Retrieval Advances of BrO/SO$_2$ Molar Ratios from NOVAC

This Master thesis has been carried out by Elsa Wilken

at the

Institute for Environmental Physics, University of Heidelberg,

Germany

under the supervision of

Prof. Ulrich Platt

Optimierte Bestimmung des Molaren BrO/SO$_2$ Verhältnisses aus NOVAC Daten

Die Messung der absoluten Menge und des Verhältnisses von Vulkanischen gas Emissionen geben Einsicht in magmatische Prozesse. Das Network for Observation of Volcanic and Atmospheric Change (NOVAC) verfügt über ein System an automatisierten UV-Spektrometern, welche die Gas Emissionen der Vulkane aufzeichnen. Der Ausstoß von BrO und SO$_2$ kann mithilfe von Differenzieller optischer Absorptionsspektroskopie (DOAS) aus den aufgenommen Spekren bestimmt werden wobei die optische Absorption in der Fahne mit einem Hintergrundspektrum verglichen wird. Dies setzt voraus, dass das Hintergrund Spektrum nicht durch Vulkanische Gase beeinträchtigt ist. Typischerweise wird das Hintergrund Spektrum für einen Scan ein Höhenwinkel gewählt welcher als außerhalb der Fahne liegend identifiziert wird. Es hat sich jedoch gezeigt, dass auch diese Spektren noch durch Vulkanische Emissionen verunreinigt sein können. Als alternative Referenzspektren könnten 1) ein theoretisches Solar Atlas Spektrum oder 2) ein nicht verunreinigtes referenz Spektrum des selben Messgeräts dienen. Option 1) hat den Nachteil einer verringerten Messgenauigkeit, da Instrumenteneffekte hier modelliert werden müssen. Option 2) setzt vorraus, dass das Referenzspektrum unter ähnlichen Wetter- und Strahlungsbedingungen aufgenommen wurde. Wir verwenden die erste Methode um Kontaminierung zu identifizieren und greifen für die Bestimmung der Gas Konzentration auf die zweite Methode zurück um eine hohe fit Qualität sicher zu stellen. Stellen unsere Methode für NOVAC Daten von den Vulkanen Tungurahua und Nevado Del Ruiz vor.

Retrieval advances of BrO/SO$_2$ molar ratios from NOVAC:

Measurements of magnitude and composition of volcanic gas emissions allow insights in magmatic processes. Within the Network for Observation of Volcanic and Atmospheric Change(NOVAC) automatically scanning UV-spectrometers are monitoring gas emission at volcanoes. The emissions of BrO and SO2 can be retrieved from the recorded spectra by applying Differential Optical Absorption Spectroscopy(DOAS) and comparing the optical absorption of the volcanic plume to the background. Therefore, the background spectrum must not be affected by volcanic influence. Classically, the background spectrum is taken from the same scan but from an elevation angle which has been identified to be outside of the volcanic plume. However, experience shows those background spectra can still be contaminated by volcanic gases. Alternatively reference spectra can be derived from 1) a theoretical solar atlas spectrum or 2) a volcanic-gas-free reference spectrum recorded by the same instrument. 1) comes with a drawback of reduced precision, as the instrumental effects have to be modeled and added to the retrieval. For 2), the alternative reference spectrum should be recorded at similar conditions with respect to meteorology and radiation. We use the first option to check for contamination and the second to evaluate the spectra to maintain a god fit quality. We present our approach and its results when applied on NOVAC data from Tungurahua and Nevado Del Ruiz.

Contents

8 Results

This chapter shows and discusses the difference of the SO_2, BrO and BrO/SO_2 ratio data when evaluating with the NOVAC-Method, or with the contamination based method. The aim is to discover the systematic differences between the different retrievals and to discuss the reliability of the data.

To obtain the reference with minimal expected BrO error, the calculation of Equation (7.3) and the corresponding coefficients from Section 7.1 (Tungurahua) and Section 7.1 (Nevado Del Ruiz) are used. For the retrieval only "Multi Add" data are used. The maximal temporal difference between measuring the reference and the plume is two weeks. The maximal temperature difference is 3.3 °C.

Figure 8.1 shows a comparison of the results of contaminated data if performing the evaluation with the NOVAC-method and the contamination based method. The x-axis shows the column density of BrO respectively SO_2 calculated with NOVAC-method, the y-axis shows the column density calculated with the contamination based method. Only data are used where the corresponding SO_2 column density lies above the plume limit ($SO2\_SCD > 7 \cdot 10^{...}$). Hereby, the column densities are evaluated with the contamination based method. Thus, the corresponding SO_2 SCDs evaluated with NOVAC could be below $7 \cdot 10^{17}$. The plots on the left side (Figure 8.1(a) and 8.1(c)) show the results from the Tungurahua volcano while the plots at the right side (Figure 8.1(b) and 8.1(d)) show the results from Nevado Del Ruiz volcano. The black solid line shows a linear fit of the data, the dotted line indicates where the both evaluation are equivalent.

