

An improved temperature correction for OMI NO₂ slant column densities from the 405-465 nm fitting window

Summary:

The Differential Optical Absorption Spectroscopy (DOAS) technique used in the satellite retrieval of NO₂ slant column densities (SCDs) requires a precise knowledge of its absorption cross-section, measured in the laboratory. The reference cross-sections used in this fitting method have been measured in the lab at a temperature of 220 °K. The actual temperature where NO₂ resides in the atmosphere differs significantly with altitude, so that the absorption cross-section spectrum is temperature-dependent. Neglecting the temperature dependency of the NO₂ absorption cross section may result in large systematic errors in the DOAS method. This Technical Note provides an improved temperature correction factor for a post hoc temperature-correction on the NO₂ slant columns. Reprocessed OMI slant columns retrieved in the 405-465 nm fitting window with NO₂ cross sections of 220 °K, 240 °K, and 294 °K are compared to obtain a new, empirical temperature sensitivity for NO₂ slant column densities. We compare the new temperature correction formula with the one used in DOMINO-2- and SP2- algorithms. The proposed temperature correction equation is similar to the SP2 correction formula for the most part of the 200-320 °K temperature interval, showing a slight disagreement at higher temperatures. In contrast, this study's correction factor diverges significantly from the one used in DOMINO-2, suggesting an improved cross-section-‘fitting’ at the corresponding slant-column-weighted (effective) temperatures.

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References

- Boersma, K. F., E. J. Bucsela, E. J. Brinksma, and J. F. Gleason (2002), NO₂, in *OMI Algorithm Theoretical Basis Document, vol. 4, OMI Trace Gas Algorithms, ATBD-OMI-04, Version 2.0*, edited by K. Chance, pp. 13-36, NASA Distrib. Active Arch. Cent., Greenbelt, Md., Aug.
- Boersma, K. F., H. J. Eskes, and E. J. Brinksma (2004), Error analysis for tropospheric NO₂ retrieval from space, *J. Geophys. Res.*, *109*, D04311, doi:10.1029/2003JD003962.
- Boersma, K. F., H. J. Eskes, R. J. Dirksen, R. J. van der A, J. P. Veefkind, P. Stammes, V. Huijnen, Q. L. Kleipool, M. Sneep, J. Claas, J. Leitao, A. Richter, Y. Zhou, and D. Brunner (2011), An improved tropospheric NO₂ column retrieval algorithm for the Ozone Monitoring Instrument, *Atmos. Meas. Tech.*, *4*, 1905-1928.
- Bucsela, E. J., N. A. Krotkov, E. A. Celarier, L. N. Lamsal, W. H. Swartz, P. K. Bhartia, K. F. Boersma, J. P. Veefkind, J. F. Gleason, and K. E. Pickering (2013), A new stratospheric and tropospheric NO₂ retrieval algorithm for nadir-viewing satellite instruments: applications to OMI, *Atmos. Meas. Tech.*, *6*, 2607–2626.
- Burrows, J. P., A. Dehn, B. Deters, S. Himmelmann, A. Richter, S. Voigt, and J. Orphal (1998), Atmospheric remote-sensing reference data from GOME: Part 1. Temperature-dependent absorption cross-section of NO₂ in the 231-794 nm range, *J. Quant. Spectrosc. Radiat. Transfer*, *60*, 1025-1031.
- Vandaele, A. C., C. Hermans, P. C. Simon, M. Carleer, R. Colin, S. Fally, M. F. Merienne, A. Jenouvrier, and B. Coquart (1998), Measurements of the NO₂ absorption cross-section from 42 000 cm⁻¹ to 10 000 cm⁻¹ (238-1000 nm) at 220 K and 294 K, *Journal of Quantitative Spectroscopy and Radiative Transfer*, Volume 59, Issues 3–5, Pages 171-184.
- van Geffen, J. H. G. M., K. F. Boersma, M. van Roozendael, F. Hendrick, E. Mahieu, I. de Smedt, M. Sneep, and J. P. Veefkind (2015), Improved spectral fitting of nitrogen dioxide from OMI in the 405–465 nm window, *Atmos. Meas. Tech.*, *8*, 1685–1699.

