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Retrieval of tropospheric column densities of NO_2 from combined SCIAMACHY nadir/limb measurements:

Supplementary material

S. Beirle[1], S. Kühl[1], J. Pukite[1], and T. Wagner[1]

[1]Max-Planck-Institut für Chemie, (Otto Hahn Institute), Mainz, Germany

Abstract.
This document provides supplementary material to the manuscript **Retrieval of tropospheric column densities of NO_2 from combined SCIAMACHY nadir/limb measurements** (Beirle et al., 2009, hereafter BE09).

1 Content

This document provides supplementary material to the manuscript Beirle et al., 2009, hereafter BE09.

Figures, Equations and Sections in BE09 are referenced by a prefix M (Manusscript), Figures, Equations and Sections in this supplement are referenced by a prefix S (Supplement).

See Table 1 in BE09 for an overview for abbreviations and symbols.

In addition to the Figures in BE09, the following Figures are provided:

- Fig. S1 displays V^*_{RS}, i.e. the mean NO_2 VCD V^* in the reference sector as function of day d and latitude Λ. See Section M2.4.1.
- Fig. S2 shows the error $\widehat{\delta W}_{\mathrm{RSM}}$ as function of day d and latitude Λ. See Section S3.2 and Eq. S1.
- Fig. S3 shows the error $\widehat{\delta W}_{\mathrm{RLC}}$ as function of day d and latitude Λ. See Section S3.3 and Eq. S2.
- Figs. S4-S9 display maps of daily V^*, L, ΔL, and the TSCDs T_{RSM}, T_{ALC}, and T_{RLC}, for additional days (April 2, 2005; July 20, 2005; October 24, 2005).
- Figs. S10 shows the latitudinal dependencies of V^*_{RS} and L_{RS} for the respective days.
- Figs. S11-16 show monthly climatologies of T_{RSM}, T_{ALC}, and T_{RLC}, their differences, and the difference in standard deviations, for April, July, and October 2003-2008.

Correspondence to: S. Beirle (beirle@mpch-mainz.mpg.de)

2 Stratospheric VCD W_{RSM}

Fig. S1 displays V^*_{RS}, i.e. the mean NO_2 VCD V^* in the reference sector, as function of day d and latitude Λ. This is the stratospheric VCD estimate W_{RSM}, as defined in Eq. M1. See Section M2.4.1.

3 Intrinsical error information

Rough estimates of the accuracy of TSCDs can be gained from - unphysical - negative TSCDs (Section S3.1). Two additional error quantities are defined: δW_{RSM} as the standard deviation of W in the reference sector (3.2) and δW_{RLC} as the mean quadratic deviation of individual LLV values ΔL from the smoothed LUT $\widehat{\Delta L}$ (3.3). Note that δW_{RSM} and δW_{RLC} are not meant to be the "one and only" error of either SES, but rather contain information on statistical and systematical errors which are calculated automatically during the RSM and RLC retrieval procedures. Increased values of δW_{RSM} and δW_{RLC} indicate systematic errors due to non-validity of the underlying assumptions of the respective method. From the error in W, the according error in T is defined by multiplication with A_{Strat} (3.4). Both error quantities are calculated during the processing of TSCDs as function of day and latitude.

3.1 Accuracy

Total (slant) column densities of nadir as well as limb measurements are potentially biased. Nadir SCDs are potentially

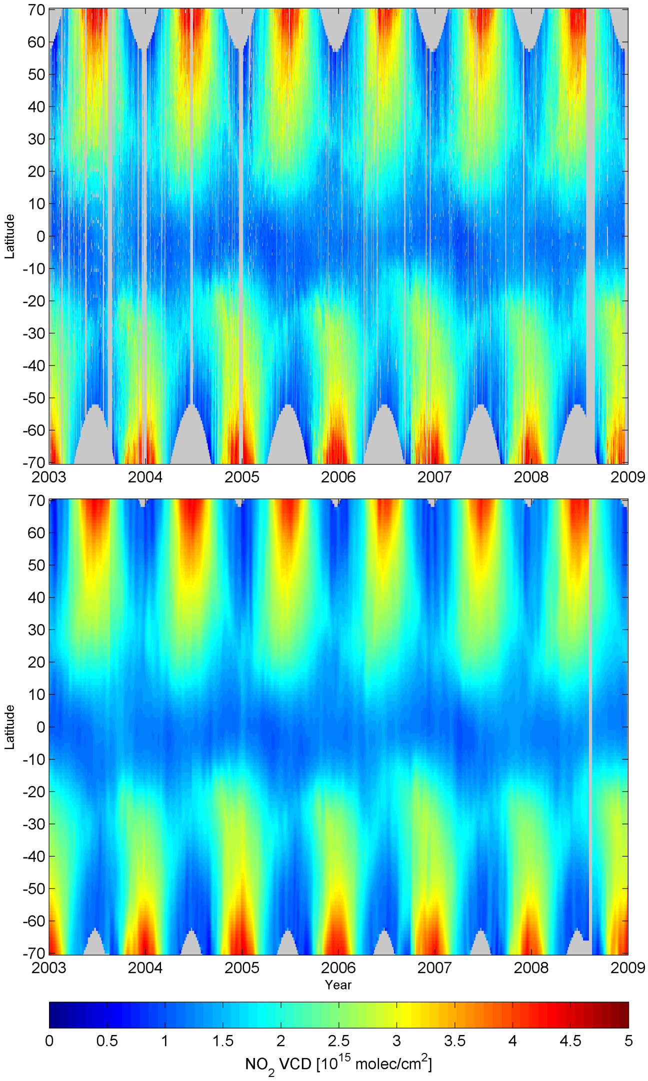

Fig. 1. Mean NO_2 VCD in the Reference Sector (RS) as function of day and latitude: $V^*_{\mathrm{RS}}(d,\Lambda)$ (top) and the smoothed LUT $\widehat{V}^*_{\mathrm{RS}}(d,\Lambda)$ (bottom).

