Retrieval Advances of BrO/SO2 Molar Ratios from NOVAC

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Contents

5 Evaluation routine

This chapter outlines the algorithm which is used for the evaluation of the spectroscopic data recorded in NOVAC. The problem of contamination of the reference is explained and possible solutions are presented.

5.1 Conventional evaluation routine

The fitting routine used for this thesis is based on the DOASIS software Kraus (2006). The equations of the DOAS retrieval of this work are slightly different from Equation (3.7). Equation (3.4) can be rewritten as:

$$\begin{aligned} ln\left(I\left(\lambda, L\right)\right) =& ln\left(I_0\right) + P\left(\lambda\right) - \int_0^L \sum_j \sigma_j\left(\lambda, p, T\right) \cdot c_j\left(l\right) dl \\ =& ln\left(I_0\right) + P\left(\lambda\right) - \sum_j \sigma_j\left(\lambda, p, T\right) \cdot S_j \end{aligned} \tag{5.1}$$

The term $P\left(\lambda\right)$ is a polynomial that accounts for all broad-band effects which approximates the scattering effects of the atmosphere.

The ~~remaining~~ task of the DOAS routine is to find a model function $F\left(\lambda\right)$ that minimizes χ^2:

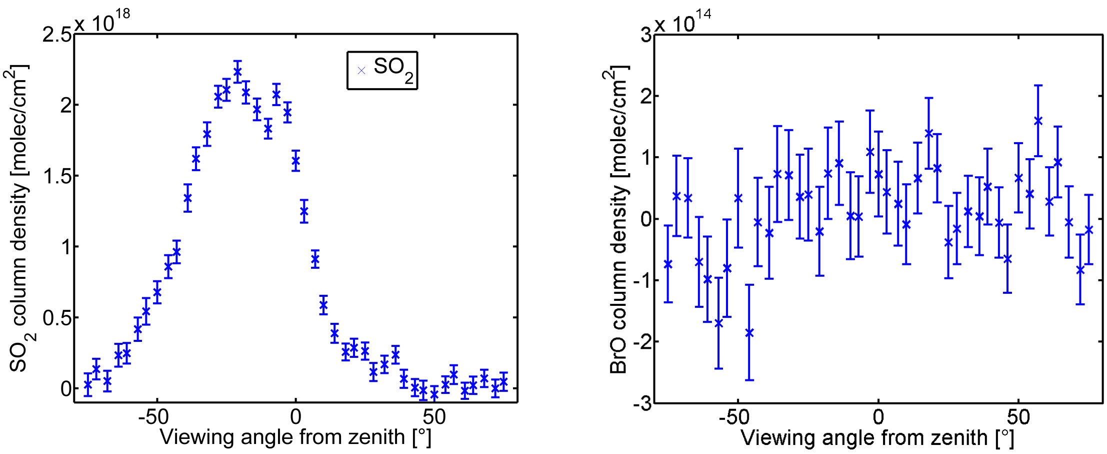
$$\chi^2 = \sum_{i=\lambda_1}^{\lambda_2} \left(ln(I(i)) - F(i)\right)^2 \tag{5.2}$$

While $F\left(\lambda\right)$ can be expressed on the basis of Equation (5.1):

$$F\left(\lambda\right) = ln\left(I_0\right) + P\left(\lambda\right) - \sum_j \sigma_j\left(\lambda\right) \cdot S_j \tag{5.3}$$

The DOAS fitting routine uses a combination of a standard least-squares fit and a Levenberg-Marquard algorithm to minimize χ^2

The SO_2 evaluation is performed for a wavelength range between 314.8 nm and 328 nm. Including a SO_2 absorption cross section recorded at a temperature of 298K Vandaele et al. (2009) and a O_3 absorption cross section recorded at 221K Burrows et al. (1999).
The BrO evaluation is performed for a wavelength range between 330.6 nm and 352.7 nm. The sum in Equation (5.3) includes for the BrO evaluation the following



(a) (b)

Figure 5.1: (a) SO_2 SCD as a function of the elevation angle with error bars computed by the DOASIS fitting routin. (b) BrO SCD as a function of the elevation angle with error bars computed by the DOASIS fitting routine. Taken from Warnach (2015)

absorption cross sections: BrO at 298K Fleischmann et al. (2004), the SO_2 and O_3 absorption cross sections described above, O_4 Hermans et al. (2003), NO_2 at 298K Vandaele et al. (1998) and CH_2O at 298K Meller and Moortgat (2000).
NOVAC provides spectral data for ≈ 50 different elevation angles. For the DOAS evaluation a reference and a measurement spectrum is needed. ~~To get the SCD's the references need to be free of any volcanic trace gas of interest~~ (this will be discussed more detailed in Section 5.2). ~~With the $F(\lambda)$ (Equation (5.3))~~ the column density of BrO and SO_2 of the measurement spectrum relatively to the reference spectrum can be calculated using ~~the calculations from above~~.