Introduction

NO₂ is one of the most important trace gases because it is a criteria pollutant and because of its essential role in ozone and aerosol formation, nitrogen deposition and the O₃ cycle (Burrows *et al.*, 1998). Furthermore, it exhibits a strong observable structured absorption feature in the visible spectral region which can be exploited by remote sensing, as for instance by the satellite-borne Ozone Monitoring Instrument (OMI) used in the current study. The algorithms for the retrieval of the OMI NO₂ amounts used in this study are:

- Dutch OMI NO₂ (DOMINO) algorithm version 2
- Standard Product (SP2) algorithm (OMNO2, version 2.1)

The OMI NO₂ slant columns version 2.0 derived from the updated slant column fitting approach by van Geffen *et al.* [2015] within the preparation of a new NO₂ retrieval processing for OMI, DOMINO version 3, are also used.

The Differential Absorption Spectroscopy (DOAS) method is applied in the OMI wavelength window of 405 nm to 465 nm, optimized for NO₂, to determine its slant column density (SCD). When low levels of air pollution are present, the slant column uncertainty is the dominant contribution to the overall retrieval error budget (Boersma *et al.*, 2004; Bucsela *et al.*, 2013). NO₂ is a gas distributed at different altitudes within the atmosphere; from the planet's surface to the upper stratosphere. Therefore its interference with the solar radiation is measured by UV-Visible instruments at notably different temperatures. By neglecting the temperature profile and assuming a homogenous NO₂ effective temperature of 220 °K, large systematic errors of the order of -20% might be present in the DOAS technique (Boersma *et al.*, 2004), so that, in principle, the cross sections should be fitted at the corresponding slant-column-weighted (effective) temperatures. Effective temperatures are determined from the atmospheric temperature profile, $T(z')$, weighted by the altitude-resolved air mass factor, $m(z')$ and the NO₂ number-density profile, $n(z')$, at altitude z' as follows:

$$T_{eff} = \frac{\int_z^{\infty} T(z') m(z') n(z') dz'}{\int_z^{\infty} m(z') n(z') dz'} \quad (1)$$

where z denotes the surface height. Since the trace gas effective temperature along the photon path is usually unknown, it is common practice to perform a spectral fit with a NO₂ cross-section spectrum obtained at one atmospheric temperature (e.g. $T_o = 220$ °K). An a posteriori temperature correction is then applied in the air mass factor calculation to compensate for the constant temperature assumption in the DOAS spectral fit (e.g. Boersma *et al.*, 2004; Bucsela *et al.*, 2013).

NO₂ cross-section temperature dependence

The temperature of 220 °K is considered to be the standard temperature for the DOAS spectral fitting. Vandaele et al. [1998] affirm the necessity to use a cross-section measured at a temperature as close as possible to the temperature of the NO₂ layer; the NO₂ bulk in the stratosphere (± 30 km) resides at a temperature close to 230 °K. The same study also reports that the NO₂ abundances calculated with the cross-sections at 220 °K are consistently 20% smaller than the amounts recorded at 294 °K, after the cross-section-convolution with the instrumental function of the IASB ground-based instrument developed for stratospheric studies. The laboratory cross-sections have been measured at 220, 240 and 294 °K (Vandaele et al., 1998) and convolved with the OMI instrument transfer function as described in van Geffen et al. [2015]. The change of the NO₂ differential absorption cross-sections with the absolute temperature is shown in Figure 1 (upper row; left panel). In the entire wavelength region (405-465 nm), the amplitude of the differential cross-sections decreases with increasing temperature, but the spectral features remain very similar. This decrease in amplitude becomes more intense at certain wavelengths.

