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Retrieval advances of BrO/SO2 molar ratios from NOVAC

This Master thesis has been carried out by Elsa Wilken

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Germany

under the supervision of

Prof. Ulrich Platt

(Titel der Masterarbeit - deutsch):

(Abstract in Deutsch)
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Retrieval advances of BrO/SO2 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 a 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

1 Introduction

Volcanic activities on Earth have always shaped the earth surface and influenced atmospheric processes. Volcanoes are often particularly recognized by their dramatic consequences of a major volcanic eruption. But volcanoes influence our lives in more than this way. Volcanic gases can effect the weather (timescales of days to weeks) or the climate (timescales of months to years) Schmidt and Robock [2015]. Examples are the lake eruption in Iceland (1783-1784) followed by a very hot summer and a cold winter in central Europa Thordarson and Self [2003] and the Tambora eruption, indonesia in 1815 which caused the "year without summer" in 1816.

Considering the plate tectonics of earth most volcanoes are caused by diverging or converging of the continental plates and therefore located at the margins of the continental plates. Another possibility for occurrence of volcanoes is the the interior of continental or oceanic shelves. Schmincke [2000]
The most abundant volatile species released during a volcanic eruption are water vapour (H_2O; relative amount of the plume: 50%-90%) and carbon dioxide (CO_2; relative amount of the plume: 1%-40%) Platt and Bobrowski [2015]. But the short effects of those two gases are rather low since there effect on atmospheric composition is negligibly due to the high abundance of atmospheric H_2O and CO_2. But on timescales of the age of the earth the volcanic emission of H_2O and CO_2 are the source of our current atmosphere. Schmidt et al. [2015]
A typically volcanic plume consists of many different gases alongside H_2O and CO_2 sulfur dioxide (SO_2) contributes with 1%-25% to the plume, hydrogen sulfide (H_2S) with 1%-10% and hydrogen chloride with (HCl) 1%-10%. Furthermore there are trace gases for example carbon disulfide (CS_2), carbon sulfide (COS) carbon monoxide (CO) hydrogen fluoride (HF) and hydrogen bromide (HBr) Platt and Bobrowski [2015]
A decrease of stratospheric ozone (O_3) has been observed after the eruption of El Chickon in 1982 and the eruption of mount Pinatubo 1991. A depletion stratospheric O_3 results in ozone holes. The depletion comes from volcanic aerosols which serve anthropogenic chlorine/bromine into more reactive forms Solomon et al. [1998].
Volcanic gases can alter the radiative balance of the earth in timescales relevant for climate change due to scatter and absorption of solar radiation Schmidt et al. [2015].
The gas composition of the volcano plume change with activity and could be a indication for the processes inside the earth.
In this work we are particularly interested in the ratio of BrO and SO_2. The halogen sulfur ratio is a proxy for volcanic processes. Therefore we make the assumption that the ratio of BrO and SO2 contains informations about its degassing source

depth. A change in BrO/SO2 prior to eruption was observed at Etna and Nevado del Ruiz.

To gain further knowledge about the volcanoes the Network for Observation of Volcanic and Atmospheric Change (NOVAC) was installed. NOVAC is a Network of DOAS Instruments located next to about 30 volcanoes in America, Africa and Europe. At every Volcano there are two to four DOAS Instruments installed, recording record back-scattered solar radiation spectra at different viewing angles.
NOVAC is a network which produces a large amount of data and we have the chance to evaluate long time periods which is a unique opportunity to study correlations of the trace gases.
Since the conditions at volcanoes are rough, the instruments need to be rather simple to keep the maintenance cheap and to assure a longer lifetime of the instruments. So we need to waive on temperature stabilization even at the expense of the quality of the data.

One possibility to measure the volcanic trace gases is to use Differential Optical Absorption Spectroscopy Platt and Stutz [2008]. DOAS exploit the wavelength dependency of the absorption of light. Here the gas emissions can be retrieved from the quotient of the absorption signal of the volcanic plume and a reference region. This will be explained in a further chapter.

The reference region, is usually treated as free of volcanic trace gases. If the reference region is for any reason contaminated by volcanic trace gases, the reference spectrum has to be replaced by a volcanic-gas-free reference. Alternative spectra could be for example a theoretical solar atlas spectrum or a volcanic-gas-free reference spectrum recorded in the temporal proximity(eg. a day before) by the same instrument. The first option comes with the drawback of reduced precision, as the instrumental effects have to be modeled and added to the retrieval. The reduction in precision is acceptable for the SO2 retrieval, but not suitable for a BrO retrieval because then most data would be below the detection limit. For the second option, the alternative reference spectrum should have been 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. We combined both options in order to achieve both, enhanced accuracy but still maximum possible precision of the SO2 and BrO retrievals. We present an algorithm which finds the optimal reference spectrum automatically. As first step, a possible SO2 contamination of the standard reference is checked by a comparison with the theoretical solar atlas. If a contamination is detected, as second step, the algorithm picks a volcanic-gas-free reference (beforehand automatically checked for contamination) from another scan.

In this work we are mainly dealing with data from Tungurahua in Ecuador in the timespan of 01.08.2008 to 30.07.2009. Later on, we will also show the results of Nevado del Ruiz a volcano located in Colombia.

Part I

Theoretical Background

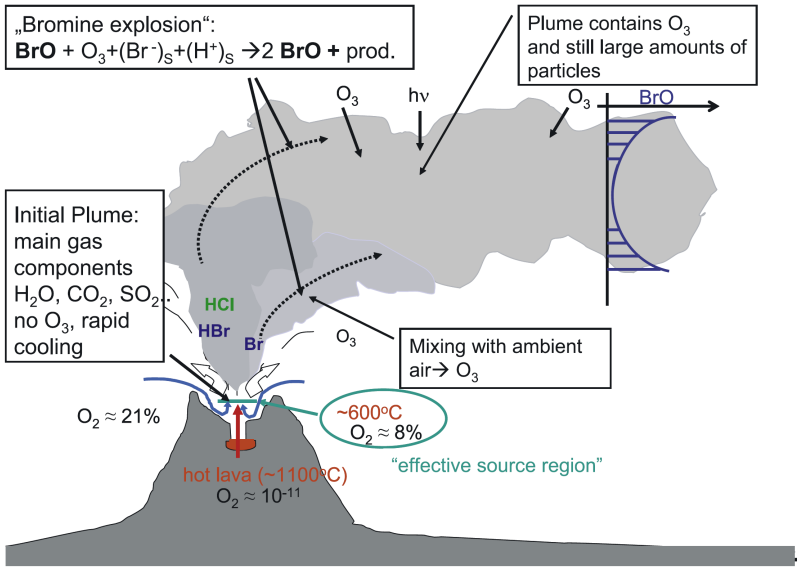


Figure 1.1:

1.1 Volcanism and volcanic chemistry

1.1.1 Volcanism

1.1.2 Volcanic degassing

1.1.3 Volcanic gases and their impact on the climate

1.1.4 Volcanic plume chemistry

1.1.5 Sulphur species

1.1.6 Bromine oxide

1.1.7 Using volcanic gases to study volcanic activity

1.2 Remote sensing of volcanic gases

1.2.1 Absorption spectroscopy

1.2.2 Scattering processes in the atmosphere

1.2.3 Beer-Lambert Law

1.2.4 Differential Optical Absorption Spectroscopy(DOAS)

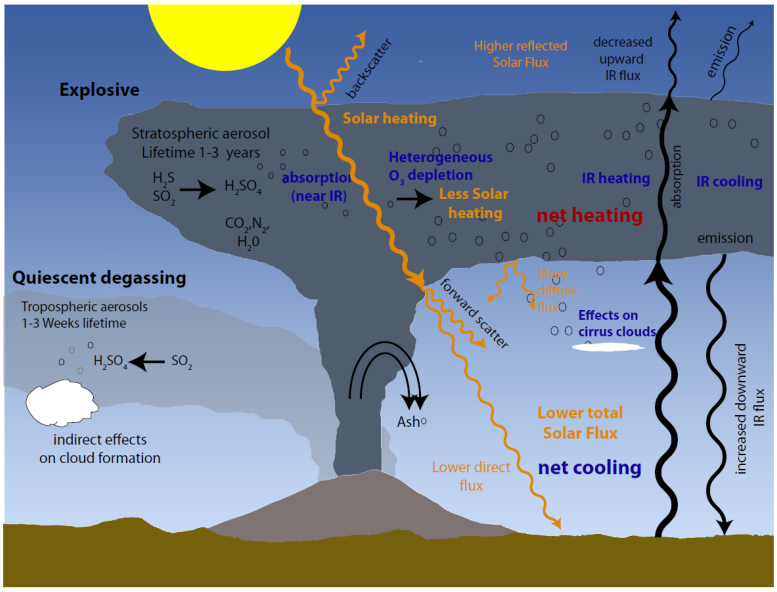


Figure 1.2:

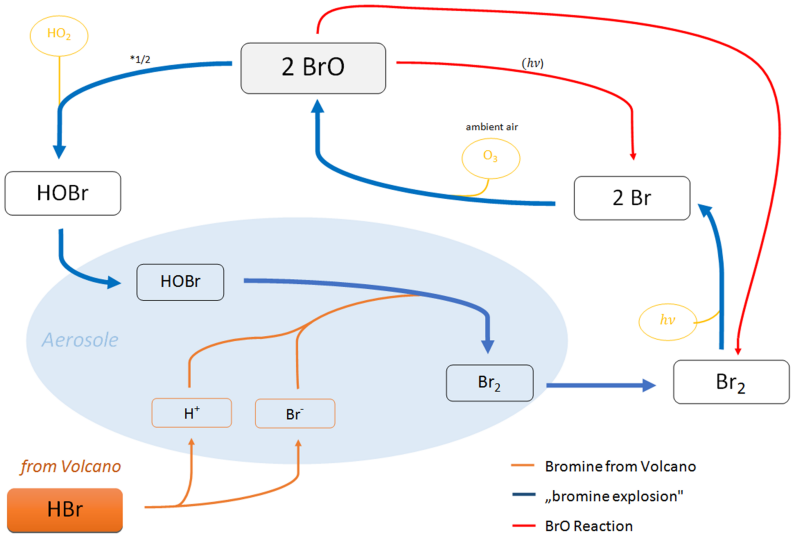


Figure 1.3:

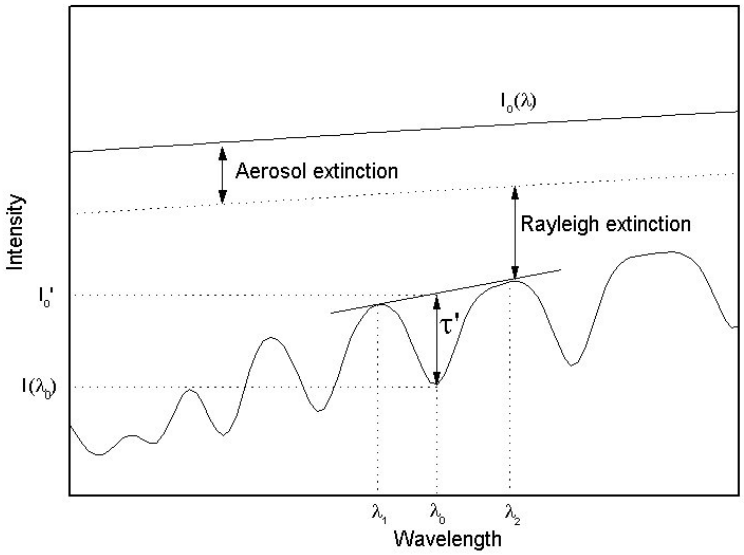

$I_0(\lambda)$
Aerosol extinction
Rayleigh extinction
Intensity
I_0'
τ'
$I(\lambda_0)$
λ_1
λ_0
λ_2
Wavelength

Figure 1.4:

Part II

Evaluation of the Data of Tungurahua and Nevado Del Ruiz

2 Network for Observation of Volcanic and Atmospheric Change

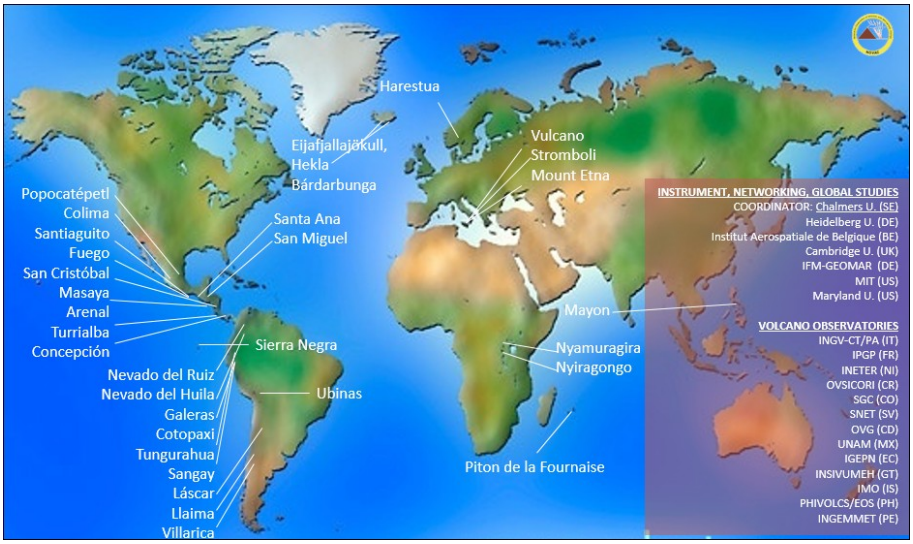
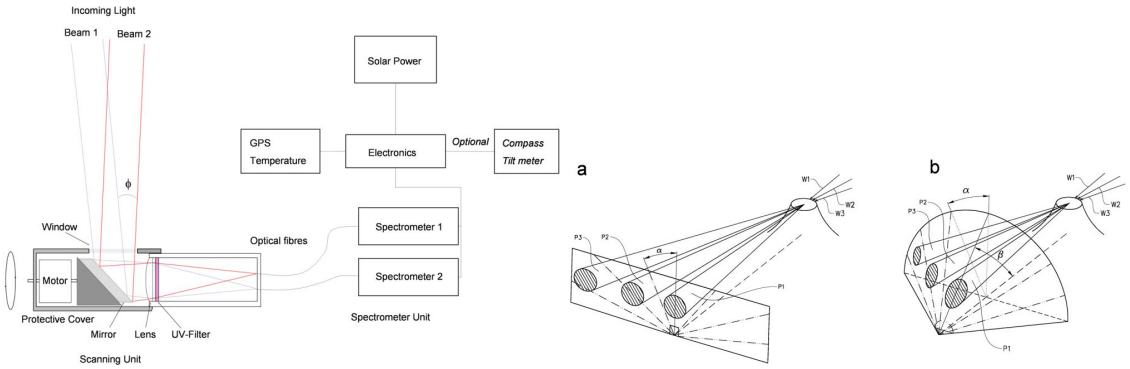