affected by unknown spectral features introduced by the optical system and the necessity to measure the direct sun spectrum damped by a diffusor plate (Richter and Burrows, 2002; Wenig et al., 2004). This bias, as well as other systematic errors, generally may depend on time and latitude. However, all systematic error compounds that are the same in- and outside the RS are eliminated in the tropospheric excess CDs T_{RSM} and T_{RLC}.

The quantification of absolute biases, i.e. the estimation of the accuracy of total, stratospheric and thus tropospheric CDs, is difficult, and generally needs knowledge on the "truth". However, the "truth" is known in so far, that negative tropospheric CDs are unphysical. I.e., from the appearance of systematic negative TSCDs (on a level beyond possible statistical fluctuations around zero), a lower estimate of the local accuracy can be gained, and the removal/reduction of negative TSCDs is one central argument for the improvement of one SES compared to another.

In addition, spatial patterns of enhanced (or reduced) TSCDs far from source regions likely indicate artefacts introduced by a insufficient stratospheric correction, and allow the quantification of accuracies of the SES.

Finally, over unpolluted regions, the mean, but as well the standard deviation (over time) of tropospheric NO_2 CDs is expected to be low. If high standard deviations are observed, this indicates fluctuations of artefacts of the stratospheric estimation. Thus, the reduction of standard deviation is also a quantitative argument for the evaluation of the SES performance.

3.2 Standard deviation in the RS: δW_{RSM}

While averaging daily total VCDs V^* in 1° bins in the RS for the calculation of W_{RSM} (Eq. M3), we also calculate the respective standard deviation (std) $s(V^*_{\mathrm{RS}})$:

$$\delta W_{\mathrm{RSM}}(d,\Lambda) := s(V^*_{\mathrm{RS}}). \quad (1)$$

δW_{RSM} is processed similar to V^*_{RS}, i.e. a LUT $\widehat{\delta W}_{\mathrm{RSM}}(d,\Lambda)$ is created and smoothed with the same settings as for $\widehat{V}^*_{\mathrm{RS}}$. Fig. S2 displays $\widehat{\delta W}_{\mathrm{RSM}}(d,\Lambda)$. Typical values are about 2.5×10^{14} molec/cm^2.

As long as the basic assumptions of the RSM are justified, i.e. the RS being free of tropospheric pollution and stratospheric CDs being independent on longitude, δW_{RSM} is dominated by statistical errors (e.g. the DOAS fit noise and natural fluctuations of NO_2 VCDs). An increased value of $\widehat{\delta W}_{\mathrm{RSM}}$, like at 20°S (Fig. S2), indicates additional systematic errors, probably due to fit artefacts over oligotrophic oceanic regions. Also stratospheric dynamics may affect the RS, especially at high latitudes, leading to increased values of $\widehat{\delta W}_{\mathrm{RSM}}$ up to 5×10^{14} molec/cm^2 at 65° S in October).

3.3 Error of the LLV: δW_{RLC}

The neglection of zonal variations in the simple RSM introduces systematic errors in the TSCDs as will be shown below. The LLC reduces these systematic errors significantly, but can not remove stratospheric patterns completely. One reason for this is the need of interpolation and smoothing of the limb VCDs (defined at the respective tangent points) over space and time. Errors thus inevitably occur in cases of strong (spatial as well as temporal) gradients. Such shortcomings of the smoothed field $\widehat{\Delta L}$ are reflected by the mean quadratic deviation of the smoothed field $\widehat{\Delta L}_i$ and the individual LLV ΔL_i, where i is an index running over all considered limb states (including the previous and the following day) within a latitude bin of 1° resolution:

$$\delta W_{\mathrm{RLC}}(d,\Lambda) := \sqrt{\sum_i \left(\Delta L_i(d,\Lambda,\Phi) - \widehat{\Delta L}(d,\Lambda,\Phi)\right)^2}. \quad (2)$$