In the following we describe the technical implementation of the DOAS approach using the data of NOVAC instruments:
The first step is to correct each spectrum of the scan for dark current and offset using the dark ~~current~~ spectrum. The next task is to locate the ~~measurement spectrum and the reference region in the volcano plume~~. ~~To do so, the~~ pre-reference (the spectrum recorded at an elevation angle of 0°) is used to perform the evaluation of the scan spectra recorded at every elevation angle. For every spectrum of the scan the SO_2 differential slant column density (dSCD) with respect to the pre-reference is calculated using Equation (5.3) by the DOASIS fit routine.

The result is SO_2 dSCDs as a function of the elevation angle. This way the elevation angle corresponding to the maximum and the minimum of the SO2 column density can be determined. The location of the SO_2 maximum defines the location of the plume. The assumption is that the minimum of the SO_2 curve corresponds to a region outside of the plume which is true in most cases. The SO_2 amount in the

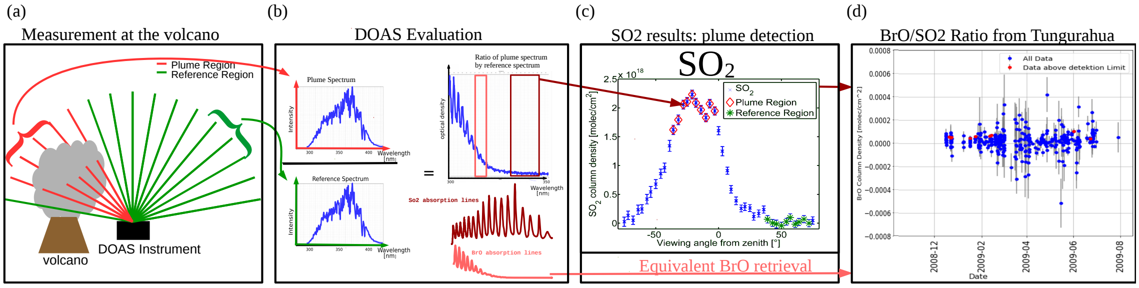
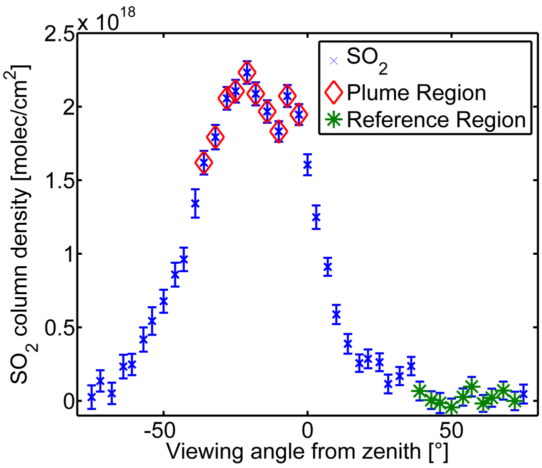
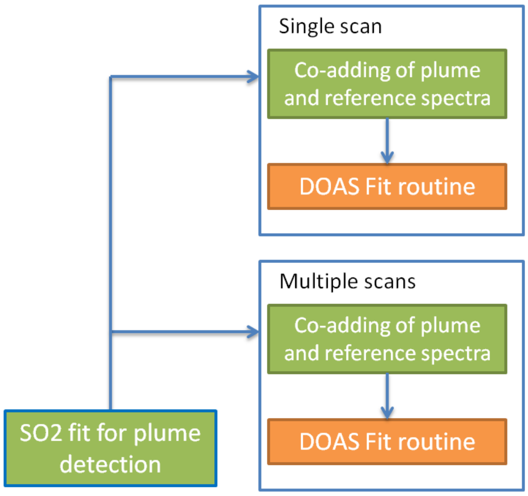


Figure 5.2: NOVAC Evaluation: (a) Measurement at the volcano (b) Evaluation of the spectral data with the DOAS routine using the absorption cross sections of BrO and SO_2. (c) Finding the location of the plume and reference (d) Computation of the ratios BrO/SO_2 at Tungurahua.