Figure 2.1: Global map of the volcanoes monitored by NOVAC. Used with friendly permission of Santiago Arellano.

Network for Observation of Volcanic and Atmospheric Change (NOVAC) is a network of instruments monitoring volcanoes over the hole world. The aim of NOVAC is to gain another tool for risk assessment, for gas emissions and geophysical researches. Also many other scientific purposes are build on the data from NOVAC. Figure 2.1 shows a map, with all volcanoes of the Network for Obersavation of Volcanic and Atmospheric Change.
NOVAC was originally funded by the European Union on the first October in 2005. The aim of NOVAC is to establish a global network of stations for the quantitative measurement of volcanic gas emissions. At the beginning NOVAC encompassed observatories of 15 volcanoes in Africa America and Europe, including some of the most active and strongest degassing volcanoes in the world. Although the EU-funding has stopped, the network has been constantly growing since it was founded. In 2017 more than 80 Instruments are installed at over 30 volcanoes in more than 13 countries.
The great advantage of the data monitored in NOVAC is the fact that NOVAC provides continues gas emission data over many years. Therefore one is able to get more statistical stable results.



(a) Bezeichnung der linken Grafik (b) Bezeichnung der rechten Grafik

Figure 2.2: Titel unterm gesamten Bild

The instruments used in NOVAC are scanning UV-spectrometer : Mini Doas instruments.
The Mini-DOAS instrument represents a major breakthrough in volcanic gas monitoring as it is capable of real-time semi-continuous unattended measurement of the total emission fluxes of SO2 and BrO from a volcano. Semi-continues means in this case that the measurement is only possible during day time when enough Sun light is there.

The basic mini-DOAS system consists of a pointing telescope fiber-coupled to a spectrograph. Ultraviolet light from the sun, scattered from aerosols and molecules in the atmosphere, is collected by means of a telescope with a quartz lens defining a field-of-view of 12 mrad. **??**
The spectrometers measure in the UV region in a wavelength range of 280 to 420 nm. In this range are the differential structures of SO2 and BrO dominant.
The Novac-instruments need to be very robust to stand the conditions around volcanoes. Therefore the design of the instruments is rather simple, this means the instruments do not have internal stabilisation features like temperature stabilization to keep the measurement independent of external parameters (for example Temperature). This comes along with a reduced precision of the data, but the huge amount of data produced by NOVAC compensates this disadvantage.

2.1 Measurement Routine

The Instruments are set up five to ten km downwind of the volcano of the volcano. To cover most of the occurring wind directions two to five instruments are installed at each volcano. Ideally the measurement plane is orthogonal to the plume, to get the best measurement results. In reality the measurement plane could be twisted.
The Instruments record spectra in different viewing angles covering a the hole sky from horizon to horizon from -90° to 90°. The zenith is at 0°. The measurement routine starts with a spectrum in zenith direction: The pre-reference. Afterwards

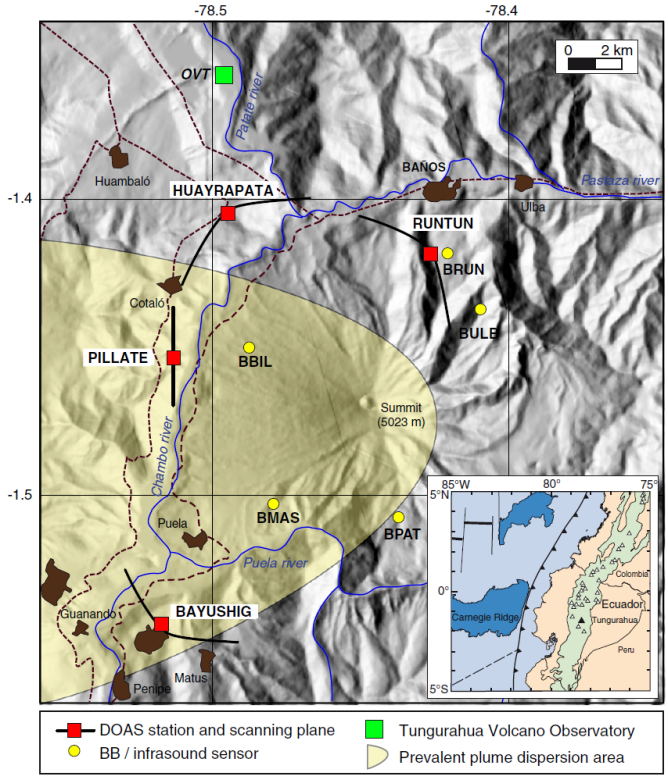


Figure 2.3:

the dark current spectrum is recorded.
Then the Instrument turns automatically to the side, recording spectra at the Elevation Angle from -90° to 90° with steps of 3.6°.
One hole measurement takes from 6 to 15 minutes.