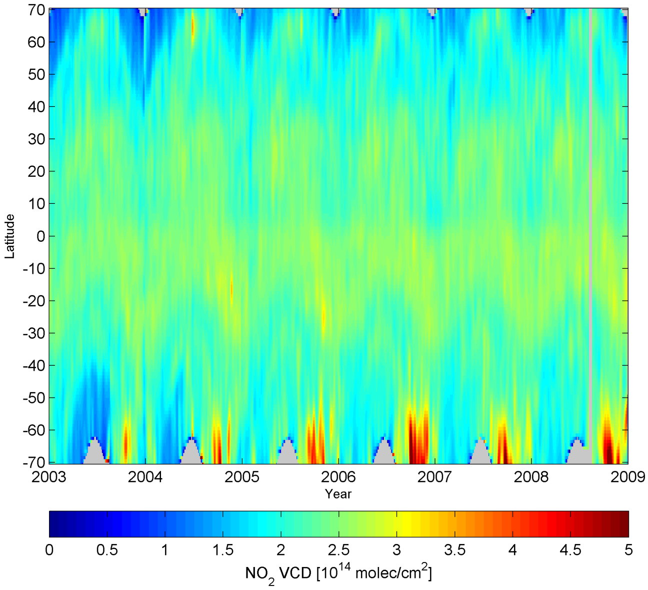

Fig. 2. Standard deviation of NO_2 VCDs in the RS $\widehat{\delta W}_{\mathrm{RSM}}(d,\Lambda)$ as function of day and latitude.

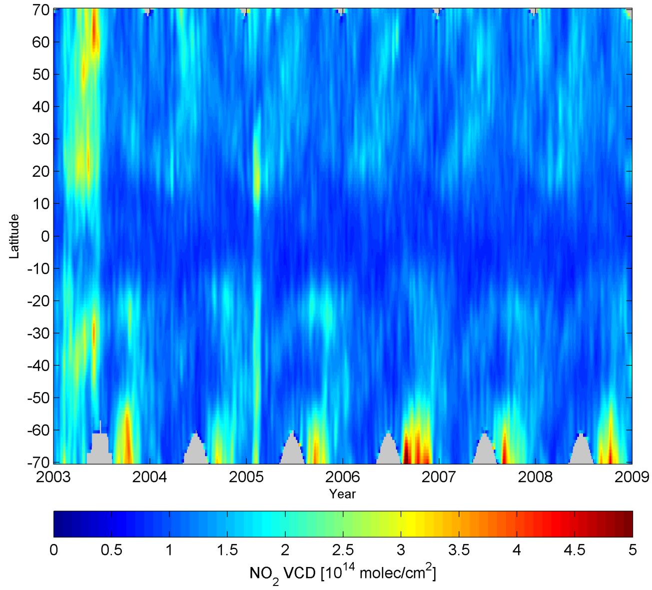

Fig. 3. Error of the LLV estimation $\widehat{\delta W}_{\mathrm{RLC}}(d,\Lambda)$.

Whenever the smoothed LUT $\widehat{\Delta L}$ is not capable of reflecting features of the measured LLV ΔL, this results in an increased error δW_{RLC}. Again, we create a smoothed LUT $\widehat{\delta W}_{\mathrm{RLC}}(d,\Lambda)$, which is shown in Fig. S3. High values of $\widehat{\delta W}_{\mathrm{RLC}}$ occur especially during autumn south from 60° S, as a consequence of strong spatial gradients of stratospheric NO_2 (see discussion).

From the difference $\Delta L_i(d,\Lambda,\Phi) - \widehat{\Delta L}(d,\Lambda,\Phi)$, in principle also a "state error" for individual states can be defined, which would retain the longitudinal dependency, which is lost in the definition of δW_{RLC}.

3.4 TSCD errors

From the errors in W, the respective errors in T are calculated by multiplication with the respective stratospheric AMF:

$$\delta T_{\mathrm{RSM}} := \delta W_{\mathrm{RSM}} \times A_{\mathrm{Strat}} \tag{3}$$

$$\delta T_{\mathrm{RLC}} := \delta W_{\mathrm{RLC}} \times A_{\mathrm{Strat}}. \tag{4}$$

δT is thus higher than δW by A_{Strat}, i.e. a factor of 2-7.

4 Daily examples

In addition to the sample day presented in BE09 (28 January 2006), Figs. S4-S10 illustrate the different SES (Figs. S4,S6,S8,S10) and the resulting TSCDs (Figs. S5,S7,S9) for three additional days in April, July and October.

5 Monthly climatologies

Figs. 11-16 show monthly climatologies of TSCDs (Figs. S11,S13,S15) and their differences (Figs. S12,S14,S16) for April, July, and October. In constrast to BE09, only differences of RSM and RLC are shown, as the ALC introduces zonal stripes throughout the year due to the different latitudinal dependencies of L and V^* (compare Fig. S10).

References

BE09: Beirle, S., S. Kühl, J. Puķīte, and T. Wagner, Retrieval of tropospheric column densities of NO_2 from combined SCIAMACHY nadir/limb measurements, amt-2009-87, AMTD, 2009.