earth atmosphere is negligible (see Section 2.4.1) so we take it as a region of zero SO_2.
~~To detect the plume region~~ we use a gauss fit of the SO_2-elevaltion-angle-curve. ~~To increase the quality and to get a more robust result~~ the sum over several plume spectra is taken. If the gauss curve is too wide we use the 10 spectra with the highest SO_2 amount. As reference we use the sum of the 10 spectra with the lowest SO_2 amount.
The absolut slant column densities (SCD's) of BrO and SO_2 can now be calculated with the previously ~~detected~~ reference and plume spectrum. In Figure 5.1 (a) an example SO_2 SCD as a function of the elevation angle is shown. The SO_2 curve has a maximum at the position of the plume at an elevation angle of approximately $-30°$ to $0°$ and a reference region at an elevation angle of $40°$ to $70°$. Figure 5.1 (b) the extrema of the BrO curve are not as distinct as it is the case for the SO_2 curve. Since the BrO column density is much lower than the SO_2 column density, and just lies slightly above the detection limit, the plume is hard to detect using the BrO column density as it is shown in fig. 5.1 (b). Therefore we use the plume location we ~~found~~ by using SO_2 to evaluate the BrO column density.
~~To further increase the fit quality~~ multiple reference and plume spectra of successive measurements are added. Figure 5.3 (b) shows the routine of adding multiple spectra of consecutive measuring times. In the following the spectra resulting from the multi adding technique will be referred to as "Multi Add Spectra" ~~"Multi Add Spectra"~~.
Taking the BrO/SO_2 ratio if the column densities are close to zero yields unpredictable and unrealistic results. Thus, spectra measured outside of the volcano plume need to be excluded. This ~~could~~ be achieved by setting a BrO or/and an SO_2 threshold. A reasonable BrO threshold needs to be at least in the order of the DOAS fit error. However this could lead to elevated BrO/SO_2 ratios, since the BrO error is often close to the detection limit. Thus, all low BrO column densities are excluded from the evaluation. The other possibility is to set an SO_2 threshold. In this thesis



(a)



(b)

Figure 5.3: (a) SO_2 SCD as a function of the elevation angle. The co-added plume region is marked with red diamonds, and the co added reference region with green stars. From Warnach (2015). (b) Flow chart of the BrO and SO_2 evaluation. From Lübcke (2014).

an SO_2 threshold (plume limit) of $7 \cdot 10^{17} \frac{molec}{cm^2}$ is used for the selection of spectra for the evaluation of the BrO/SO_2 ratio. $7 \cdot 10^{17} \frac{molec}{cm^2}$ is a hight threshold for the column density. However, this ~~this~~ approach assures that only strongly significant gas amounts are accounted. This way, the BrO/SO_2 ratio will not be significantly influenced (Lübcke et al., 2014) and ~~that~~ all utilized measurement spectra are inside of the volcano plume.
Increasing a plume limit leads to an decrease of usable data. The ratio of usable data as a function of the plume limit is shown in Figure 5.4. An exponential decrease of data can be observed. The plot is based on the data of Tungurahua. Plume limits below $7 \cdot 10^{17}$ are shaded in yellow. A plume limit of $7 \cdot 10^{17}$leads to a ratio of usable data of approximately 10%.

5.2 Contamination problem

To assure that the reference is volcanic gas free a high resolution solar atlas spectrum (see Section 5.2) is used to evaluate the reference. In some reference spectra an amount of SO_2 different from zero is found. Thus we can conclude, that there are some references which contain a non-negligible amount of volcanic trace gases. In rare (ca. 10% of the data) scenarios, the volcanic plume covers the whole scan region. This could happen if for example the volcanic plume of the day before s extend over the hole scan area as a consequence of windless conditions. In consequence, the reference is contaminated with volcanic trace gases. Thus, the gas

