for the method used but argue for a slightly smaller offset. The remaining differences between GOME and ground-based

ACPD

7, S8739–S8749, 2008

data can not be explained by uncertainties in the normalisation procedure.

P15085, line 6: here, for the first time, the overall error budget of 10-12% is being mentioned. This should already have been done. -> We have included a sentence in the errors sections. Numbers are updated to 12-14% since the uncertainty in the reference content was missing.

P15086, line 3-5: I suggest replacing "points to" by "confirms previously established". -> Yes, this is a fair comment. Problems with ERA-40 are well known. We will change this in the final version.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 15067, 2007.

ACPD

7, S8739–S8749, 2008

Interactive Comment