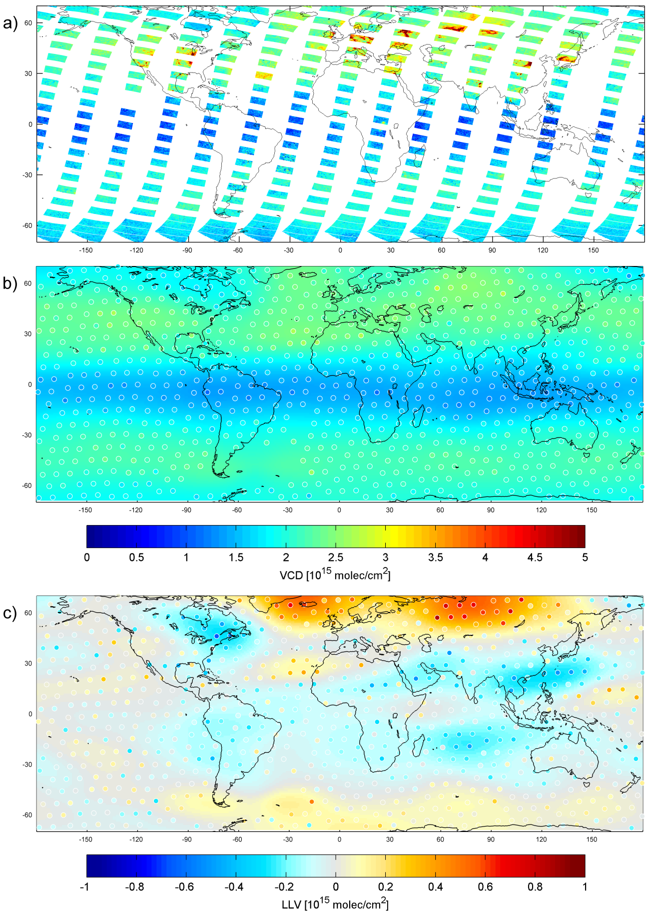

Fig. 4. Results for 2 April 2005. a) Total nadir VCD V^* b) Stratospheric limb VCD L c) Longitudinal Limb Variation ΔL. Colour-coded disks in b) and c) indicate individual limb states (including the previous and following day), while the maps show the respective interpolated and smoothed fields.

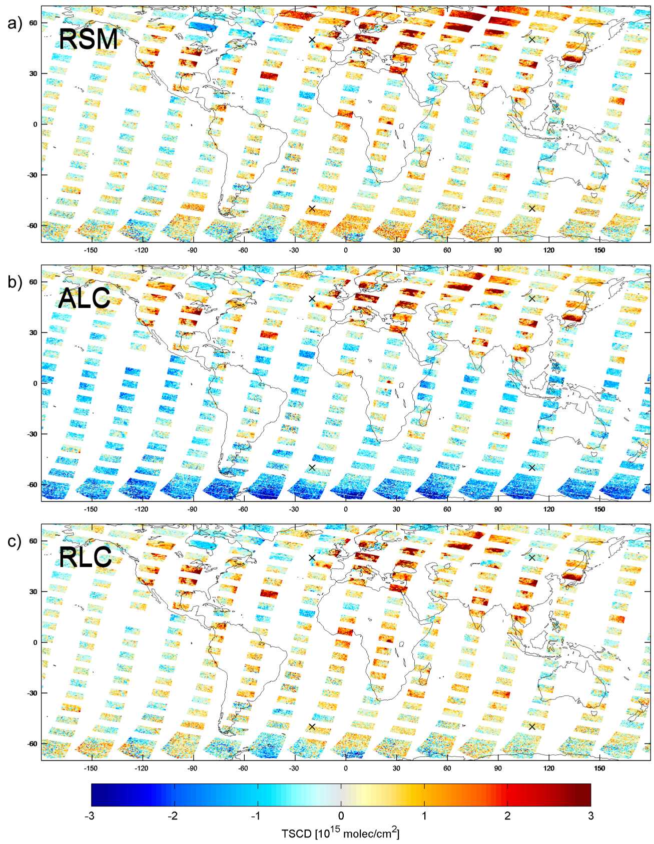

Fig. 5. Tropospheric SCDs for 2 April 2005.
a) T_{RSM}: Reference Sector Method.
b) T_{ALC}: Absolute Limb Correction.
c) T_{RLC}: Relative Limb Correction.

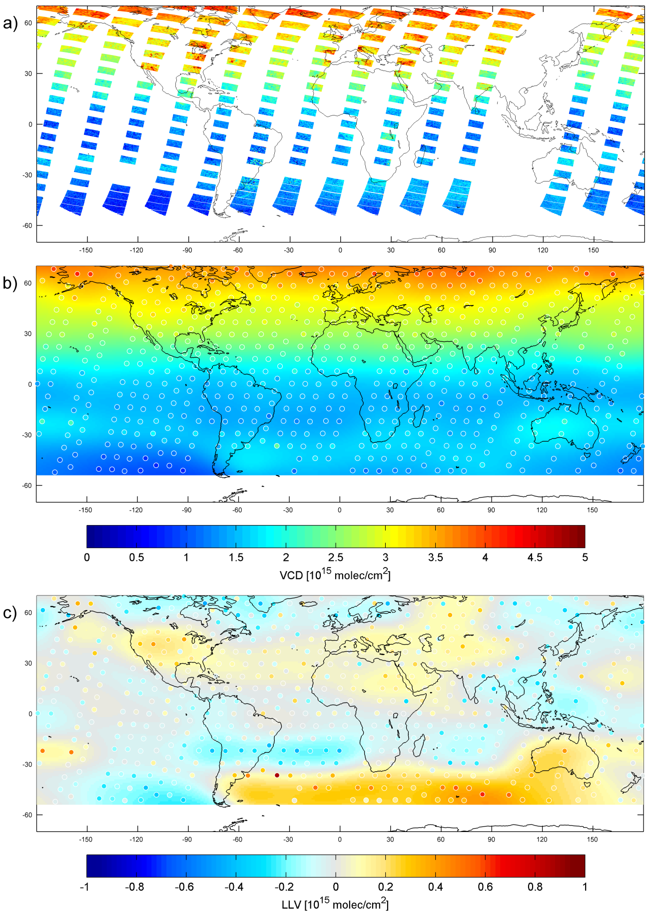

Fig. 6. Results for 20 July 2005. a) Total nadir VCD V^* b) Stratospheric limb VCD L c) Longitudinal Limb Variation ΔL. Colour-coded disks in b) and c) indicate individual limb states (including the previous and following day), while the maps show the respective interpolated and smoothed fields.