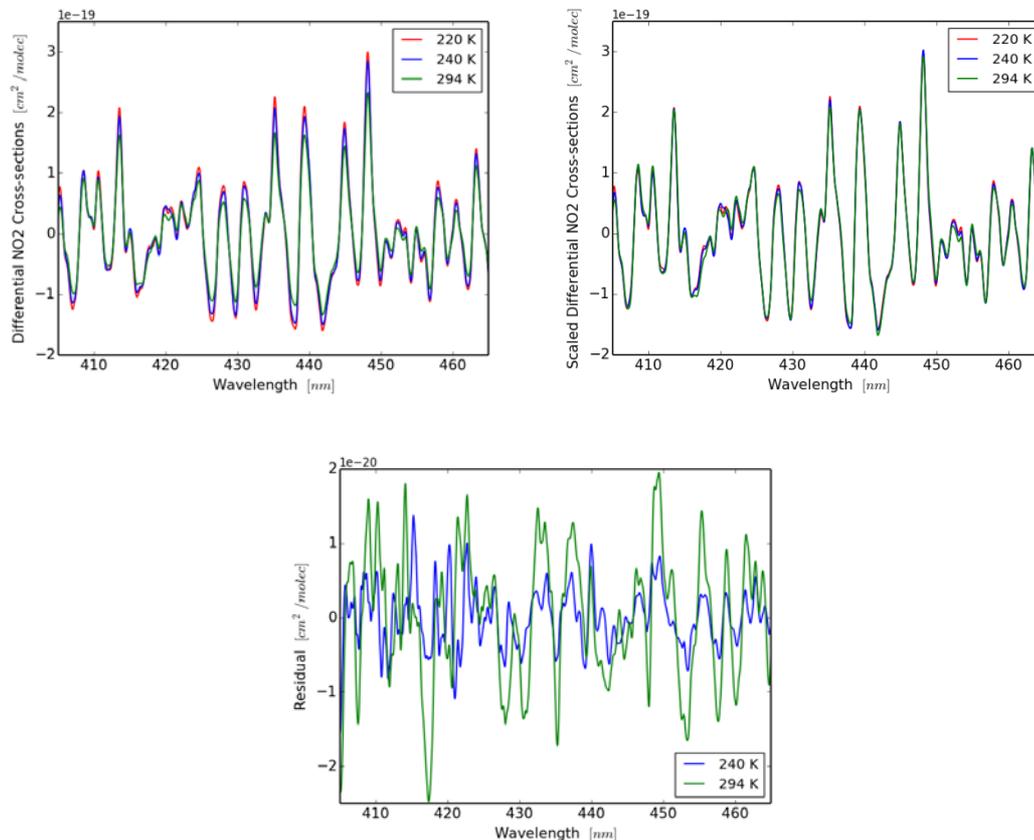


Figure 1: The NO₂ differential cross-sections (upper row; left panel) and the NO₂ scaled differential cross-sections (upper row; right panel) for different temperatures as a function of the wavelength and the respective scaled-differential-cross-section residual (bottom row).

As the simplest approach to determine the temperature dependence of the NO₂ cross-sections, the 240°K- and 294°K- differential cross-sections have been scaled to the 220°K- differential cross-sections by minimization of the root mean square (*rms*) of the differences between the scaled 220 °K and the original differential cross-sections expressed as

$$rms = \sum (\sigma_i^T - A^T \sigma_i^{T_o})^2 \quad (2)$$

where T_o is the 220 °K fixed fitting temperature, T is the temperature of the original, unscaled cross section for each wavelength, i , and A^T is the scaling factor. In Figure 1, upper right, we show the scaled cross sections after minimizing the rms (Eq. 2), and in the lower panel we show the differences between the scaled and the 220 °K cross sections. This difference indicates that the cross section shapes are slightly different, and this difference will be one contribution to the “DOAS fitting residuals”, after accounting for all absorbing species and the Ring effect.

The scaling factor A in Equation (2) is derived from the minimization of the residual rms and is found to be 0.939 and 0.789 for the effective temperature of 240 °K and 294 °K, respectively. In other words, the 220°K-cross-section amplitude is 6.5% larger than the 240°K- and 26.7% larger than the 294°K- cross-section. By scaling the cross-sections with the scaling factors, A , they are brought into reasonable agreement as shown in Figure 1 (upper row; right panel).