3 Evaluation Routine

3.1 NOVAC-Evaluation

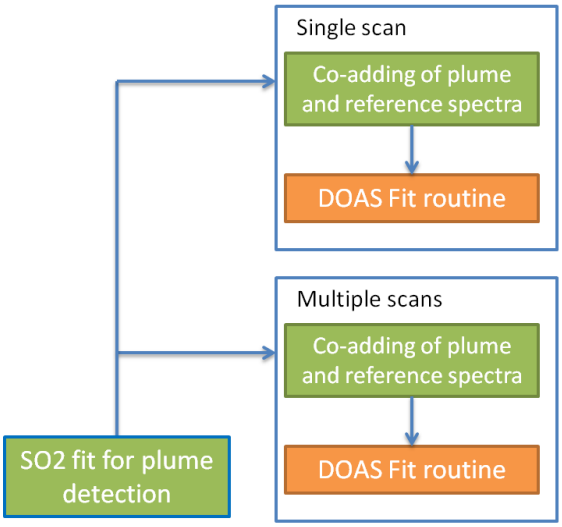
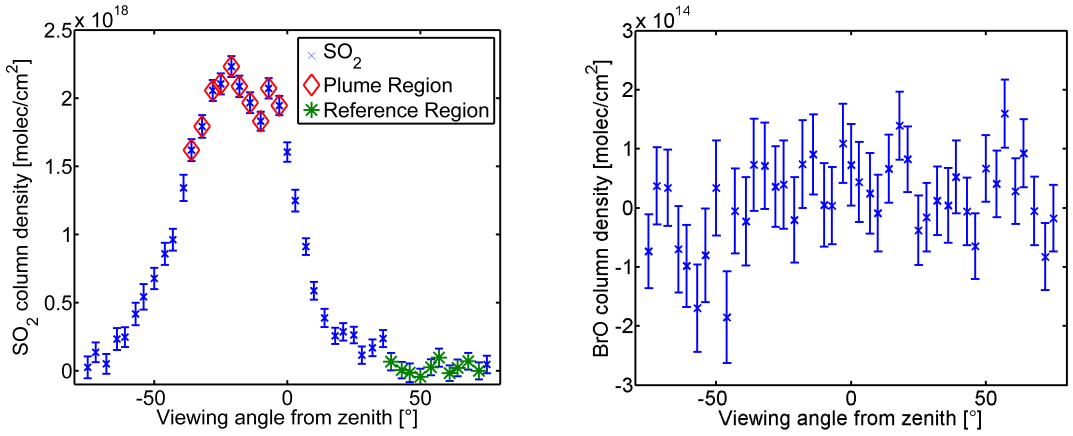


Figure 3.1:

In the following we describe the technical implementation of the DOAS approach using the data of NOVAC instruments:
The first important task is to locate volcano plume and the reference region using the data from te measurement routine described above.

To do so we use the pre-reference (the spectra recorded at an elevation angle of 0°) to evaluate spectra for SO2 at every elevation angle as described in chapter 1.2.4, that means we divide each recorded spectra by the pre-reference and take the logarithm to get rid of the Frauenhofer structures and to be able to just look at the important structures of the plume. To get the gas amounts of the evaluated spectra, one fits the absorption spectrum of all important gases on the spectrum. In our case we take all gases written in tab. ?? into account. The result will be an SO2 curve as it is shown in fig. ??. Figure ?? shows the relative SO2 column density to the pre-reference as a function of the elevation angle. We can clearly observe a a maximum of SO2 and a minimum. Inside the plume the SO2 amount is much higher than in the outside the plume. Therefore we assume that the location of the SO2 maximum match with the location of the plume. We assume that the minimum of the SO2 curve refers to a region outside of the plume which is in most



(a) Bezeichnung der linken Grafik

(b) Bezeichnung der rechten Grafik

Figure 3.2: Titel unterm gesamten Bild

times the case. The SO2 amount in the earths atmosphere is negligible so we take it as a region of zero SO2. Now it is possible to locate the plume region as the SO2 maximum, whereas the minimum of the SO2 curve the reference region is.
To technically detect the plume region we use a gauss fit of the So2 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 only the 10 spectra with the highest SO2 amount. For the reference we use the sum of 10 spectra with the lowest SO2 amount.
The so found reference spectrum is used to fit it on the SO2 absorption lines of Gases to get the absolute column densities of SO2 and BrO in the plume spectrum

Since the BrO column density is much lower than the SO2 column density and lies just slightly above the detection limit the plume is hard to detect using the BrO column density as it is shown in fig. **??**. Therefore we use plume location we found by using SO2 to evaluate the BrO column density.
For the evaluation we use the data of more than one measurement, to increase the fit quality.
We are mainly interested in the BrO/SO2 ratio, with the calculations described above it is now possible the get this ratio. In **??** is the NOVAC Evaluation visualized.

3.2 Contamination Problem

It might occur that 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 still extend over the hole scan area as a consequence of windless conditions. In consequence, the reference is contaminated with volcanic trace gases.

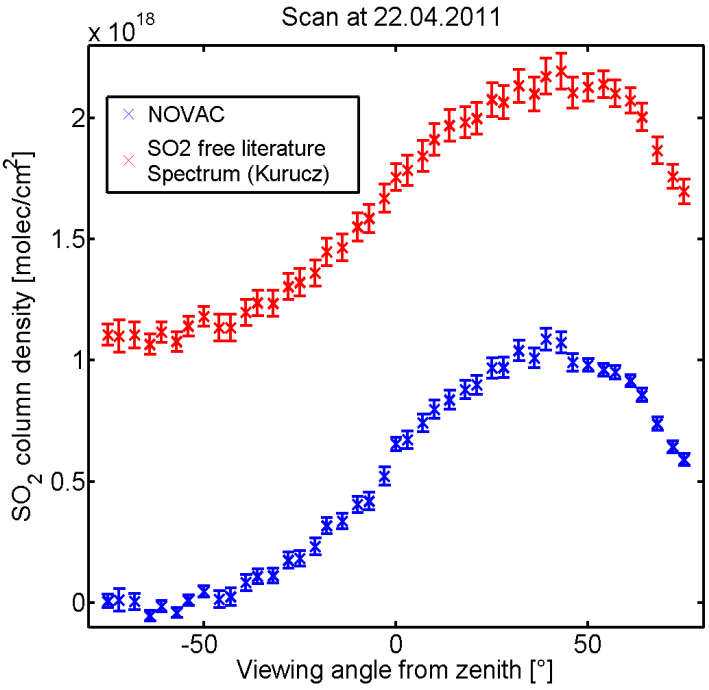


Figure 3.3:

Thus the gas amount is underestimated by the NOVAC-Evaluation: In fig. 3.3 we see an example from April 2011 (Tungurahua) where the reference region is contaminated by volcanic trace gases. The blue SO2 curve shows our calculations with the NOVAC-Evaluation, but since there is still SO2 in the reference region, therefore the assumption, that the SO2 amount could be set to zero in the reference region is wrong. The red curve shows the real SO2 curve, and we will underestimate the total SO2 amount of the plume. Contamination occur in approximately 10% of the data.

If the reference region is for any reason contaminated by volcanic trace gases, the reference spectrum has to be replaced by a volcanic-gas-free reference. Alternative spectra are a theoretical solar atlas spectrum (the use of a solar atlas spectrum will be described in section 3.2) ore a a volcanic-gas-free reference spectrum recorded by the same instrument.

In the following we will discuss both of these options:

Evaluation using a Solar Atlas Spectrum

An alternative to choose 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]. The advantage of using a solar atlas spectrum as reference is, that we know that there are no volcanic trace gases, we do not need to assume, that the minimum SO2 amount is zero. 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 SO2 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 SO2 amount in the reference.