Figure 8.1(a) and 8.1(b) show the results for the BrO retrieval:

- The BrO column densities retrieved with the contamination based method have become larger on average compared to the NOVAC method.

- An almost constant offset of $1.2 \cdot 10^{13}$ (Tungurahua) and $2.0 \cdot 10^{13}$ (Nevado Del Ruiz) can be observed.

Figure 8.1(c) and 8.1(d) show the results for the SO_2 retrieval:

- The SO_2 column densities retrieved by the contamination based method become larger for almost every measurement compared to the NOVAC method.

- An almost constant offset of $6.5 \cdot 10^{17}$ (Tungurahua) and $7.4 \cdot 10^{17}$ (Nevado Del Ruiz) can be observed.

(a) Data of Tungurahua

(b) Data of Nevado Del Riz
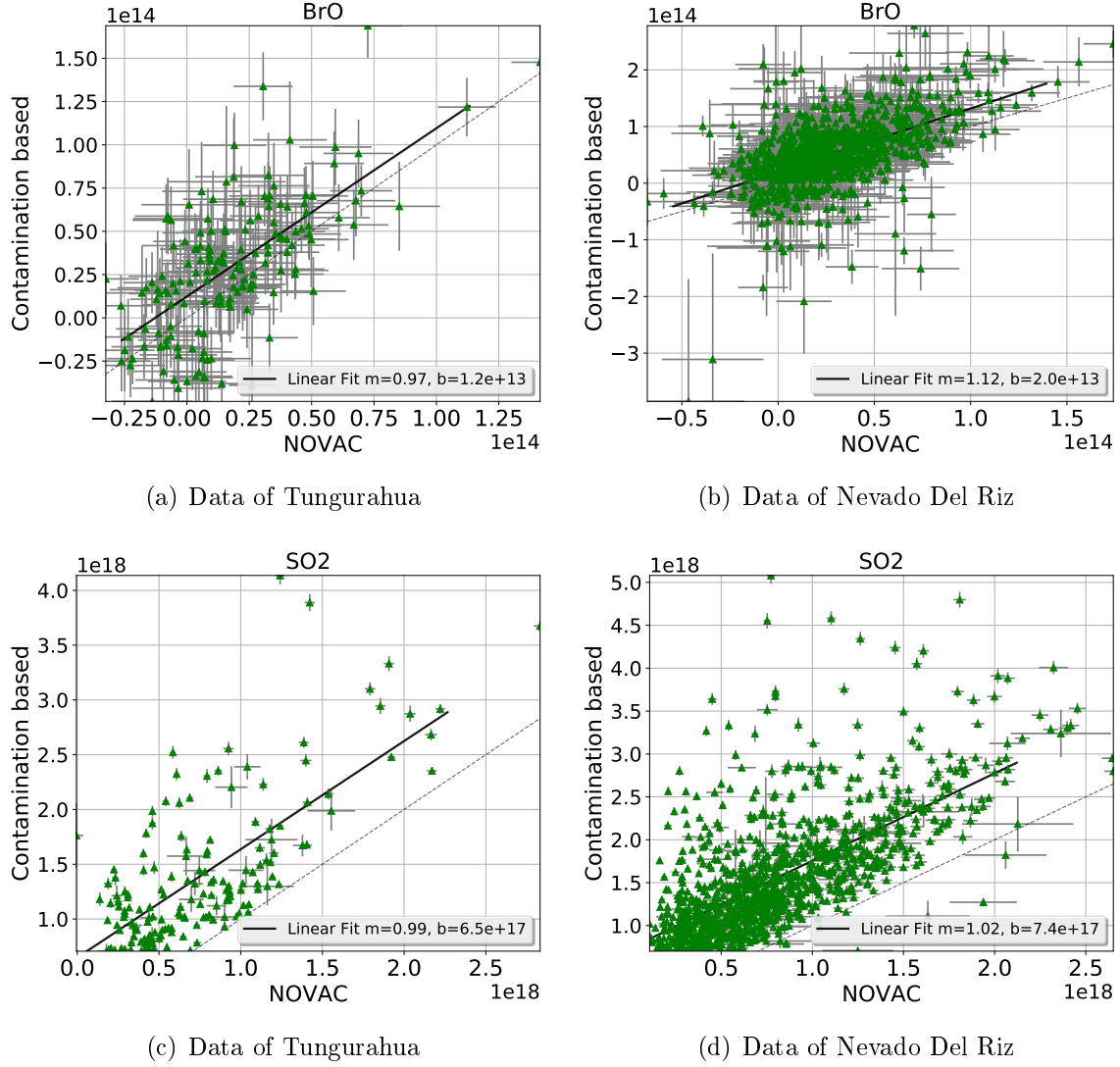
(c) Data of Tungurahua