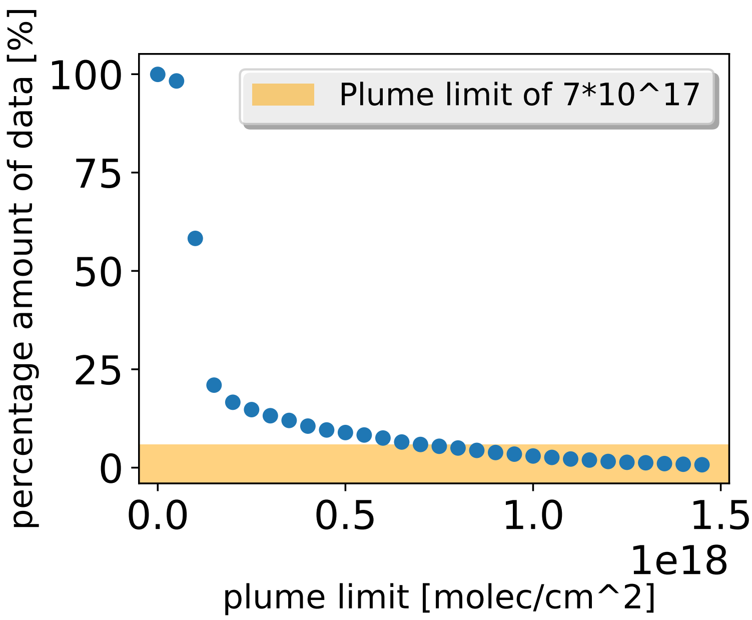


Figure 5.4: The decrease of the amount of usable data as a function of the plume limit. The plume limits below the actual plume limit of $7{\cdot}10^{17}$ are marked with a yellow shade.

amount is underestimated by the NOVAC-evaluation: In Figure 5.5 we see an example from April 2011 (Tungurahua) where the reference region is contaminated by volcanic trace gases. The blue SO_2 curve shows the calculations with the NOVAC-evaluation, but since there is still SO_2 in the reference region, the assumption, that the SO_2 amount could be set to zero in the reference region is wrong. The red curve shows the real SO_2 curve, which lies significantly above the NOVAC -curve.

If the reference region for any reason is contaminated by volcanic trace gases, there are two possibilities: excluding the contaminated data from the evaluation or the reference spectrum has to be replaced by a volcanic-gas-free reference. Alternative spectra are a theoretical solar atlas spectrum or a volcanic-gas-free reference spectrum recorded by the same instrument.

In the following we will discuss the two alternative reference spectra.

Evaluation using a Solar Atlas spectrum

An alternative for choosing the region with the lowest column density as reference region is to use a theoretical high resolution solar atlas spectrum as reference Chance and Kurucz (2010). The use of a theoretical solar atlas spectrum as a reference which is completely volcanic-trace-gases-free was first proposed by Lübcke et al. (2014).

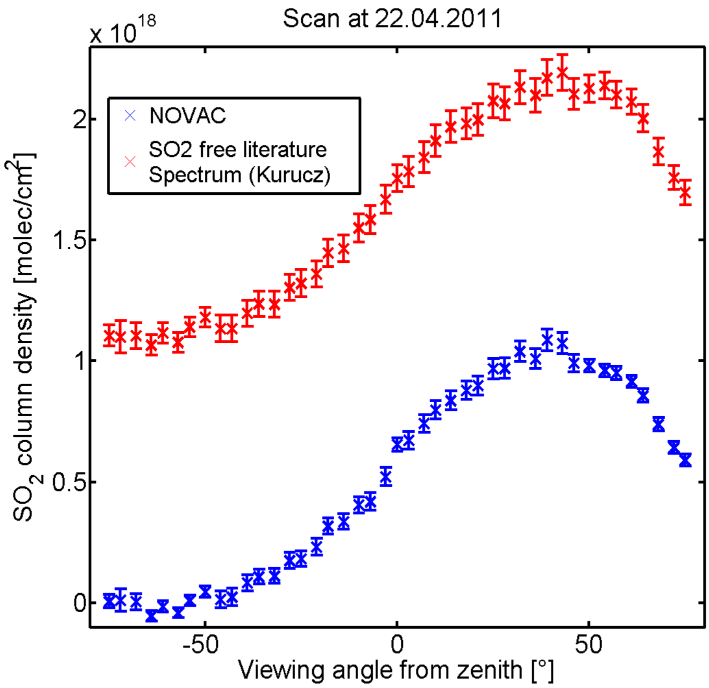


Figure 5.5: Scan with a contaminated reference spectrum from April 2011. From Warnach (2015)

The advantage of using a solar atlas spectrum as reference is, that we know that there are no volcanic trace gases and do not need to take this fact as a possibly inadmissible assumption. The disadvantage is, ~~that~~ using a solar atlas spectrum comes along with a drawback of precision: A theoretical solar atlas spectrum is far more precise than the spectra of the NOVAC instruments. Therefore the instrument functions ~~need~~ ~~to be~~ modeled and added to the retrieval.
The reduction of precision is acceptable for the SO_2 retrieval but not suitable for a BrO retrieval because then most data would be below the detection limit.

Possible contaminations can be checked by a theoretical solar atlas spectrum to evaluate the SO_2 amount in the reference.