Evaluation using a Spectrum of the same Instrument

An alternative reference spectrum coud be a a volcanic-gas-free reference spectrum recorded by the same instrument. When using such a reference several problems occur:
As described in chapter 2 the instruments used in NOVAC do not include features like temperature stabilisation due to that the measurements are not independent from 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 when the plume was recorded.

In this work we will combine both options in order to achieve both, enhanced accuracy but still maximum possible precision of the SO2 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.

In the following we will discuss how to find the an optimal reference from another scan automatically.

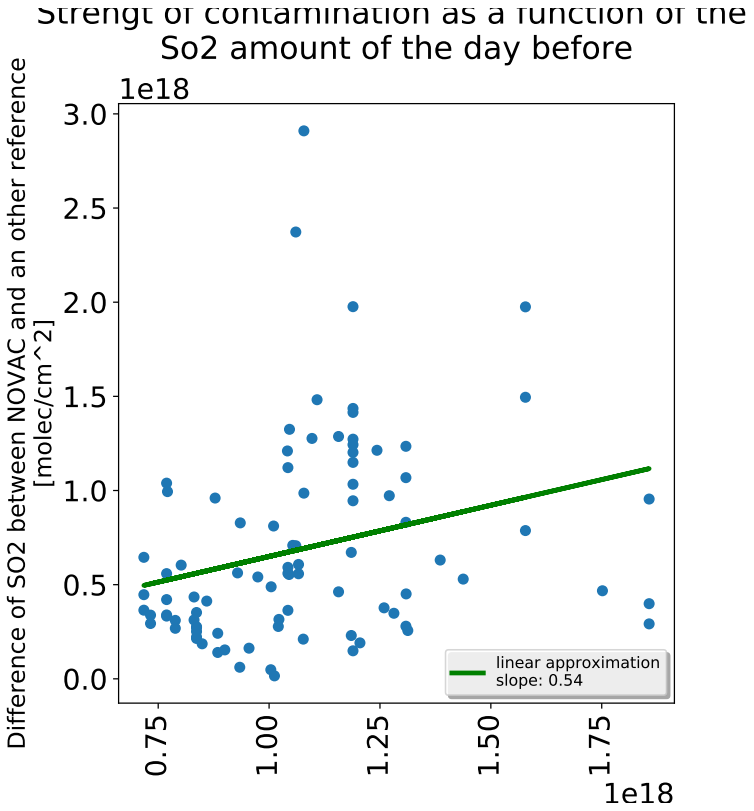

Strengt of contamination as a function of the
So2 amount of the day before
Difference of SO2 between NOVAC and an other reference
[molec/cm^2]
1e18
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.75
1.00
1.25
1.50
1.75
1e18
linear approximation
slope: 0.54

Figure 3.4:

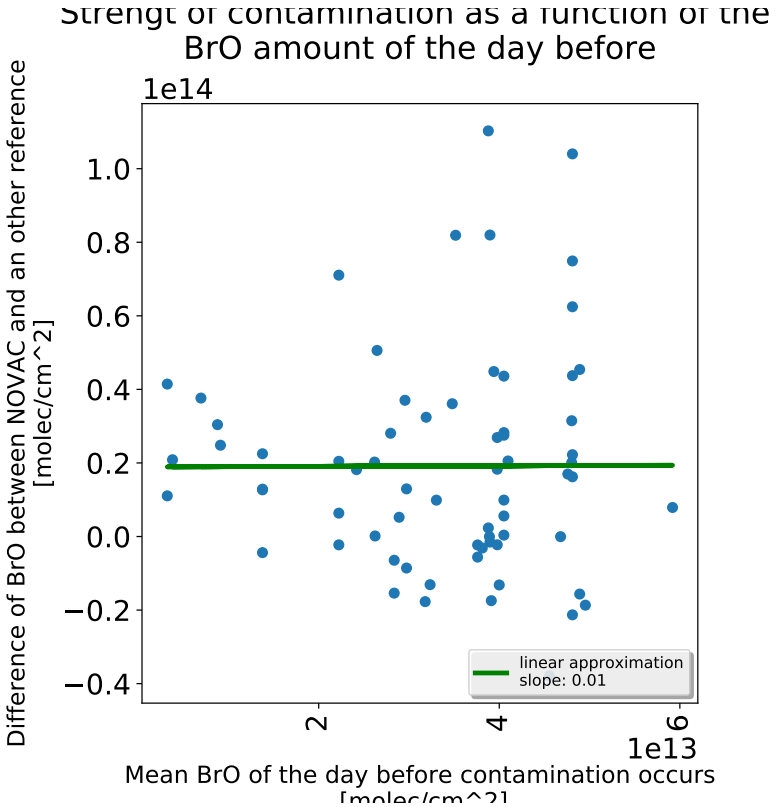

Strengt of contamination as a function of the
BrO amount of the day before
1e14
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
Difference of BrO between NOVAC and an other reference
[molec/cm^2]
linear approximation
slope: 0.01
2
4
6
1e13
Mean BrO of the day before contamination occurs

Figure 3.5:

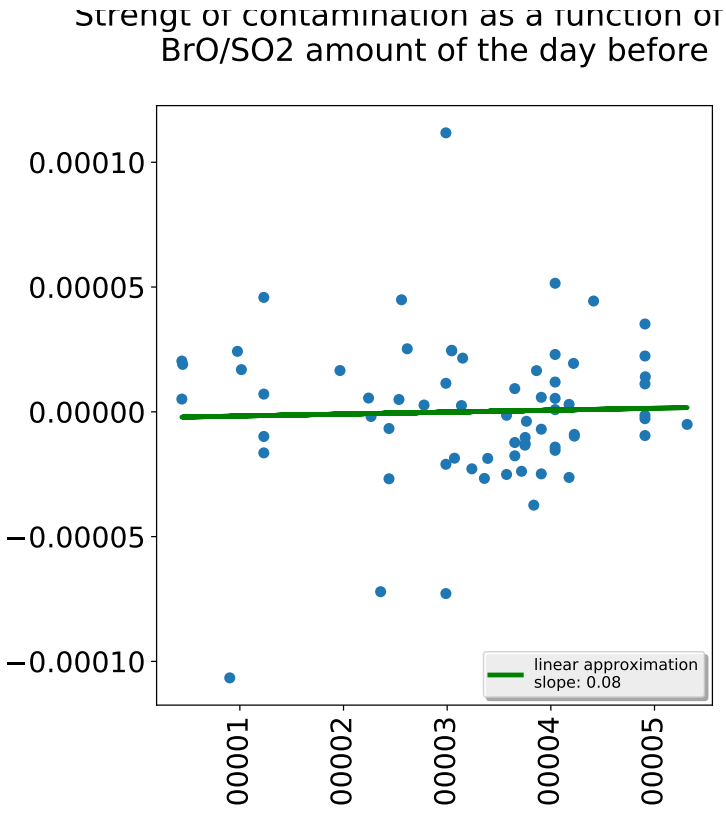

Strengt of contamination as a function of the
BrO/SO2 amount of the day before
0.00010
0.00005
0.00000
−0.00005
−0.00010
linear approximation
slope: 0.08
00001
00002
00003
00004
00005