(d) Data of Nevado Del Riz

Figure 8.1: Comparison of the results of contaminated data for performing the evaluation with the NOVAC-method and the contamination based method. Only data are used where the corresponding SO_2 column density (retrieved from the contamination based method) lies above the plume limit of $SO2\_SCD > 7 \cdot 10^{17}$. The black solid line shows a linear fit of the data, the dotted line indicates where the both evaluation are equivalent. (a) Results for the BrO column densities from Tungurahua; (b) Results for the BrO column densities from Nevado Del Ruiz; (c) Results for the SO_2 column densities from Tungurahua; (d) Results for the SO_2 column densities from Nevado Del Ruiz

Figure 8.2 shows the difference of the SO_2/BrO ratio when performing the evaluation with the NOVAC method and the contamination based method. The results

for Tungurahua are visualized on the left side (Figure 8.2(a) , 8.2(c)) and the results for Nevado Del Ruiz are shown on the right side (Figure 8.2(b) , 8.2(d)). Figure 8.2(a) and 8.2(b) show the results of the contamination based method plotted against the results of the NOVAC method. Figure 8.2(c) and 8.2(d) show the actual difference between both methods. The column density calculated with NOVAC is subtracted from the corresponding column density retrieved with the contamination based method. The black valid line indicates a linear fit of the data, the dotted grey line shows where the difference is zero. That means that both evaluations lead to the approximately same ratio.

- For low BrO/SO_2 ratios around below zero, the ratios calculated with the contamination based method are higher than the ratios retrieved with the NOVAC method. For higher BrO/SO_2 ratios (above zero) the ratios calculated with the NOVAC method are larger.

- The absolute difference between both evaluation methods increases with the increase of the absolute ratio.

Due to the increase of the SO_2 column density when performing the evaluation with the contamination based method more SO_2 SCD lies above the plume limit of $7 \cdot 10^{17} \quad \frac{molec}{cm^2}$. This leads to an increase of the amount of reliable data.
In the following we discuss the results for the Tungurahua volcano and the Nevado Del Ruiz.

	Tungurahua	Nevado Del Ruiz
Total amount of data	6500	14005
Percentage of data above plume limit	6.7%	12.8%
Contaminated data	0.060	0.099

Table 8.1: Results for Tungurahua and Nevado Del Ruiz. The absolut amount of data and the amount of data within the plume limit and the amount of contaminated data are shown.

8.1 Tungurahua

In the considered timespan from June 2008 to August 2009, 6500 multi add spectra are recorded.
Using the conventional NOVAC-method to perform the evaluation and ignoring contamination results in an amount of 6.7 % of SO_2 column densities within the plume limit. Thus 6.7 % of the data can be used for the examination of the volcanic gas

Contaminated data		Tungu rahua	Nevado Del Ruiz		Not contaminated data	Tungu rahua	Nevado Del Ruiz
Within plume-limit	NOVAC	0.192	0.399		Within plume-limit	0.055	0.088
	Cont. based	0.419	0.779				
not analysable		0.025	0.078				

Table 8.2: Results for Tungurahua and Nevado Del Ruiz. Left: The amount of contaminated data which are evaluated with the contamination based method above the plume limit are shown. Due to a lack of appropriate references a small amount of the contaminated data is not analysable. This amount is also listed in this table. Right: The results for the not contaminated data are shown.

emissions in this timespan.

6.0 % of all spectra are found as contaminated and thus need to be excluded from the conventional NOVAC-evaluation. From the remaining data, if the contaminated spectra are excluded, only 5.5 % of the SO_2 column densities are above the plume limit (see Table 8.2).

A higher amount of spectra within the SO_2 plume limit can be found in the contaminated data even if the contaminated data are evaluated with the NOVAC-method. Here, the percentage of data in the plume-limit is: 19.2%. This means that the contaminated data are 2.86 times more frequently above the detection limit. This leads to the presumption, that the probability of getting contaminated data increases with the gas amount leaving the volcano.

The following paragraph deals only with the contaminated data. When performing the evaluation of the contaminated data with the contamination based method 41.9% of the resulting SO_2 column densities are in the plume limit. Thus, the reliable amount of contaminated data increase by 118.7% while the total amount of data increase by 45.2%. Thus 7.99% of all data are above plume limit when using the contamination based method.

