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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Retrieval of nitrogen dioxide stratospheric profiles from ground-based zenith-sky UV-visible observations: validation of the technique through correlative comparisons" *by* F. Hendrick et al.

F. Hendrick et al.

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At first, we would like to thank Dr H. K. Roscoe for his helpful comments and suggestions.

Referee comment: However, this success has led to the exposure of what I believe is a conceptual mistake concerning the smoothing error, also to be found in our own earlier work (Preston et al. 1997). The mistake is now obvious because the variability of NO2 from the new climatology is much larger than our earlier guess. This results in a smoothing error that is at least 5 times the sum of all other errors, often over 10 times their sum (Hendrick et al. 2004, Figure 1). This surely cannot be correct. The formalism for the covariance of the smoothing error on p2875 is correctly quoted as Ss

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= (A-I)Sx(A-I)T, where A is the matrix of averaging kernels and Sx is the covariance matrix of the true NO2 profile. The authors, like us, then equate Sx to the covariance matrix of the a priori profile, Sa. From the variability of satellite measurements, together with the correlation of values between adjacent altitudes, the authors have for the first time been able to derive an accurate value of Sa, where the diagonal elements are the squares of the variabilities and the off-diagonal elements are the correlations. However, equating Sx to Sa cannot be correct, as the true profile cannot have a standard error as large as the variability the authors show from NO2 climatology, which is 50% at 25 km (Hendrick et al. 2004, Figure 1), even though Rodgers (2000) justifies it: “Because the true state is not normally known, we cannot estimate the actual smoothing error... What is required is a description of the statistics of the error, which must be calculated from ... some appropriate ensemble of states, which may or may not be that described by ... Sa”. Rodgers (2000) goes on to a more subtle discussion of the meaning of smoothing error: “Many remote observing systems cannot see spatial fine structure, the loss of which contributes to smoothing error. To estimate it correctly, the actual statistics of the fine structure must be known”. This argues that the smoothing error is not concerned with the variability of NO2 (the diagonal elements of Sa), only with size of fine structure, or wiggliness, of likely true profiles (the off-diagonal elements). If the diagonal elements of Sa were set to zero, might this then provide a better estimate of smoothing error Ss? The smoothing error in Figure 1 of the manuscript would certainly have more reasonable values. Fortunately, this knotty philosophical problem can be bypassed. Rodgers (2000) exposes another conceptual mistake that we have all been making for many years: “it may be better to abandon the estimation of the smoothing error, and consider the retrieval as an estimate of the smoothed version of the state, rather than an estimate of the complete version of the state”. In the manuscript, the validations compare retrieved ground-based profiles with smoothed balloon-borne and satellite profiles, so the retrieval is indeed considered an estimate of the smoothed version of the state. This is also true of most literature discussions of profiles from remotely-sensed measurements, necessarily so if the profile is shown at altitudes spaced by the

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vertical resolution of the retrieval. Is it appropriate in the manuscript and most of the literature to abandon the concept of smoothing error?

Reply: One of the aims of our paper is to characterize the profiles retrieved from ground-based DOAS observations. This can only be achieved through a complete error budget including the main error source, which is the smoothing error in the case of measurements with low vertical resolution such as the ground-based UV-visible or FTIR spectroscopy. We agree with the Rodgers statement in the Dr H. K. Roscoe's comments "it may be better to abandon the estimation of the smoothing error, and consider the retrieval as an estimate of the smoothed version of the state, rather than an estimate of the complete version of the state". However the complete Rodgers statement (Rodgers, 2000, page 49) starts by "If the real covariance is not available, it may be betterĚ.". In our study, we have built a covariance matrix Sx based on a real ensemble of states (HALOE profiles) and, according to Rodgers, we can therefore estimate the smoothing error. It is also the first time that the smoothing error associated with ground-based UV-visible profiling is calculated using a Sx matrix based on a real ensemble of states. That is the reason why the smoothing error is so large, because the "true" variability is large compared to the one corresponding to the Sa matrices which have been used - in a erroneous way - to calculate the smoothing error up to now. Similar results have been obtained with the ground-based FTIR spectroscopy. For example, Barret et al. (2002) have characterized the retrieval of ozone profiles from solar IR spectra. Using a Sx matrix based on a real ensemble of states, they obtained a smoothing error which is also 5 or 10 times the sum of all other errors, as in our study. Another important point is that we did not equate Sx to Sa as claimed by Dr H. K. Roscoe. The Sa matrix has been constructed empirically (see page 2873, lines 10-19 in our paper) whereas the Sx matrix has been constructed using HALOE profiles (see page 2876, lines 2-20 in our paper). The reason is that, if we use in the retrieval a Sa matrix identical to the Sx matrix, which presents large variability on its diagonal, undesired oscillations in the retrieved profiles often occur. Thus, Sa has been determined empirically for "technical" reasons. Setting the diagonal elements of the Sx