Figure 3.6:

4 Limitations for the evaluation of BrO

Since the SO2 amount in a volcano plume is rather high (magnitude of SO2 at Tungurahua $\approx 1e^{18}$, Warnach [2015]) , the evaluation of SO2 is unproblematic compared to BrO.
Evaluating BrO is more difficult since the amount is much smaller and the measurement error relative to the column density much larger. Since we want to get the BrO/SO2 we need to maximize the accuracy of BrO. Therefore the aim is to choose the reference with respect to the BrO error, to minimize the BrO Error and to increase the amount of reliable BrO/SO2 ratio data.
We figured out, that the BrO Error depends strongly on the surrounding conditions when recording the plume and the reference. In the following, we will take a closer look at the dependence of the BrO error on external parameters.

4.1 BrO Error dependence on external parameters

The measurement and evaluation depends on the surrounding conditions like temperature or cloudiness Lübcke [2014]
If choosing a new reference we need to take the surrounding conditions into account
The better the surrounding conditions of the time where the reference is measured coincide with the conditions of the time when the plume is measured, the lower is the BrO error
The surrounding conditions we take into account are temperature, colorindex, exposure time, elevation-angle, daytime and the temporal difference.
In almost all cases (99%) the absolute BrO Error is minimal when using the reference recorded at the same time as te plume spectrum. So we won't be able to get an BrO Error which is smaller than the "Same Time Error".

4.1.1 Time

Due to instrument drifts the fit quality decreases with the time difference between recording the plume and the reference. Therefore it is better to use an reference in temporal proximity.

Figure 4.1 shows the Instrumental drift as a function of time, to create fig. 4.1 we used Tungurahua data, 2008 from June to November. We can observe that the drift changes with time. If we use the reference and plume spectra of the same time, we do not need to care about these effects, since the shift is equal for the plume and reference spectrum, but if the recording time is not the same the quality of the fit changes with the differences in wavelength shift which increases with the time

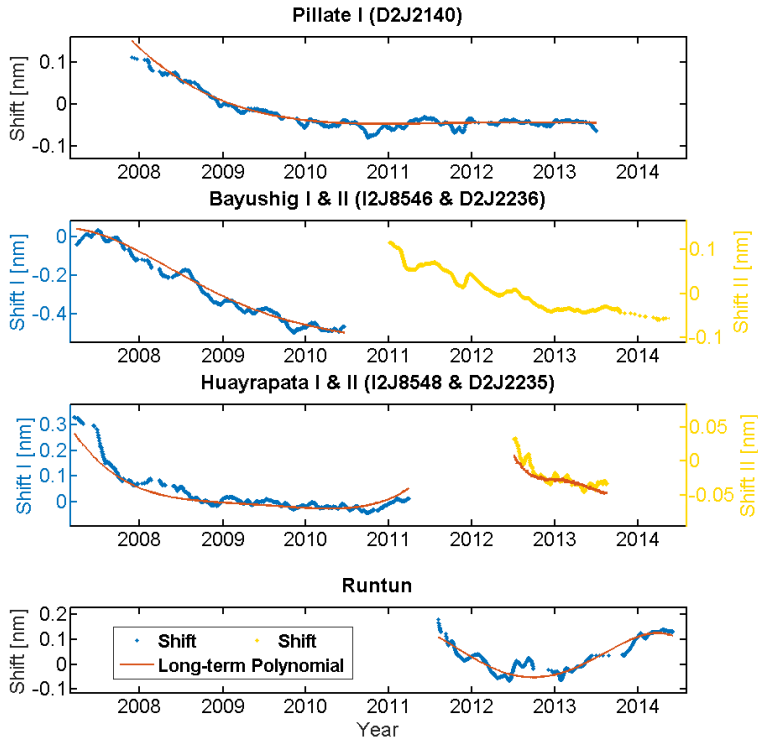


Figure 4.1:

difference.
In fig. 4.3 the BrO Error as a function of the time difference between recording the plume and the reference is shown. The running mean is drawn with a black line. The BrO Error increases with time difference.
To evaluate the maximal time difference, were we still get reliable results we calculated for all possible reference-plume pairs the corresponding BrO Error. With this data we are able to find for all plume spectra the associated reference where the BrO Error is minimal. In **??** a histogram is plotted with the probability of picking the best reference as a function of the time difference. Obviously the best results are if the day of measuring the reference is the same day as measuring the reference that means, if the time difference is smaller than one day. We allow all time difference which are in one sigma area.

We found out that the time interval where it is still reasonable to use references is about 14 days. Therefore we only use references where the recording time difference between plume and reference is smaller than two weeks. When using a references with a temporal difference to the plume of more than 14 days the probability, that the fit quality and thus the BrO error increases to much for our purposes.

4.1.2 Temperature

The Instrument design of the NOVAC instruments compromise between accuracy and longetivity as explained in chapter 2. In particular there are no internal thermal stabilizations installed as an attempt to reduce the need for power. This can influence the recorded spectra.

• For DOAS analysy it is crucial to assign the wavelength range of photons collected by each pixel to te respective pixel. THe wavelength to pixel mapping (WMP) is commonly performed by a Mercury lamp ore by comparison with the hig hdefined kuruz spectrum. The WMP depends on optcal alignment of the spectrometer and therfore it is not constant. This optical alignment depends on the temperature. Pinardi et al. [2007] has shown that variations of the Instruments temperature can cause changes in the instrument line function and can also cause shifts in the WMP. Warnach [2015] showed the dependency of short term shifts on the instrument temperature Figure 4.4.

The above discussed temperature dependence of the WMP causes a reduction of the fitquality with increasing instrument temperature between plume and reference. Thus the BrO Error increases as well with the temperature difference. To quantify the BrO error dependency on the temperature all plume spectra of Tungurahua from August 2008 to August 2009 (Nevado del Ruiz from .... to ....) where evaluated with all plume spectra of the same time. In this time span 1647 "multi-add" spectra from tree different instruments where recorded, so we get approximately 1646^2 plume reference pairs and their corresponding BrO error and temperature. The BrO error as function of the temperature difference can be seen in fig. 4.5. The blue dots shows the mean BrO error at the specific temperature difference, the standard deviation is illustrated with gray bars.
When compare the data of Tungurahua and Nevado Del Ruiz it is noteworthy that the BrO error on temperature dependence of the Data of Nevado Del Ruiz is stronger and the deviation is weaker than at Tungurahua, this may occur due to the larger temperature fluctuation at Nevado Del Ruiz. ?????????? quellen bitte!
When looking at all discussed external parameters, temperature has the strongest impact on the BrO error due to the strong impact on the WMP. [h!]