By using trace gas free references instead of contaminated references about 45.2 percent more data are available.

Due to the very small amount of BrO column densities above the detection limit often the daily mean of the BrO/SO_2 ratios is used. Hereby at least tree to four "Multi Adds" per day in the plume limit need to be recorded. Thus, performing the evaluation of contaminated data with the contamination based method leads to more data. 12.5% more daily mean data can be retrieved when using the contamination based method. The amount of daily means increases less than the total amount of data, this effect can be explained due to a higher occurence of contamination if

the SO_2 column densities are high, thus more data are retrieved for days with a high SO_2 amount.

8.2 Nevado Del Ruiz

At Nevado Del Ruiz a larger time span is examined. Thus, there is a higher amount of "Multi Add" data of 14005. The total amount of contamination data is 1392. This is equivalent to 9.9% of all data. Evaluating the contaminated data with the NOVAC-method in 39.9% of the cases yields SO2 SCDs within the plume limit. of the SO_2 SCDs within the plume limit. As at Tungurahua the occurrence of data above the plume limit within the contaminated data is larger as for not contaminated data (by a factor of 3.4).

The following paragraph only deals with the contaminated data. If using the contamination based method 77.9% of the SO_2 column densities are above the detection limit. Thus, an increase of SO_2 SCDs above the plume limit within the contaminated data of 95% is observable. In total the amount of SO_2 SCDs above the plume limit increases by 68.8%. percent. As a result 12.8% of all data are above the plume limit.

For the same reasons as described for the Tungurahua volcano we are also interested in the daily means: In total we get 22.6 percent more daily means in the timespan for Nevado Del Ruiz.
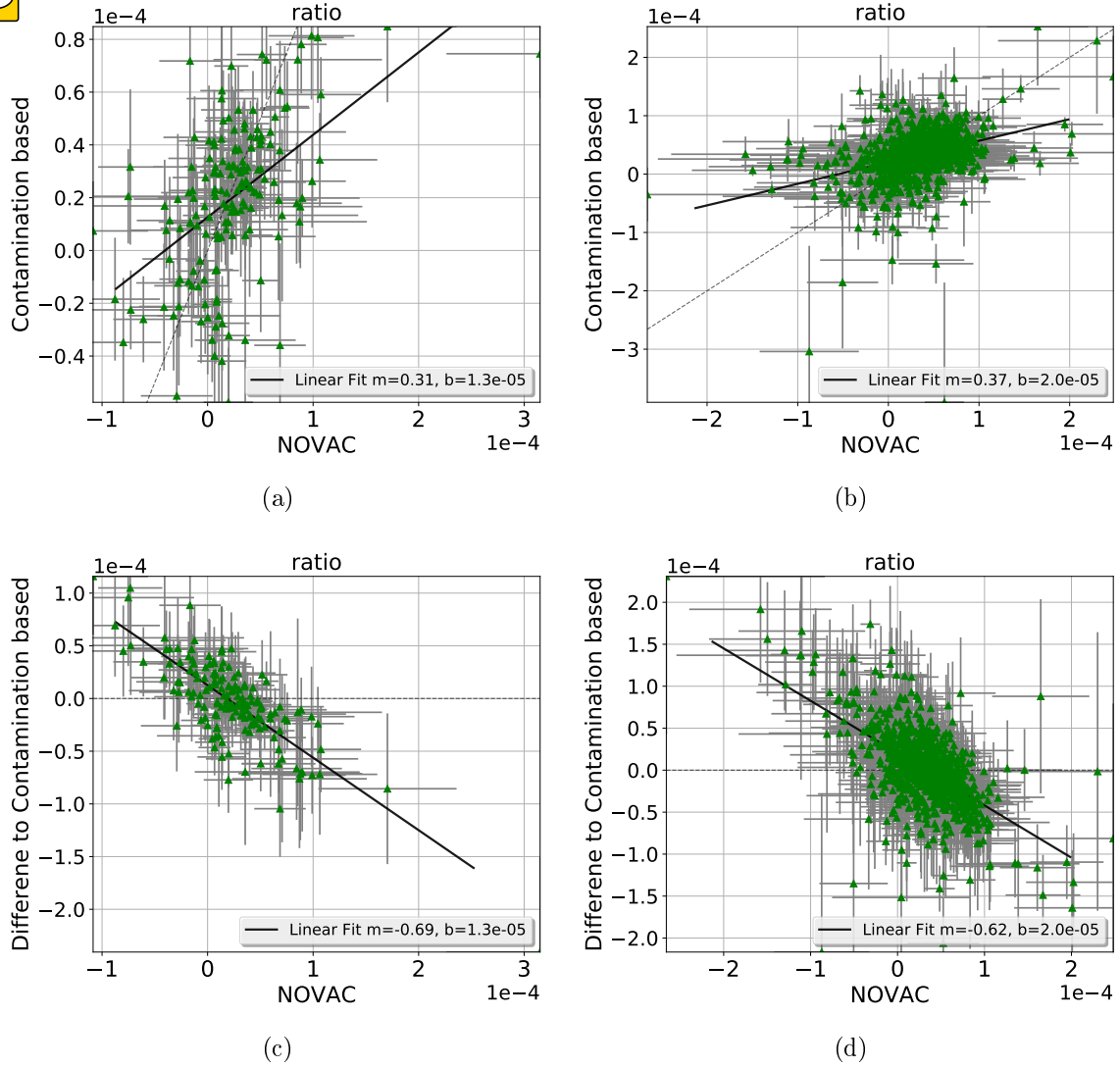
(a)