This technical note introduces an improved temperature correction factor for OMI NO₂ slant column fitting in the 405-465 nm spectral window. In section 3 we show the temperature correction factors currently used in DOMINO v2 algorithm (Sect. 3a) and NASA’s Standard Product v2.1 (Sect. 3b). Likewise, Sect. 3c describes this study’s temperature correction factor and its retrieval process in detail. The differences found between the aforementioned studies are discussed in Sect. 4, followed by conclusions in Sect. 5.

Temperature correction factor

The NO₂ vertical column density, N_v , is the ratio of the slant column density to the air mass factor, M , expressed as

$$N_v = \frac{N_s}{M} \quad (3)$$

The temperature correction is applied to the air mass factor:

$$M = \frac{\int_0^\infty m(z') C[T(z'), T_o] N(z') dz'}{\int_0^\infty N(z') dz'} \quad (4)$$

where $m = d(N_s)/d(N_v)$ is the altitude-resolved air mass factor. $N(z')$ denotes the NO₂ number density profile (molecules cm⁻² per layer) while the temperature correction factor $C[T(z'), T_o]$ accounts for the temperature difference between the fitting temperature, T_o , and the local atmospheric temperature, $T(z')$ (Boersma *et al.*, 2002).

a) DOMINO-2 temperature correction factor

Boersma *et al.* [2004] found that the temperature dependence of the DOAS slant column fit is well described within the narrow wavelength window of 425-450 nm (for e.g. GOME) by the correction term C for layer z' expressed as

$$C(T) = \frac{T_o - 11.39}{T - 11.39} \approx 1 - 0.0048 \cdot [T - T_o] \quad (5)$$

with T as the temperature of NO₂ in layer z' and the nominal spectral NO₂ -fitting temperature of $T_o = 220$ °K. The GOME-temperature-correction factor was also implemented in the DOMINO v2 algorithm instead of the correction factor that was introduced in the OMI Algorithm Theoretical Basis Document (OMI ATBD - Volume IV) for OMI Trace Gas Algorithms [2002] and later confirmed by the Bucseła et al. [2013] study.

b) SP2 temperature correction factor

Boersma et al. [2002] (OMI ATBD for OMI Trace Gas Algorithms), later confirmed by Bucseła et al. [2013], suggested an a posteriori correction for the difference between the current nominal spectral NO₂ fitting temperature of $T_o = 220$ °K and the actual atmospheric temperature. The proposed temperature-correction formula in those studies for the wider wavelength window of 405-465 nm is expressed as

$$C(T) = 1 - 0.003 \cdot [T - T_o] \quad (6)$$

where T represents the temperature of the atmosphere at a certain altitude and $T_o = 220$ °K is the fixed-NO₂-cross-section temperature used in the slant column fitting. The coefficient 0.003 (units °K⁻¹) is obtained empirically by fitting synthetic radiance spectra with NO₂ cross sections measured at several temperatures (Bucseła et al., 2013).

c) New temperature correction factor

Here we use results obtained from actual OMI level-1b data (Collection 3), processed by the improved OMNO2A fitting routine (see *van Geffen et al.*, 2015) in the 405-465 nm wavelength interval. OMI NO₂ slant columns version 2.0 provide a good opportunity to obtain an improved temperature correction for use in DOMINO v3 and QA4ECV retrieval algorithms.

The observational data was extracted from an OMI orbit in July 2005. The reason for not choosing a more recent orbit is the well-known “row anomaly” (RA) phenomenon in OMI data since 2007. The extent of the RA has increased since the first time it was noticed and currently affects approximately half of OMI’s pixels.

The OMNO2A processor, hosted by NASA, uses OMI level-1b spectra to calculate the standard OMI NO₂ SCD data, with cross-sections (*Vandaele et al.*, 1998) convolved with the instrument transfer function (ITF) or slit function prior to the DOAS fit (*van Geffen et al.*, 2015). Here we compare the 220°K-cross-section OMI NO₂ SCDs v2.0 with the NO₂ slant columns derived from adopting 240°K and 294°K cross sections. Figure 2 illustrates the ratio of the NO₂ slant column density using the 240 °K cross sections (left panel) and the 294 °K cross sections (right panel) as a function of the SCD at 220 °K. The black points indicate that the ratios of the SCDs are largely independent of the SCD itself. To obtain a weighted average ratio, we assign each binned SCD-ratio a weight, w , that determines the relative importance of each bin on the average, since the respective number of occurrences per bin (gray line, as indicated by the right y-axis) varies strongly with SCD. The new temperature correction values in Figure 2 are calculated as