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matrix to zero would obviously lead to an erroneous estimation of the smoothing error. Smoothing error calculation has to be made with a covariance matrix with correct diagonal elements in case no off-diagonal elements are available. This can be highlighted by the statement by Rodgers concerning the interpretation of off-diagonal elements in a covariance matrix (Rodgers, 2000, page 39): "the non-diagonal covariance has a larger variance at large scales, and smaller variance at small scales, in contrast to the diagonal covariance which has variance at all scales equally". This means that the off-diagonal elements of Sx are responsible for an enlargement of the structures or that a diagonal matrix has finer structures than a full covariance matrix. Therefore, a diagonal covariance matrix would lead to a realistic but overestimated smoothing error. A covariance matrix with diagonal values set to zero -as suggested by Dr H. K. Roscoe for a "more reasonable" estimation of the smoothing error- has no real physical meaning. The correlation matrix corresponding to such a covariance matrix has undetermined diagonal elements, and infinite off-diagonal elements!

Referee comment: In the validation exercise, the algorithm adopted for smoothing the high-resolution profiles to the lower resolution of the ground-based inversions (p2880 line5) is excellent if the high-resolution profile extends over a large altitude range. However, when its range is limited to 20 km or less, as in the Figures 6 and 8, the algorithm smoothes the high resolution profile inside its range with the a priori outside it. If the a priori is less than the high-resolution profile, the smoothed profile is biased downwards, as is clear in the Figures. This cannot possibly be the smoothing imparted by the retrieval scheme to true high-resolution profiles, they do not stop at 30 km. One way to proceed would be to repeat the retrieval using the previous result as the a priori. Another would be to replace the a priori in the smoothing alogorithm by the retrieved profile. Best might be to extend the balloon or satellite profiles by a smooth and continuous function (e.g. cubic spline) that became equal to the a priori at, say, 40 km. Certainly the current result is unsatisfactory because in most cases it makes the comparison with ground-based data look better than it should be.

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Reply: The correlative profiles cover a limited altitude range (e.g., 13-29 km for the SAOZ balloon) but according to the smoothing method, they have to be extended over the same altitude grid as the averaging kernels. For all the results presented in the manuscript, the correlative profiles have been completed below and above their covered altitude range by the a priori profile. As noted by Dr H. K. Roscoe and Referee #2, this is unsatisfactory because the smoothed correlative profiles are biased downwards since the a priori profiles are generally less than the correlative profiles, which makes the comparison with ground-based data look better than it should be. In the revised version of the manuscript, the correlative profiles are completed below and above their covered altitude range by the a priori profile scaled by the ratios between the correlative and a priori profiles at the lower and upper altitude limits of the correlative profile, respectively; e.g., a SAOZ balloon profile is completed below 13 km by the a priori profile scaled by the ratio between the SAOZ balloon and a priori profiles at 13 km, and above 29 km by the a priori profile scaled by the ratio of the SAOZ balloon and a priori profiles at 29 km. This scaling avoids the presence of large discontinuities at the lower and upper limits of the original altitude range of the correlative profile and results in higher smoothed correlative profiles than previously, especially for the SAOZ balloon profiles. Due to these changes, all the Figures and Tables are updated in the revised manuscript. The scaling also generally improves the agreement between smoothed and unsmoothed correlative profiles. However, low biases in the smoothed correlative profiles can still be observed as in Figure 7 for the Harestua 13.8.98 and Andoya 27.3.03 cases at low and high altitudes, respectively. The fact that the smoothed profile does not match the unsmoothed one is inherent to the smoothing method and observational technique used: the information content retrieved from the GB UV-visible measurements becoming significantly lower below 20km and above 30km, the second term of the Eq. 9 (p2880) is smaller at these altitudes due to the low values of the corresponding elements in the A matrix, resulting in an increase of the weight of the a priori profile in the smoothed correlative profile. This behaviour can be amplified in some cases, e.g. when the SZA sampling of the measurements is not optimal (low

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SZA upper limit and/or large SZA intervals above 90° SZA).