(b)

(c)

(d)

Figure 8.2: Comparison of the results of contaminated data for performing the evaluation with the NOVAC-method and the contamination based method. Only data are used where the corresponding SO_2 column density (retrieved from the contamination based method) lies above the plume limit of $SO2\_SCD > 7 \cdot 10^{17}$. (a)+(b): The black solid line shows a linear fit of the data, the dotted line indicates where the both evaluation are equivalent. (a) Results for the BrO /SO_2 column densities from Tungurahua; (b) Results for the BrO /SO_2 column densities from Nevado Del Ruiz. (c) +(d) The column density calculated with NOVAC is subtracted from the corresponding column density retrieved with the contamination based method. The black valid line indicates a linear fit of the data, the dotted grey line shows where the difference is zero. That means both evaluations lead to the same ratio. (c) Tungurahua (d) Nevado Del Ruiz

8.3 BrO/SO₂ time series

This section presents the final time series of SO2, BrO and BrO/SO_2 for Tungurahua and Nevado Del Ruiz.

Figure 8.3 shows the results for the Nevado del Ruiz volcano. The plot at the top of Figure 8.3 shows the results for SO2. If the contaminated data would be excluded from the evaluation only the green data points can be used for the evaluation of the time series.

The middle plot of Figure 8.3 shows the corresponding BrO time series. The green data points indicates BrO SCDs where the corresponding SO_2 amount is above the detection limit, while the red BrO SCDs show contaminated data above the detection limit.

The plot at the bottom of Figure 8.3 show the BrO/SO_2 ratio time series. The increase of usable data can be seen. Figure 8.4 shows the equivalent plot for the Tungurahua volcano.