$$C = \frac{\sum w_i c_{i,mean}}{\sum w_i} \quad (7)$$

where $c_{i,mean}$ is the average slant column ratio (black circles) for each bin, and w_i is the weight $1/\sigma_{i,mean}^2$ for each bin characterized by its uncertainty of the mean, $\sigma_{i,mean}$, as the ratio of the standard deviation, σ_i , (i.e. 1σ ; green bars) and the square root of the number of observations, n_i .

By doing so, we arrive at a temperature correction factor of 0.938 (red line in Figure 2; left panel) and 0.785 (red line in Figure 2; right panel) for the 240°K- and 294°K- cross-section cases, respectively. The 240°K- SCDs are 6.6% larger and the 294°K- SCDs are 27.4% larger than the 220 °K- SCDs. It is evident that the magnitude of the correction factor derived from Equation (7) is dominated by the $w_i, C_{i,mean}$ pairs from the bins in the range of $\sim 0.5 \cdot 10^{16}$ - $2 \cdot 10^{16}$ molec/cm² interval of the 220°K- slant column density, exactly where the number of observations is highest. The ratio for the high SCD values corresponds very well with the weighted mean in contrast to the smaller –more noisy- SCD ratios where the difference between the slant columns is larger. In this case small absorption features not accounted in the DOAS fit may interfere with the NO₂ features and influence the fit results somewhat.

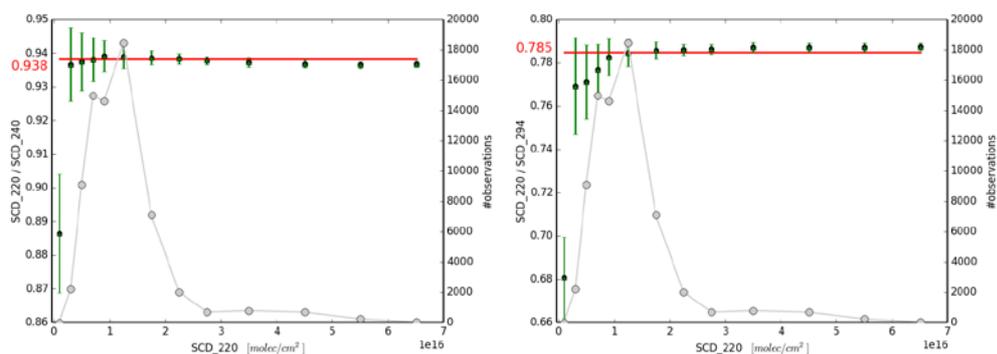


Figure 2: Temperature correction factor using the 240°K-cross sections (left panel) and 294°K-cross sections (right panel) (red line). The black circles indicate the mean slant column ratio per bin while the gray line describes the number of occurrences in each bin.

We now compare the temperature correction factor, C , to the scaling factors, A , derived earlier. The wavelength window used in the DOAS fit between modeled and observed reflectance spectra by OMI is wider (405-465 nm) than the one in GOME's case (425-450 nm). Attempting to quantify this difference and considering that the temperature correction factors, C , are numerically substantially close to the scaling factors, A , for the large spectral window, a new pair of scaling factors for the narrow wavelength window is calculated instead as seen in Table 1 below:

Table 1: Scaling factors, A , and temperature correction factors, C , for two different spectral windows. These values are used as test bed on OMI level-1 data after the cross-sections convolution to the instrument's slit function.

Wavelength Window (nm)	A (240 °K)	C (240 °K)	A (294 °K)	C (294 °K)
405 – 465	0.939	0.938	0.789	0.785
425 – 450	0.935		0.773	

The scaling factors for both spectral windows agree well, especially at lower temperatures. The temperature correction factors are numerically close to the scaling factors for both temperatures in the wide spectral window of 405-465 nm.