- The BrO error has the strongest dependence on the temperature difference. At Tungurahua (Nevado Del Ruiz) the BrO error increases by factor of $3.53 \cdot 10^{12}$

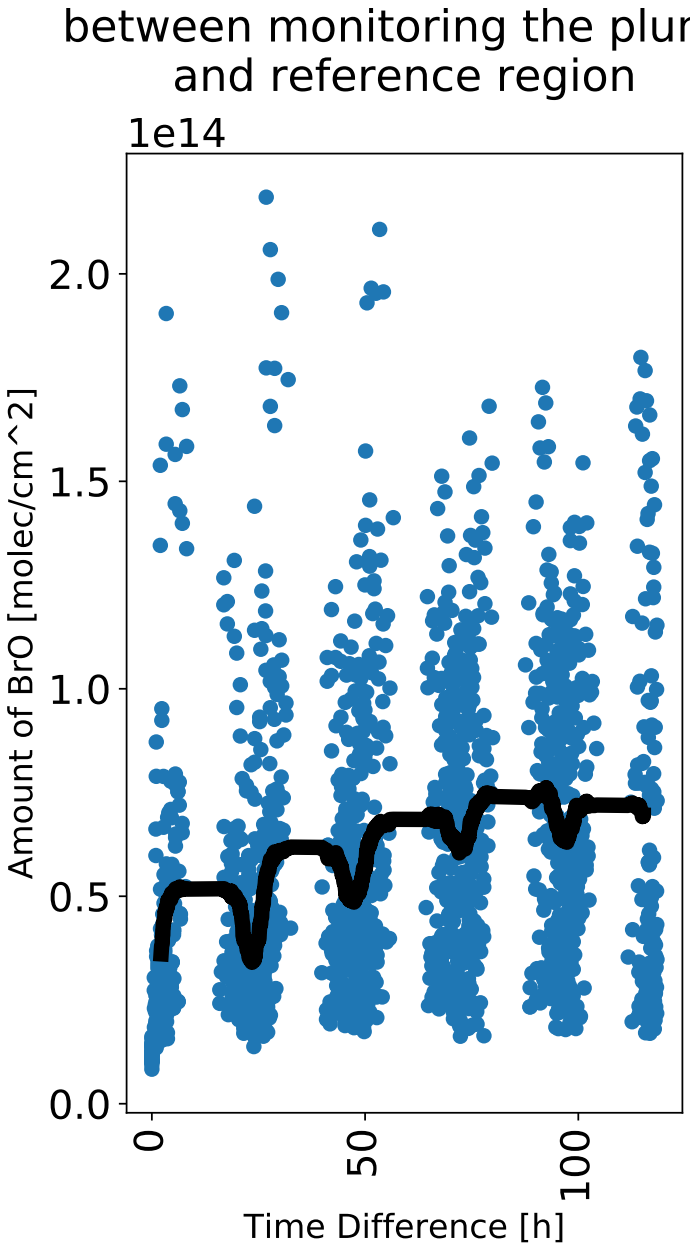

between monitoring the plume
and reference region
1e14
2.0
1.5
1.0
0.5
0.0
Amount of BrO [molec/cm^2]
0
50
100
Time Difference [h]

Figure 4.2:

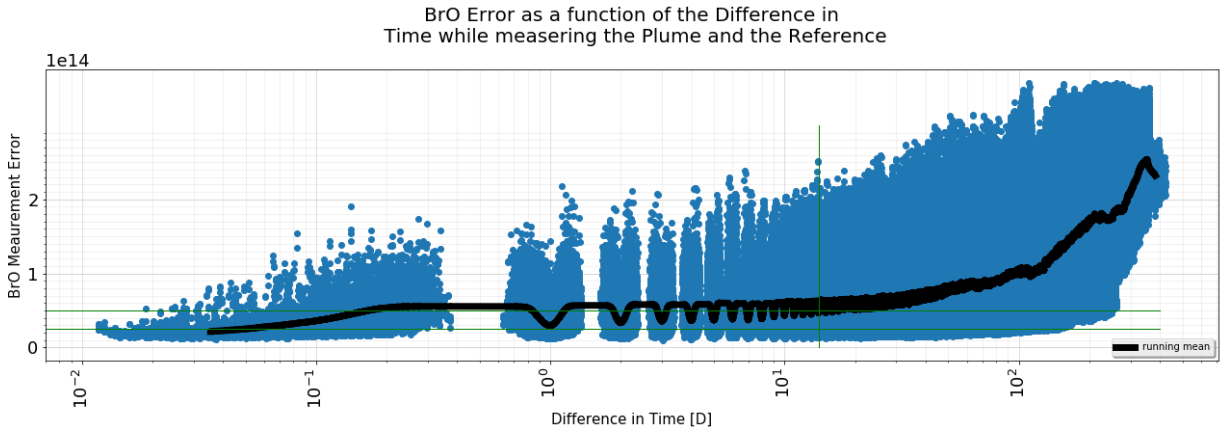
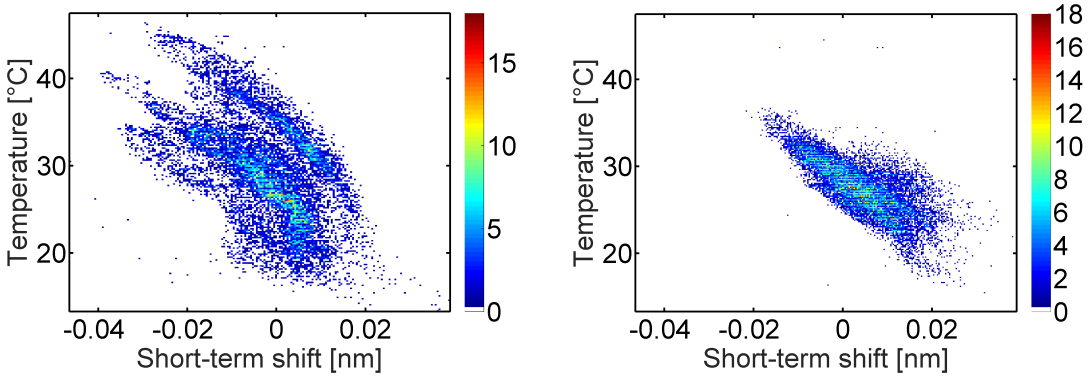


Figure 4.3:



(a) Data of Tungurahua

(b) Data of Nevado Del Riz

Figure 4.4: Titel unterm gesamten Bild

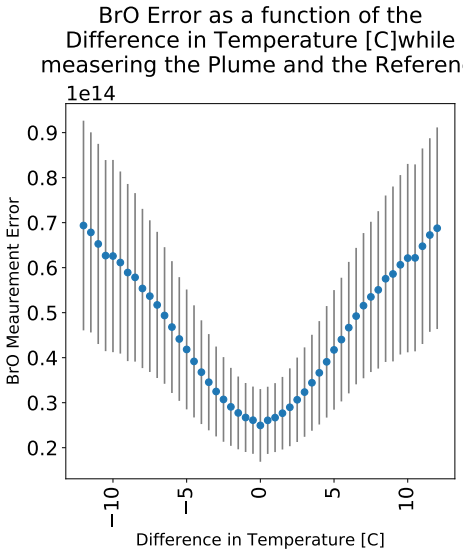
per degree.