Figure 8.5 shows a time series of Daily means of the BrO/SO_2 ratio. The minimum amount of valid data point within one day is above 4. Days where 3 or less valid data where recorded are not considered in this figure. Thus all considered ratios have an SO_2 SCD above the plume limit. The red marked ratios shows data which are only able to use, if the contaminated data are used as well.
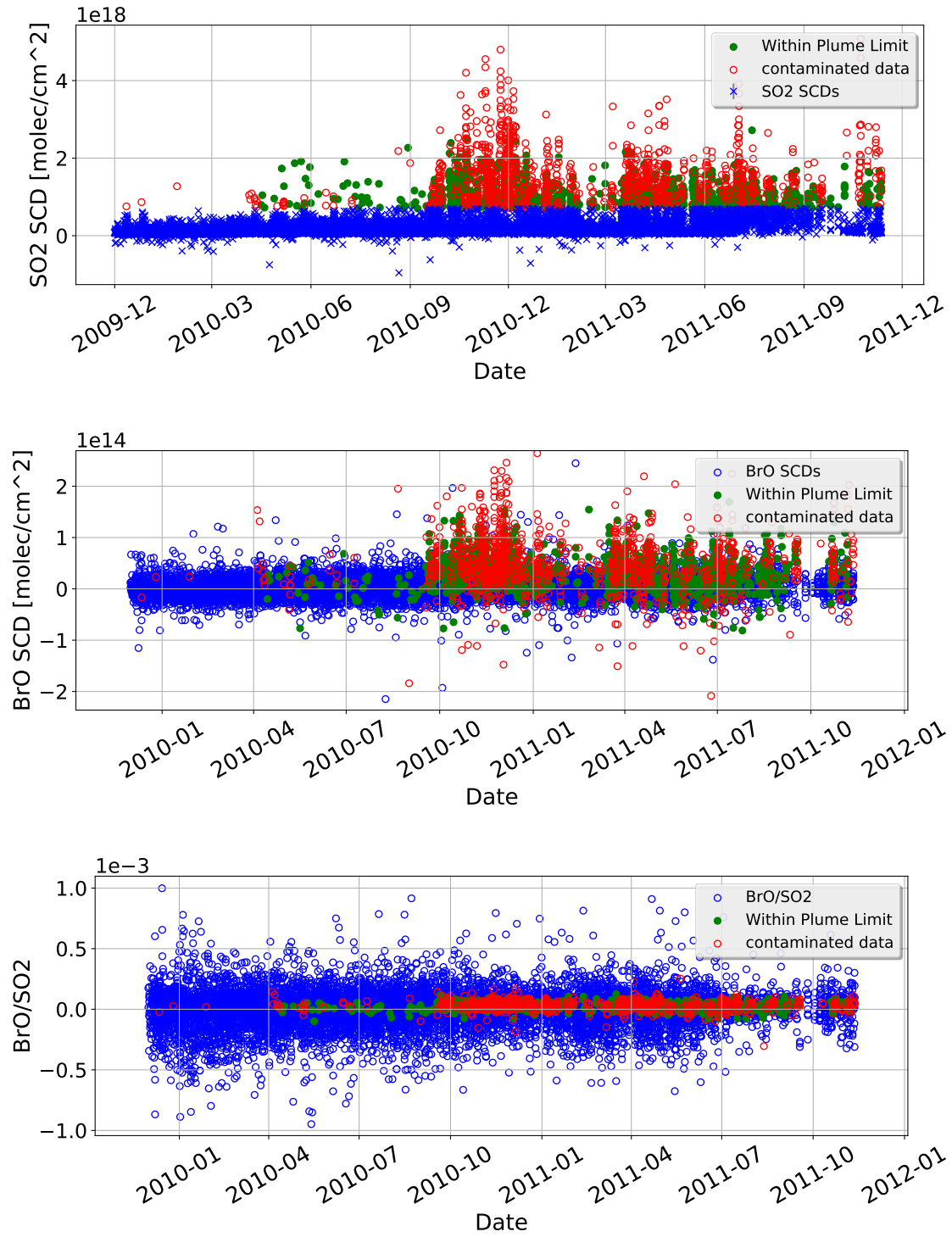
Figure 8.3: Time series of BrO, SO2 and the BrO/SO$_2$ ratios for Nevado del Ruiz . The contaminated data are evaluated by using the contamination based method. Blue data points are below the detection limit, green data points are not contaminated, valid SO$_2$ SCDs. Red data points are contaminated data, evaluated with the contamination based method. The contaminated data points are only marked in red, if the SO$_2$ SCD is above the plume limit. Contaminated data below the detection limit are not particularly marked.