Boersma et al. [2004] and Bucsela et al. [2013] approached the temperature correction problem linearly as evident from Eq. (5) and (6). Here we test the relevance of including non-linear terms in the correction factor as a function of temperature. A quadratic polynomial fit was used on the C -values obtained for the 220, 240, and 294 °K cross section spectra (i.e. 1.0, 0.938 and 0.785, respectively) and the best fit through the data is expressed as

$$C(T) = 1 - 0.00316 \cdot (T - T_o) + 3.39 \cdot 10^{-6} \cdot (T - T_o)^2 \quad (8)$$

which defines the new temperature correction formula.

Figure 3 shows the temperature correction factor $C(T)$ vertical profile averaged over all pixels in one orbit. Implementing the atmospheric temperature profile extracted from the ECMWF database in the new correction formula (Eq. 8), we collected the mean temperature correction profile over one entire OMI orbit on 15 January 2005. Every blue star represents one of the 34 layers of the TM5 model whilst the red line indicates the temperature correction factor when the layer-temperature is equal to the nominal fitting temperature of 220 °K. Apart from the region where the actual temperature is equal (or significantly close) to 220 °K, the correction values deviate notably from unity (1). Neglecting the temperature effect will lead to appreciable underestimation or overestimation of the NO₂ columns, especially if a relatively large amount of NO₂ is present in layers with correction factors substantially different from 1. For example, such oversight will reduce boundary layer (denoted by the 5th-6th star) NO₂ observations by about 20%, which emphasizes the importance of accounting for the cross-section temperature dependence and the need for accurate temperature correction estimation.

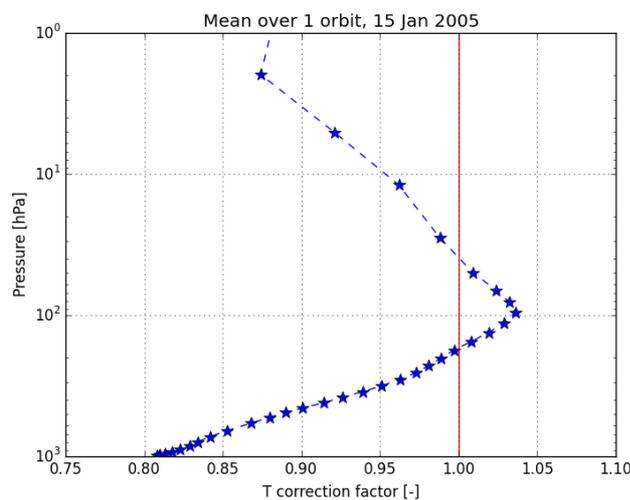


Figure 3: Mean temperature correction factor vertical profile over one orbit on 15 January 2005. The blue stars indicate the 34 TM layers and the red line pinpoints the correction factor when the atmospheric temperature is equal to the fixed fitting temperature of 220 °K.

Discussion

In this section we present the differences seen between the three temperature correction factors discussed in section 3. The temperature sensitivity derived from four research groups is tabulated in Table 2.

Table 2: Overview of temperature sensitivities from the literature

Authors	Wavelength Window	Temperature Sensitivity
<i>Boersma et al. [2002]</i>	405 – 465 nm	0.3% °K ⁻¹
<i>Boersma et al. [2004]</i>	425 – 450 nm	0.48% °K ⁻¹
<i>Bucsela et al. [2013]</i>	405 – 465 nm	0.3% °K ⁻¹
<i>This study</i>	405 – 465 nm	0.32% °K ⁻¹

Our new coefficient (linear approximation) of 0.0032 (per °K) is in line with the temperature coefficient proposed in Boersma et al. [2002] and Bucsela et al. [2013]. But it differs significantly from the one determined by Boersma et al. [2004], which was based on GOME-data. Our new correction (in the 200-320 °K temperature interval) is shown in Figure 4 (green line). Our new temperature correction factor is in excellent agreement with the Bucsela et al. [2013]- factor up to ~ 280 °K. For higher temperatures, there are differences up to -2.4%.