Evaluation using a spectrum of the same instrument

An alternative reference spectrum could be a volcanic-gas-free reference spectrum recorded by the same instrument at a different time. When using such a reference several problems occur:
As described in Chapter 4 the instruments used in NOVAC do not include features like temperature stabilization. Due to that the measurements are not independent of external parameters. So we need to choose a reference recorded at similar conditions with respect to meteorology and radiation as well as in the temporal proximity

due to instrumental changes with time and ambient conditions. Ideally the external conditions should be equal to the conditions at the time when the plume was recorded.

In this work we combine both options in order to achieve both, enhanced accuracy but still maximum possible precision of the SO_2 and BrO retrievals. So we use the solar atlas spectrum to check for contamination and a reference spectrum recorded in temporal proximity by the same instrument as reference.

~~Thus,~~ if contamination occurs it is possible to choose from a list of gas free alternative references. In theory, for ideal instruments all references should lead to the same results for the gas retrievals. But instruments are imperfect (see Chapter 4) thus the reference need to be chosen carefully in order to ensure reliable results.

As discussed above it might occur, that, that the reference is contaminated for example by the plume of the day before. If that happens, we underestimate the gas amount by using a contaminated reference. But another possibility is, that the plume itself is also contaminated. This might be the case if the volcanic gas of the volcano is not taken away by the wind, but accumulates at the instrument. If this is the case, using an other reference would lead to an overestimation of the column density of gases. With the data retrieved by the NOVAC instruments it is very difficult to discover whether the plume is contaminated or not.
Figure 5.6 shows the strength of contamination as function of the mean SO2 amount of the day before. The strength of contamination is measured as the difference ~~when perform~~ the evaluation for SO2 with ~~the~~ contaminated reference recorded ~~as~~ the same time as the plume spectrum was recorded and ~~when~~ using a gas free reference. The data where fitted with a linear function. The left plot shows data from the Tungurahua volcano. In the right plot the data of Nevado Del Ruiz are visualized. Even though both plots show a slight increase of contamination strength with the mean amount of SO2 of the day before, the increase is not significant.

However this thesis is build on the assumption, that the plume is free of additional contamination. In the following we discuss how to ~~find the~~ an optimal reference from another scan ~~automatically~~.

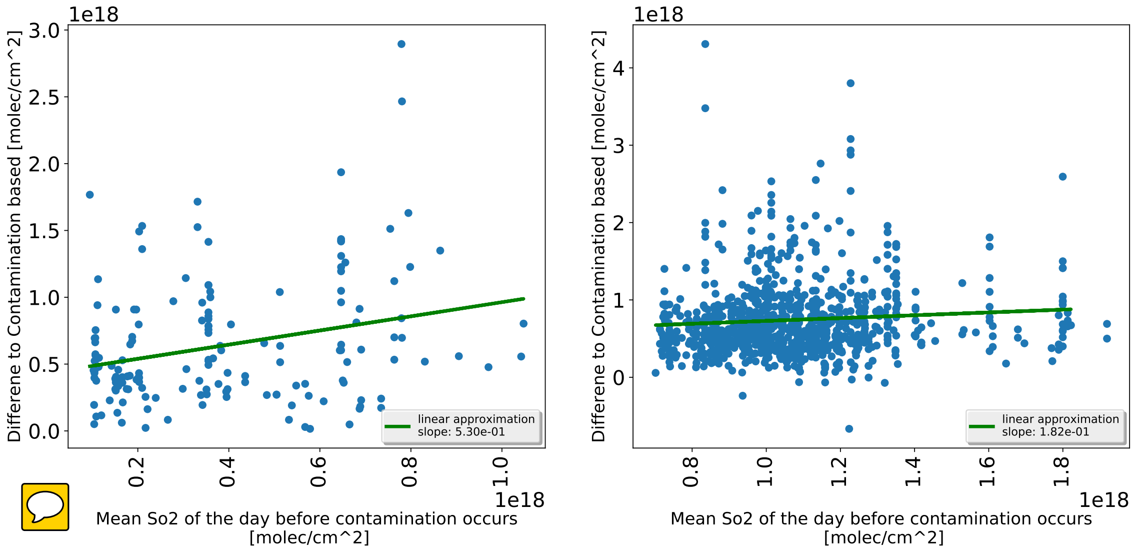


Figure 5.6: The strength of contamination as function of the mean SO2 amount of the day before. The strength of contamination is defined as the difference in SO2 SCD when evaluation with an alternative reference, or neglect the contamination. Left: data from Tungurahua. Right: data from Nevado Del Ruiz.