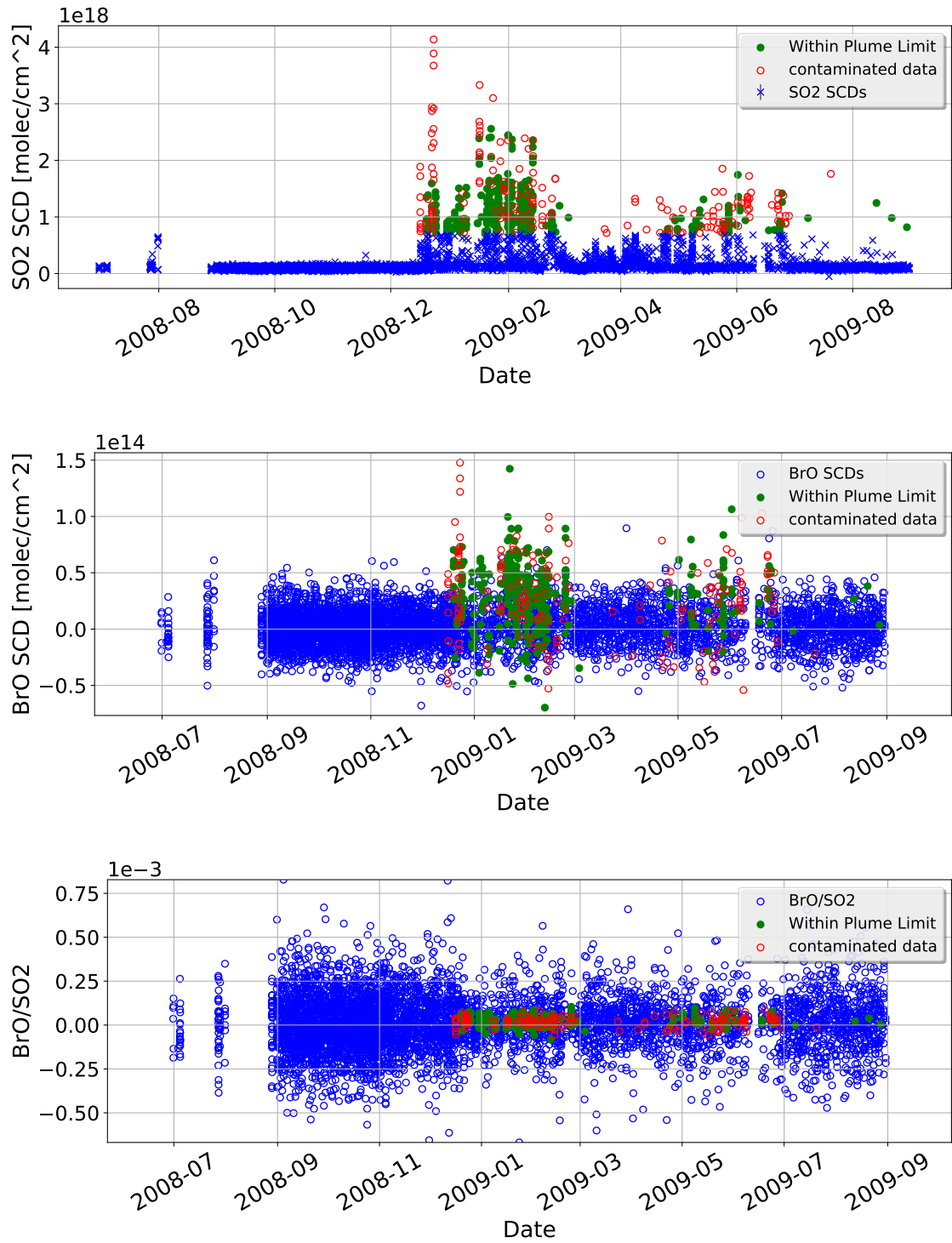
Figure 8.4: Time series of the BrO/SO$_2$ ratios for Tungurahua. The contaminated data are evaluated by using the contamination based method. Blue data points are below the detection limit, green data points are not contaminated, valid SO$_2$ SCDs. Red data points are contaminated data, evaluated with the contamination based method.
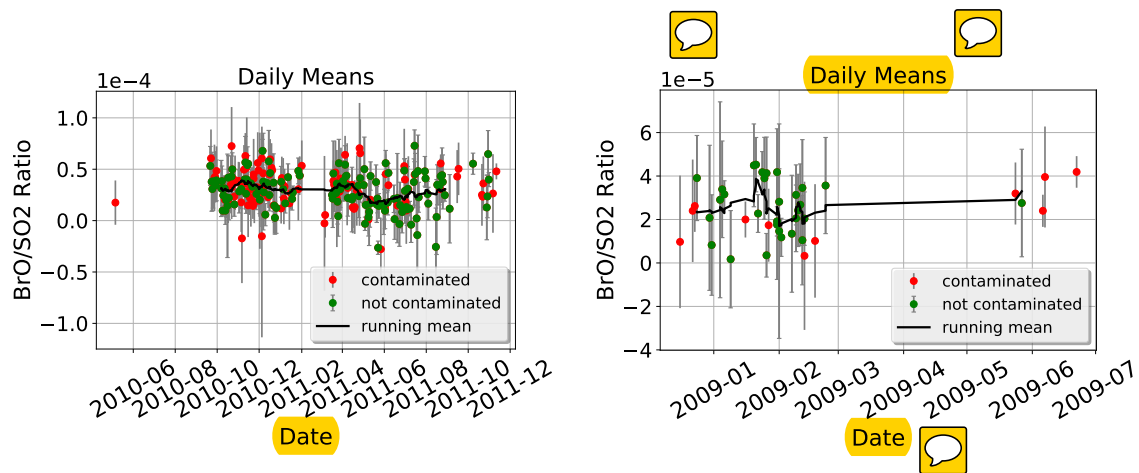
Figure 8.5: BrO/SO$_2$ ratio daily mean time series for Nevado del Ruiz (left) and Tungurahua (right). SO$_2$ SCDs used for this plot are above the plume limit of $7 \cdot 10^{17}$. The minimum amount of data per day are four. Days where less than four valid ratios are recorded are not considered in this plot. As a result of using the contaminated data as well more daily means are available, since more days have an amount of valid data's above four. Those dates are marked with red. The other data are colored in green.