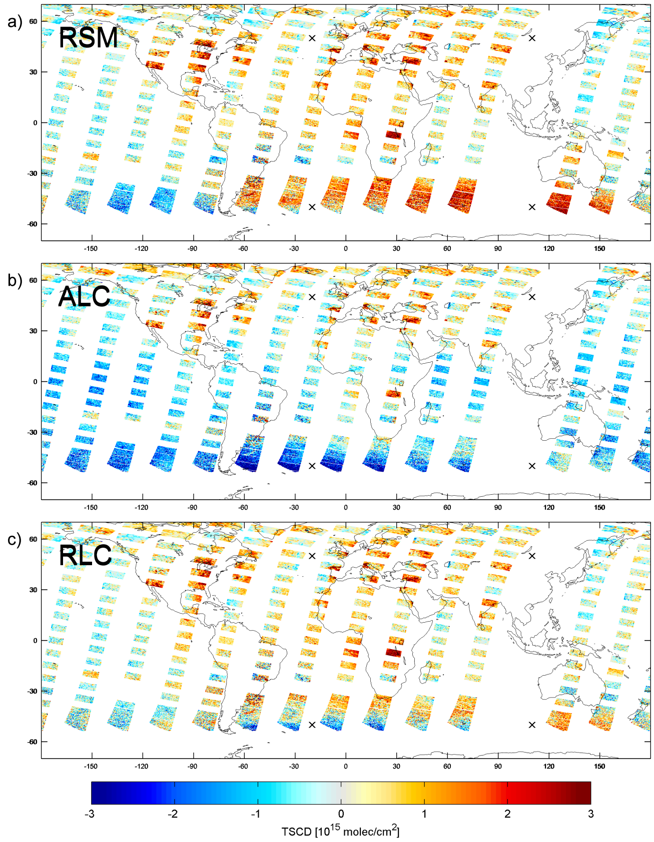

Fig. 7. Tropospheric SCDs for 20 July 2005.
a) T_{RSM}: Reference Sector Method.
b) T_{ALC}: Absolute Limb Correction.
c) T_{RLC}: Relative Limb Correction.

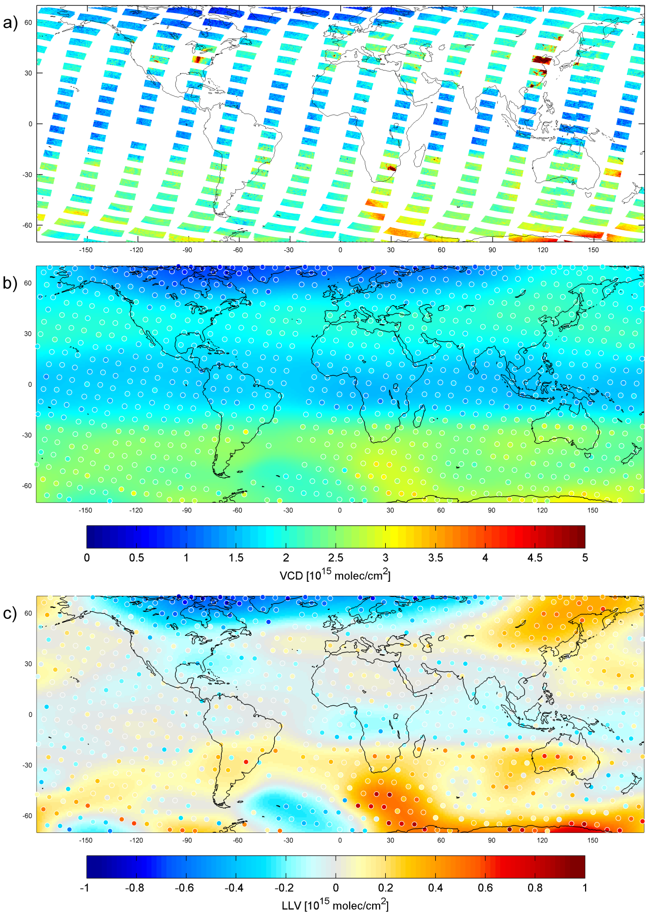

Fig. 8. Results for 24 October 2005. a) Total nadir VCD V^* b) Stratospheric limb VCD L c) Longitudinal Limb Variation ΔL. Colour-coded disks in b) and c) indicate individual limb states (including the previous and following day), while the maps show the respective interpolated and smoothed fields.