DOMINO-2 adopted Equation (5) from Boersma et al. [2004] as its temperature correction formula. The DOMINO-2 correction (Figure 4; red line) deviates from both our new- and Bucsela- factors over the entire temperature range by up to 4% (at T=200 °K), and 6% (T=320 °K). At the nominal temperatures of 240 and 294 °K the relative difference between the Boersma [2004] and the reference line is -2.7% and -6%, respectively. This implies a considerable understatement on the correction that has been applied within the DOMINO-2 algorithm for high temperatures, because it was based on the 425-450 nm window for GOME. Based on the scaling factors for the narrow window in Table 1, a re-estimation of the red line is performed. It is seen that the use of different wavelength windows during the fitting process could explain approximately 1/4th of the difference seen between the Boersma [2004]- and our new- correction. Other features such as different satellite overpass times and the differences between boundary layer thickness at midday- and afternoon- hours also play a role.

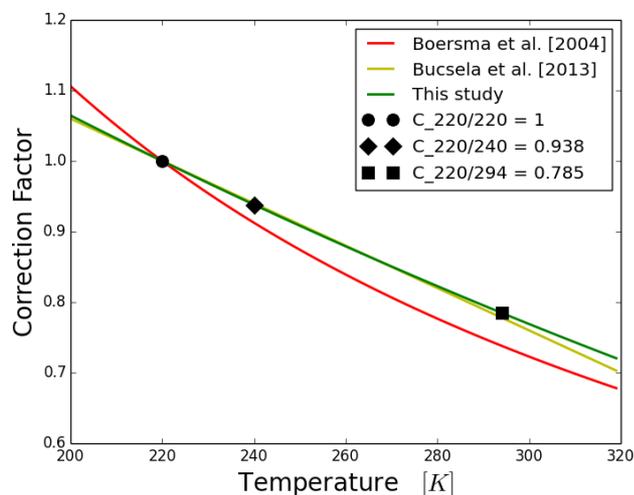


Figure 4: Temperature correction factors used in OMI NO₂ algorithms from this work (green line), Bucsela et al. [2013] (yellow line), and from Boersma et al. [2004] (red line) as a function of temperature. The temperature correction factor in Boersma et al. [2004] was based on GOME data and the 425-450 nm fitting window.

Conclusions

This Technical Note proposes an improved temperature correction factor and compares it with the correction factors used in DOMINO-2 and SP2 algorithms. The new correction factor is in an excellent agreement with the SP2-correction formula throughout the 200-320 °K temperature interval. The notable difference with the DOMINO-2 factor motivates us to recommend for the (re)processing of OMI NO₂ (DOMINO-3 and QA4ECV) the following equation to correct for temperature sensitivity of the NO₂ slant column densities in the 405-465 nm window:

$$C(T) = 1 - 0.00316 \cdot (T - T_o) + 3.39 \cdot 10^{-6} \cdot (T - T_o)^2$$

with T the atmospheric temperature at a certain altitude and $T_o = 220$ °K is the fixed-NO₂-cross-section temperature used in the DOAS fit.



The comparison of the differential NO₂ cross-section spectra at 220, 240, and 294 °K indicates that the cross-section shapes are slightly different. These spectral differences are not taken into account when fitting with one reference temperature NO₂ cross-section (220 °K for OMI). This implies that for situations with effective temperatures are substantially higher than 220 °K (such as in polluted situations), such differences will contribute to the "DOAS fitting residuals", after accounting for all absorbing species and the Ring effect.

For the QA4ECV project, we recommend to investigate the temperature-dependence of NO₂ SCDs obtained from the GOME, SCIAMACHY, and GOME-2 level-1 data in the 425-450 nm spectral windows. A similar comparison as done here, wherein NO₂ SCDs obtained by using NO₂ cross-sections at different laboratory temperatures are analyzed for a complete orbit from these three instruments would provide us with a robust test of the 425-450 nm temperature-correction derived by Boersma et al. [2004] for the GOME-instrument. Since that study, spectral fitting approaches have been improved substantially, so that a new investigation is both timely and relevant.