8.4 Issues of the contamination based method

The presented method is questionable since it does not consider contamination of the plume due to a lack of information. Moreover, we do not consider the different lifetimes of SO$_2$ and BrO. This leads to a faster depletion of BrO.

8.4.1 Contamination of the plume

As discussed above it occurs, that, the plume is contaminated as well. 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 contamination free reference of another time would lead to an overestimation of the column density of gases.

~~The contamination of the plume is visualized in Figure 8.6.~~ This is one possible occurence of contamination. As it can be seen gas of the old plume affects the measurement of the reference and the plume. However, for this example the influence on the measurement of the reference is much larger since the light path trough the old plume (coloured orange in Figure 8.6) is longer for the reference than for the measurement of the volcanic plume. Thus, we underestimate the gas amount if we do not use a gas free reference, but might overestimate if we do so. The real gas amount might be between the measured amount with and without using a reference measured at another time.

The contamination setup could differ from Figure 8.6. This would lead to different
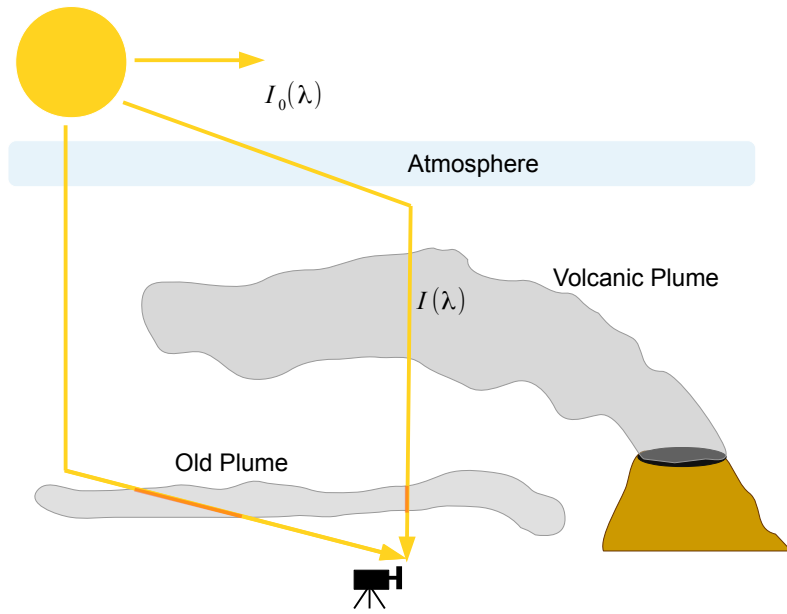
Figure 8.6: Visualization of the contamination of the plume. Due to a lack of wind the old plume sinks down an accumulates above the instrument. The light path trough the old plume is longer when recording the reference spectra (orange).
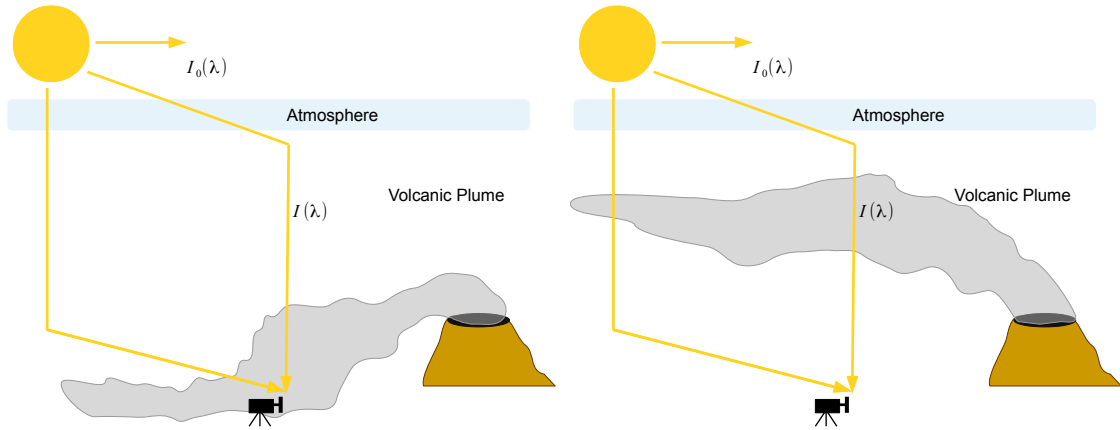

Figure 8.7: Visualization of possible scenarios for contamination. Left: the plume sinks in a way that the instrument is within the plume, therefore, all elavation angles will contain volcanic trace gases, while the plume is not additionally contaminated. Right: the plume covers the hole sky, thus all elvation angles "see" volcanic trace gases.

results. However, the reference region is in most cases at a larger elevation angle than the plume. Thus, the assumption that the light path trough the old plume is in average longer for the reference, if both, reference and plume are contaminated.

With the data retrieved by the NOVAC instruments it is very difficult or even impossible to discover whether the plume is contaminated or not.