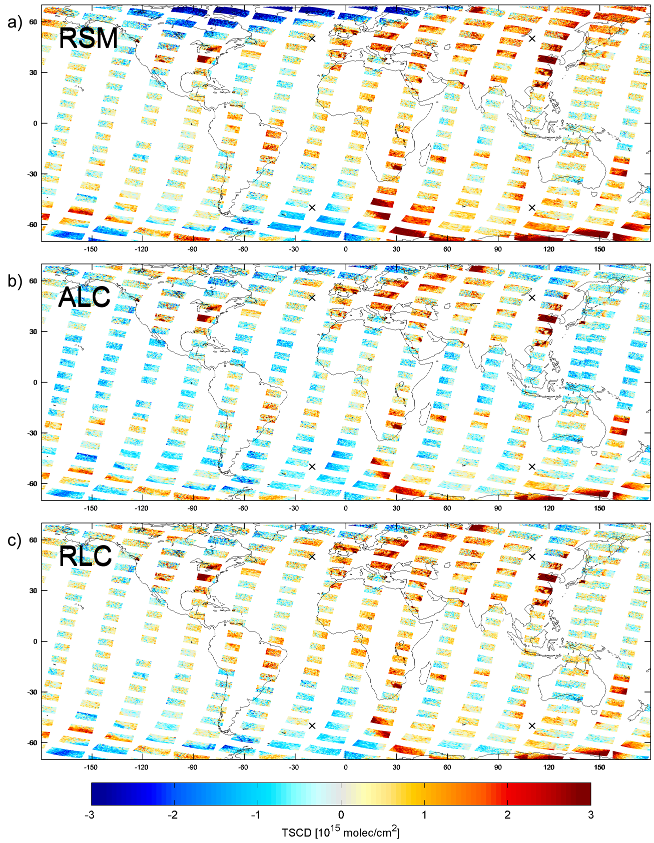

Fig. 9. Tropospheric SCDs for 24 October 2005.
a) T_{RSM}: Reference Sector Method.
b) T_{ALC}: Absolute Limb Correction.
c) T_{RLC}: Relative Limb Correction.

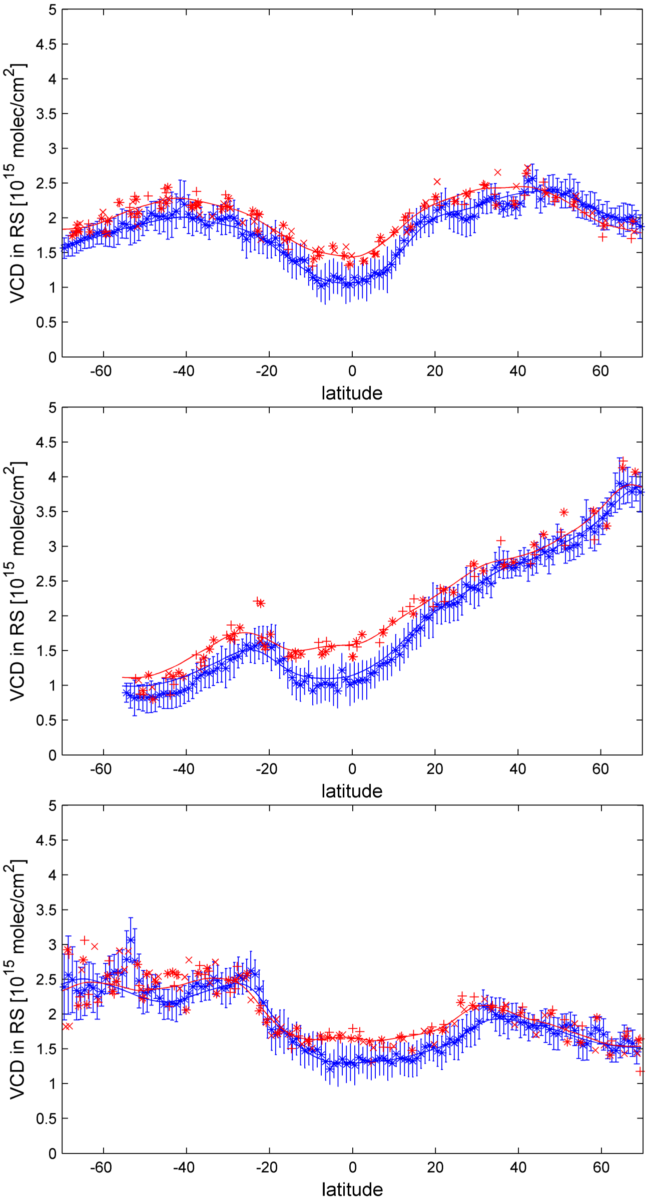

Fig. 10. Latitudinal dependencies of V^{*}_{RS} (blue) and L_{RS} (red) for 2 April 2005 (top), 20 July 2005 (middle), and 24 October 2005 (bottom).
Nadir measurements are binned in 1° bins and displayed as mean (*) and standard deviation (bar). Limb measurements are displayed for the acutal day (*) as well as for the previous (+) and the following (x) day. The curves show the respective smoothed LUTs $\widehat{V}^{*}_{\mathrm{RS}}$ and $\widehat{L}_{\mathrm{RS}}$.