Referee comment: The authors determine the amount in the reference spectrum from the retrieval itself, justifying this as avoiding a Langley plot (p2871 line14). This is a circular argument, as the use of a Langley plot is identical to the addition of the extra parameter of amount in the reference into the retrieval, if the Langley plot uses the retrieved profile in the radiative transfer model when calculating air mass factors (AMFs). The advantage of the authors' method is that it avoids systematic errors in the reference amount that could be introduced by a Langley plot using the a priori profile for calculating AMFs. The disadvantage is that prior Langley plots can derive intercepts for a whole data series, which can then be averaged to reduce random errors in reference amount. The best of both techniques would be achieved by averaging the reference amounts from the authors' method over the whole data series, then re-retrieving with this average as a forced reference amount.

Reply: We agree with the fact that the use of a Langley plot for determining the amount in the reference spectrum prior to the retrieval is identical to the addition of the amount in the reference spectrum as extra parameter into the retrieval. So we have rephrased this part by simply saying that a Langley plot prior to the retrieval is identical to the addition of the amount in the reference spectrum as extra parameter into the retrieval. Since we used DOAS data with daily reference spectra, the method suggested by Dr H. K. Roscoe (averaging the reference amounts obtained from the retrieval over the whole data series, then re-retrieving with this average as a forced reference amount) cannot be applied here.

Referee comment: The authors introduce systematic errors in the measurements into the error budget (p2875 line22). But unless these are of a pseudo-random nature with Gaussian distribution, they cannot be lumped in with random measurement errors in this way. Many systematic errors have a rectangular distribution with different upper and lower limits -how could such a distribution be included here?

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Reply: The part describing the retrieval error due to the measurement noise is rephrased. Since the residuals from the DOAS fitting were found to be in most cases dominated by the random noise of the detector, the measurement error is determined in the present study using a diagonal Se matrix (covariance matrix of the noise in the measurements) with values corresponding to the statistical errors on the NO2 DOAS fitting. So only random measurement errors and not systematic and random measurement errors as mentioned on line 22 p2875.

Referee comment: The number of independent pieces of information is determined from trace of A, the matrix of averaging kernels. The manuscript contains several examples of the dependence of its maximum value on various retrieval parameters, including a rather ambiguous statement about the upper limit of solar zenith angle (SZA) (p2878 line18). This is a critical point - could the authors please give a definitive statement or, better, a figure or table? Also important is the dependence of trace of A on the sampling - it presumably increases if the measurements go from intervals of 1° to 0.5° SZA, but does it further increase if they are at intervals of 0.25° SZA?

Reply: We have performed calculations of the trace of A using different SZA upper limit values and three fixed SZA intervals (1°, 0.5°, and 0.25°) in addition to the original SZA intervals of the measurements. Synthetic measurements with fixed SZA intervals have been generated by using a polynomial fit through the sunset Harestua May 25, 2001 measurements and interpolating on the desired SZA grid. A plot of the trace of A as a function of the SZA upper limit for the four SZA intervals is added in the revised manuscript. This plot shows that the trace of A increases with a decrease of the SZA intervals: e.g., when the SZA upper limit is 93.28°, the values of the trace of A for intervals of 1°, 0.5°, and 0.25° SZA are 1.82, 2.07, and 2.36, respectively, that means an increase of 30% from 1° to 0.25° SZA. The trace of A also increases with an increase of the SZA upper limit as expected. These results should be taken into account when new DOAS instruments are developed in order to maximise the number of independent pieces of information contained in the measurements.

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Referee comment: The authors have an unusual notion of an ill-posed problem (p2872 line20). They state that there are more elements in the state vector x than in the measurement vector y. If true, the problem would be underdetermined, the equivalent of 3 simultaneous equations in 5 unknowns, and there is no unique solution. But this is not usually true in ground-based zenith sky measurements - the state vector should have few elements (6 altitudes between 5 and 45 km), whereas spectra are measured at intervals of 0.5° SZA over a range from 88° to 94° SZA (12 measurements). Hence the problem is overdetermined, and there would be conflict but for noise on the measurements, which if large enough also results in the lack of a unique solution. Either problem would usually be thought of as ill-posed.

Reply: We agree with Dr H. K. Roscoe concerning the inappropriate use of the notion of ill-posed problem. Due to the noise on the measurements, the number of linearly independent equations is smaller than the number of unknowns. According to Rodgers (2000, page 27), the problem is in this case not ill-posed but “ill-conditioned”. The sentence is now: “Because the retrieval problem is ill-conditioned (the error on some measurement components of the vector y can be large enough that these components become useless, resulting in the lack of a unique solution to Eq. 1), a priori constraints are necessary to rejectĚ”

Referee comment: The authors rightly set the tropospheric amount in the a priori profile to a negligibly small value (p2873 line3). But their explanation is only true if xa is defined as concentration (molec cm-2) not mixing ratio (ppbv). Although the Figures show that xa is indeed concentration, they are introduced later in the paper. For clarity, the definition should be given at this earlier point.

