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Comment

## ***Interactive comment on “NO<sub>2</sub> climatology in the northern subtropical region: diurnal, seasonal and interannual variability” by M. Gil et al.***

**M. Gil et al.**

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First we would like to thank the reviewer for the very detailed positive review of our manuscript and his/her constructive remarks. In relation to his/her general comments, we will try to improve the English in the final version of the paper.

Specific comments:

P. 15070, L. 8: please add general references for the GOME, SCIAMACHY and OMI instruments. -> References are added.

P. 15070, L. 14: this sentence can be hardly understood. What is the meaning of the wording "useful in extreme"? Please rephrase to improve clarity. -> The words "Ground-based" were missing at the beginning of the sentence. We hope it is clear now.

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P.15070, L. 23: remove "...from diurnal to interannual scales". The whole sentence should be re-written for clarity. -> The sentences has been re-written.

P. 15071, L. 15: typo change "Differencial" by "Differential" -> OK.

P. 15072, L. 19: what is the photochemical box model used in this work? -> The sentence in the "Diurnal variation" section has been modified for clarification: "The diurnal cycle has been simulated for the same day and latitude by vertically integrating in 1-minute step the output profile of a photochemical box model derived from the SLIMCAT-3D (Denis et al., 2005)". More details of the model (altitude levels, chemicals, reactions) can be found in the Denis et al., paper.

P. 15074, L. 24: add "nm" after "325-460". -> OK

Also the "RASAS" acronym should be introduced. -> Following the suggestion the paragraph has been re-written for clarification. Most of instruments specifications are now in a table.

P. 15076, L. 15-18: what is the rationale for using different fitting intervals with each instrument? Please comment on possible instrumental reasons and how this could possibly affect the consistency of the combined data set. -> Two instruments data have been used to analyse the NO<sub>2</sub> series. The consistency has been satisfactorily checked by the cross-correlation during two years of data and results are shown in the draft. We think this is the important fact. Reasons for different ranges, as the referee assume, are instrumentally related. The first one (EVA) is a scanning and was scheduled for 430-450 nm (a sample every 0.1 nm). When the diode-array detector instrument was installed in the field, the range was extended essentially for two reasons: Larger range reduce the interpolation noise due to a lower oversampling, and also to measure O<sub>3</sub>.

P. 15075, L. 18: to my knowledge, the NO<sub>2</sub> absorption cross-sections are far from being Gaussian in shape. I suggest to leave this consideration off. -> NO<sub>2</sub> cross-section spectrum in the visible is Gaussian but certainly not in the measuring ranges.

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We have corrected the sentence "The NO<sub>2</sub> absorption cross-sections in the visible are highly structured, Gaussian in shape, with a large number of optically active transitions with irregular fine structure superimposed, due to the strong coupling between the ground and first excited electronic states (Orphal, 2002)".

P. 15076, L. 1: add more details on the nature of the cross-section used to correct stray-light effects, or provide adequate reference. -> The sentence has been extended as follows: "Finally, the inverse of the reference spectrum was included as a pseudo-cross-section to account for stray light inside the spectrograph and detector residual dark current".

P. 15076, L. 5: justify why a single scattering approach is accurate enough for NO<sub>2</sub> AMF calculation. What is the error due to the neglect of multiple scattering effect?. -> Retrievals are performed for 89 deg.- 91 deg. At these szas for 500 nm and a high altitude station, the multiple scattering contribution is of 1.5% or lower in the AMF values. Test has been performed using the SCIATRANS code for the AFGL tropical profile.

P. 15076, L. 20: I find the wording "observational error" not precise enough. Why not simply use "errors on slant columns"? -> We have changed by "errors in the retrieval"

P. 15076, L. 27: If possible give a reference where the need for daily profiles is highlighted. -> AMF are dependent on the NO<sub>2</sub> vertical profile. The shape changes along the year due to photochemistry and in scale of days dynamically as well. Consequently a perfect calculation of the AMF would require the vertical shape of the profile for every condition, which is unfeasible. However, the error introduced by this effect at low latitudes can be neglected as compared with other sources of errors since the stratospheric flow is essentially zonal and seasonality is small.

In the same paragraph, the discussion on the NO<sub>2</sub> retrieval errors misses to address errors due to rotational Raman scattering (Ring effect) and the smoothing effect it induces on the NO<sub>2</sub> absorption structures. This effect is systematic and highly significant

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(approx. 5% at twilight) as first reported in a paper by Fish et al. in the mid-nineties. -> Fish et al. (1995) found an underestimation in NO<sub>2</sub> retrieval due to differences in the amount of Raman scattering which is dependent on the analysis wavelength range, on the multiple scattering and also on the altitude of the station. For the typical amount of Raman scattering measured at our station we found errors much smaller than those reported by Fish et al. (2-3%) when performing sensitivity tests by synthetic spectra and not including Raman in the retrieval. In any case this error is minimised or even eliminated in the present data since a cross-section based in Raman theory (Windoas package) and offset corrections are included in the analysis.

P. 15079, L. 24: it is maybe worth to stress the fact that this is only true as long as the noon measurements are not contaminated by tropospheric NO<sub>2</sub> contents (which is usually the case at Izana, as indicated before in the text). -> OK. We have added to the sentence "in unpolluted environments"

P. 15082, L. 24: please add a reference for the gradients effects. -> Planetary wave activity distorts the zonal flow inducing zonal gradients between the polar vortex (very low NO<sub>2</sub>) and mid-latitude air (larger NO<sub>2</sub> and higher bulk). A number of papers in the nineties deal with this issue when interpreting large NO<sub>2</sub> column increase in short time scales. We have included the Solomon et al., JGR, 1994 reference in which a section is devoted to dynamical NO<sub>2</sub> effects.

P. 15083, L. 8-15: what about the possible impact of the different NO<sub>2</sub> absorption cross-section data sets used for GOME, SCIAMACHY and the ground-based measurements? How consistent are these data? If I remember well, the GOME FM98 cross-sections display significant differences in comparison to Vandaele et al. (in the range of 15%). Could this partly explain the observed disagreement? -> We agree with the reviewer that differences in the cross-sections used are a potential source of uncertainty for the comparison of the ground-based and satellite measurements. As the reviewer points out, the GOME-FM NO<sub>2</sub> cross-sections have a smaller differential cross-section than suggested by Vandaele by about 10%. This should lead to an

overestimation of the GOME NO<sub>2</sub> columns relative to the ground-based values by a constant factor of 1.10. While this is an important point, it can not explain the seasonally varying differences observed between the two data sets.

In response to the reviewers comment, we now explicitly mention the uncertainty of the cross-sections in the text:

"Therefore, a normalisation over the Pacific region is used assuming a constant NO<sub>2</sub> column in that region (Richter et al., 2005a) which strongly limits the information content of GOME measurements at low latitudes. In addition, the Burrows et al. cross-sections used for GOME show differences of up to 10% compared to the cross-sections used for the ground-based measurements which can introduce a corresponding scaling error."

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

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