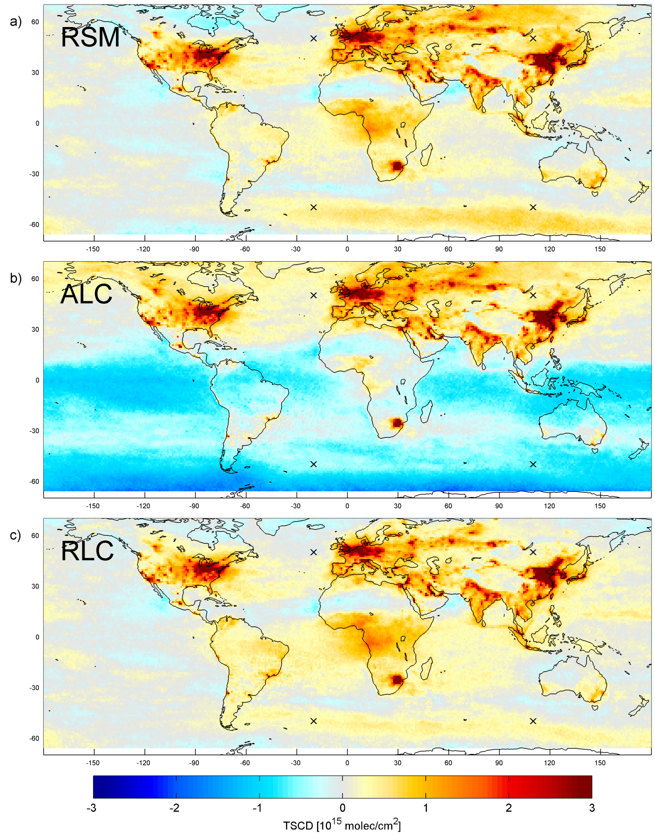

Fig. 11. Mean tropospheric SCDs for April 2003-2008. a) T_{RSM}: Reference Sector Method. b) T_{ALC}: Absolute Limb Correction. c) T_{RLC}: Relative Limb Correction.

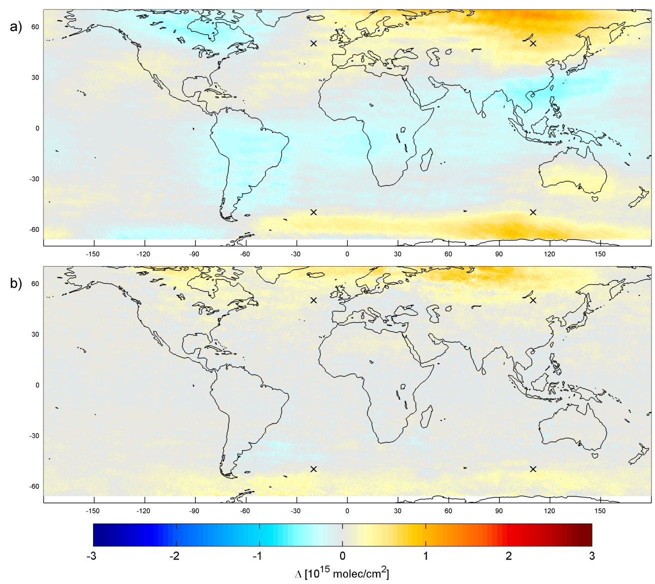

Fig. 12. Difference of RSM and RLC for April 2003-2008.
a) Difference of mean tropospheric SCDs T_{RSM}-T_{RLC}
b) Difference of standard deviations: $s(T_{\mathrm{RSM}})$-$s(T_{\mathrm{RLC}})$.

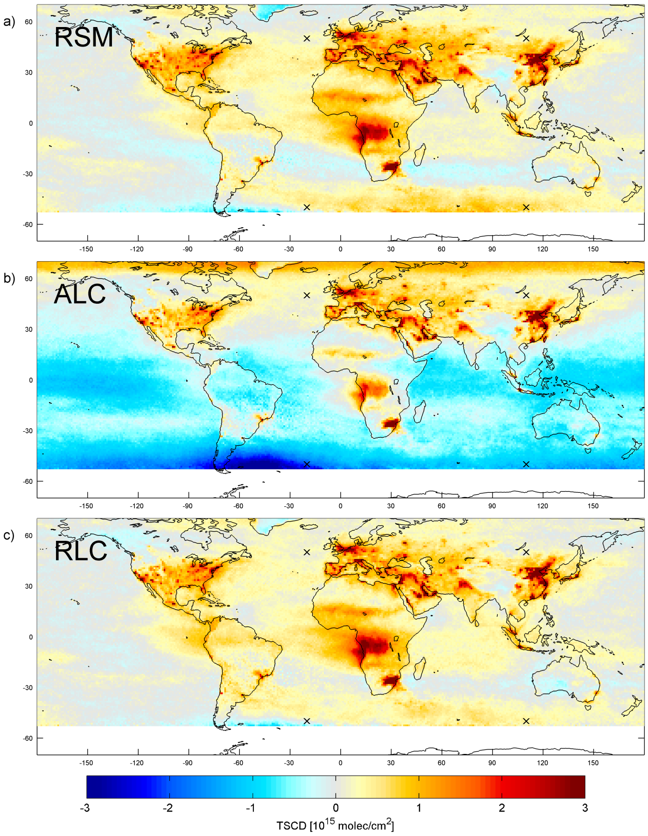

Fig. 13. Mean tropospheric SCDs for July 2003-2008. a) T_{RSM}: Reference Sector Method. b) T_{ALC}: Absolute Limb Correction. c) T_{RLC}: Relative Limb Correction.