Reply: In order to take this comment into account, the sentence “The NO2 a priori profiles are taken from the output of a stackedĚ” is replaced by “The NO2 a priori profiles used in the present study are defined as concentration (molecule/cm3) and are taken from the output of a stackedĚ.”

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Referee comment: The authors beg many questions by introducing an “ideal observing system” (p2874 line5), a phrase that could lead to many hours of debate. The system described is one where each measurement corresponds exactly to one element in the state vector, so inversion is unnecessary.

Reply: We have replaced an “ideal observing system” by an “ideal inverse method”, which is less confusing.

Referee comment: The description of the balloon-borne measurements in sections 7 and 9 as being “solar occultation techniques” is rather odd considering that only measurements in ascent are used in the manuscript (occultation refers to the sun passing behind the earth, sunrise or sunset). Furthermore the ascent measurements could well be much finer than the 1 km vertical resolution quoted.

Reply: We agree and have deleted “solar occultation” for describing the ascent measurements. The vertical resolution of these is indeed finer than the 1 km quoted. However, the SAOZ balloon data are provided with a 1 km vertical resolution.

Referee comment: The authors make repeated points about whether the satellite data is inverted with chemical correction or not, but do not say the likely size of the correction. In fact at the higher altitudes of the validation data it is small, almost certainly less than 1% at sunset (Roscoe & Pyle 1987).

Reply: According to Randall et al. (2002) and Newchurch et al. (1996), neglecting a correction for the variations of NO2 along the line of sight leads to a systematic overestimation of NO2 which can reach 20 % at 20 km. This rather large correction magnitude is clearly in contrast with the findings of Roscoe and Pyle (1987). The uncertainty on the diurnal effect correction seems therefore to be very large, mainly because this correction strongly depends on the photochemical model used for calculating it. Nevertheless, the absence of such a correction in the POAM III retrievals could at least partly explain the large discrepancies systematically observed between the GB profile retrievals and POAM III below 25 km since this explanation is consistent with the

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significantly better agreement observed with HALOE - which includes a correction for the diurnal effect - than with POAM III in sunset spring and summer conditions. The comparison of the relative differences in these conditions (below 20% for HALOE and comprised between 20% and 40% for POAM III) suggests that the magnitude of the diurnal effect correction could reach at least 10%. This effect could also play a significant role in the difference observed between sunrise and sunset in the agreement between GB retrievals and HALOE data (larger discrepancies at sunrise than at sunset) since the uncertainty on it can be 2 to 3 times larger at sunrise than at sunset (Gordley et al., 1996). More investigations - which are beyond the scope of the present study - are required to go one step further in the determination of the exact impact of this error source as well as others (e.g., the errors due to interfering absorbers and uncertainties on spectral parameters) on the agreement between GB retrievals and satellite instruments.

Referee comment: The authors see a consistent seasonal pattern in the comparison of ground-based and POAM results (p2882 line11, and Figure 10), which my eye cannot see. They state the mean overestimation by POAM is 6% in spring and 12 % in summer, but in midsummer 1998 (June) the overestimation averages about 9%; and in spring 1999 (April) all values exceed 12%. Only the year 2000 exhibits anything like the pattern described in the manuscript.

Reply: We agree with Dr H. K. Roscoe that it cannot be concluded that there is a seasonal dependence, except perhaps in 2000. Therefore, this point is cancelled.

Referee comment: In the caption to Figure 5, the use of ““fit “” is obscure and its quotes do not help; and the statement about error bars is ambiguous - is the full length 5e14 or are they ’s5e14, and are they one or two-sigma?

Reply: We have deleted the term ““fit “”. The statement about the error bars is indeed ambiguous. Typical error values amount to 5x1014 molecules/cm2, which means that the corresponding error bars amount to 1x1015 molecules/cm2. The corrected caption

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is: “Comparison between measurements and SCDs calculated using the a priori and retrieved profiles for the Harestua May 25, 2001 at sunset retrieval. The error bars on the measurements are contained within the symbols (typical error values amount to 5x1014 molecules/cm2 and correspond to one standard deviation of the statistical error from the DOAS fitting).”.

References

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