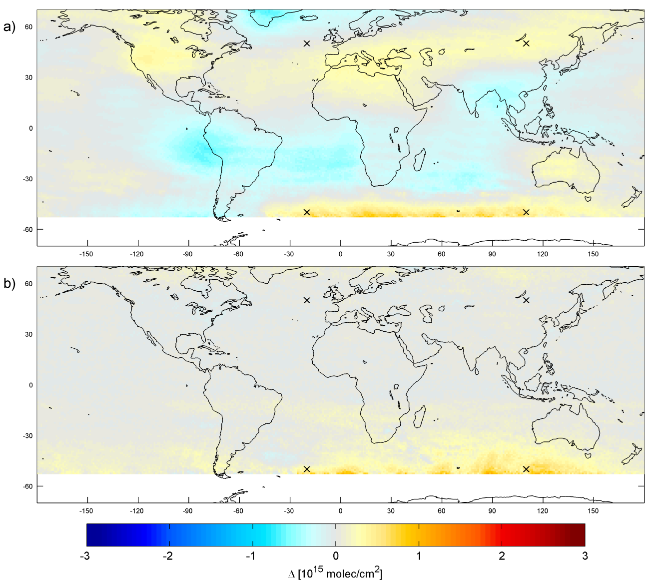

Fig. 14. Difference of RSM and RLC for July 2003-2008.
a) Difference of mean tropospheric SCDs T_{RSM}-T_{RLC}
b) Difference of standard deviations: $s(T_{\mathrm{RSM}})$-$s(T_{\mathrm{RLC}})$.

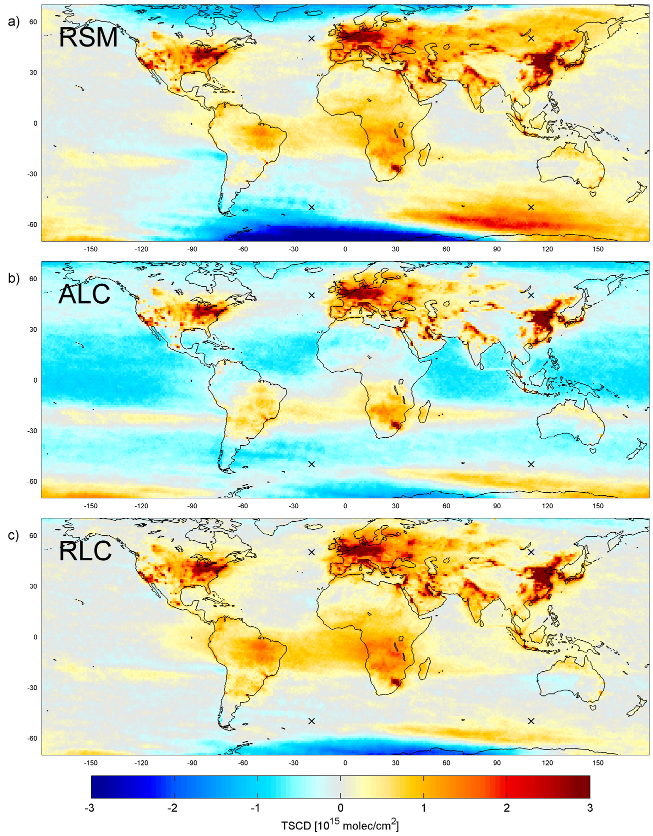

Fig. 15. Mean tropospheric SCDs for October 2003-2008. a) T_{RSM}: Reference Sector Method. b) T_{ALC}: Absolute Limb Correction. c) T_{RLC}: Relative Limb Correction.

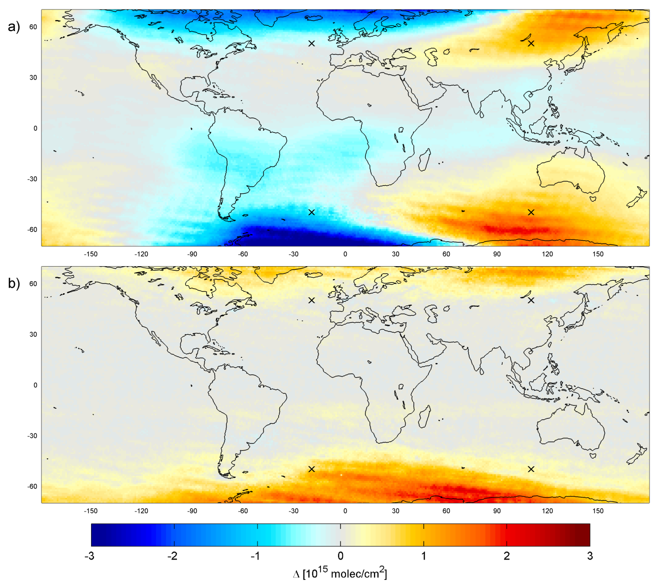

Fig. 16. Difference of RSM and RLC for October 2003-2008.
a) Difference of mean tropospheric SCDs T_{RSM}-T_{RLC}
b) Difference of standard deviations: $s(T_{\mathrm{RSM}})$-$s(T_{\mathrm{RLC}})$.