$$\rightarrow BrO_{Error} = f(ext.P) + 3.53 \cdot 10^{12} \cdot \frac{\Delta T}{1C^{\circ}} + \mathcal{O}() \qquad Tungurahua$$

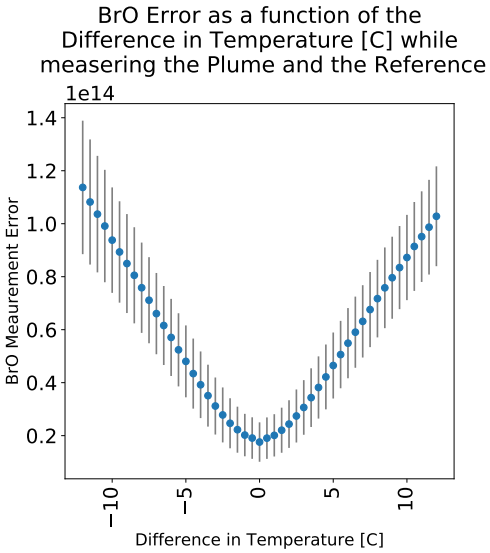
$$\rightarrow BrO_{Error} = f(ext.P) + 7.56 \cdot 10^{12} \cdot \frac{\Delta T}{1C^{\circ}} + \mathcal{O}() \qquad NevadoDelRuiz$$

4.1.3 Daytime

During the day o al lot of external parameters like temperature, solar altitude etc. change. In particular the solar altitude could have an impact on the fit quality since the light path of the sun is much longer at the evening than at noon. Figure 4.6 shows the dependency of the BrO error on the daytime. The data are calculated as



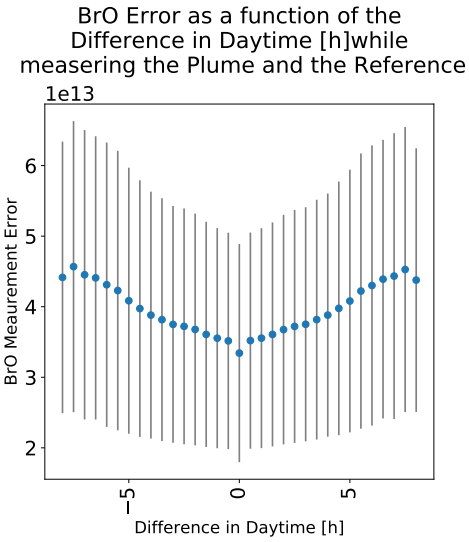
(a) Data of Tungurahua



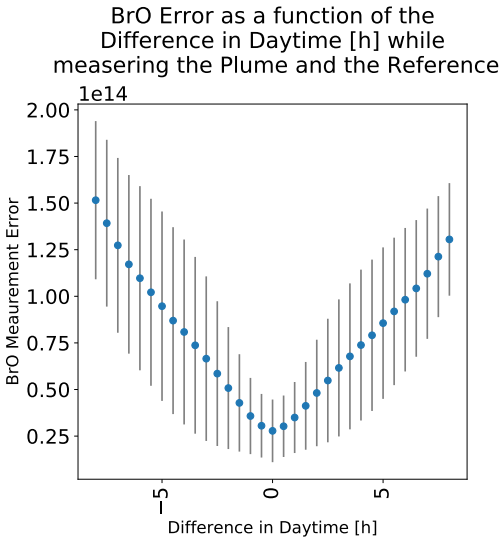
(b) Data of Nevado Del Riz

Figure 4.5: Titel unterm gesamten Bild

described for the temperature. As for the temperature the dependence of Nevado Del Ruiz is much larger than of Tungurahua, this might occur during the larger distance from the equator of Nevado Del Ruiz -> besser beschreiben



(a) Data of Tungurahua



(b) Data of Nevado Del Riz

Figure 4.6: Titel unterm gesamten Bild

- We found a dependency of the BrO error on the daytime. We assume, that

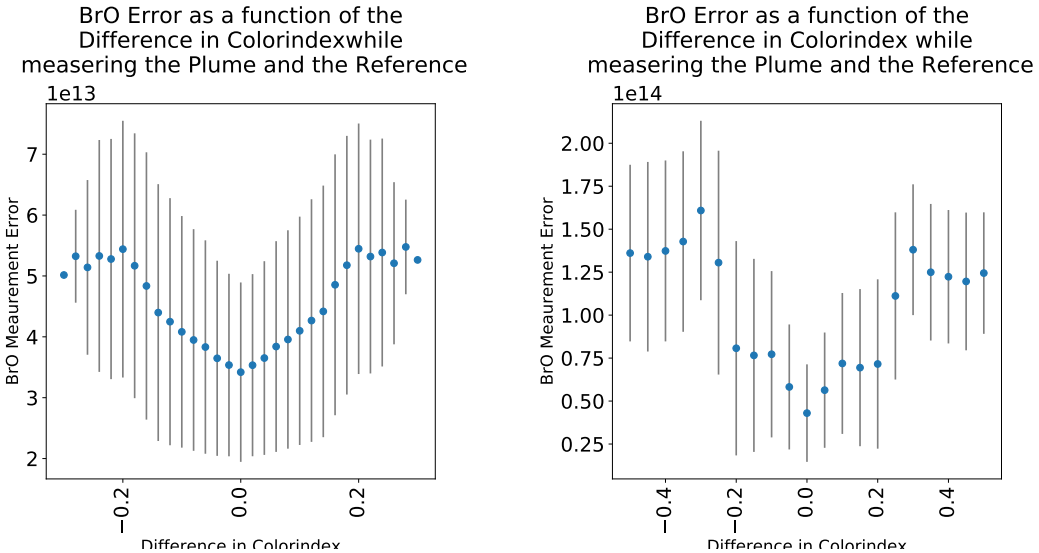
this dependency comes from other external parameters which change during the day.

- The BrO Error increases with the daytime differences like:

$$\rightarrow BrO_{Error} = f(ext.P) + 1.33 \cdot 10^{12} \cdot \frac{\Delta DT}{1h} + \mathcal{O}() \qquad Tungurahua$$

$$\rightarrow BrO_{Error} = f(ext.P) + 1.58 \cdot 10^{13} \cdot \frac{\Delta DT}{1h} + \mathcal{O}() \quad NevadoDelRuiz$$

4.1.4 Colorindex



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

Figure 4.7: Titel unterm gesamten Bild

Clouds have a strong influence on the atmospheric radiative transfer and thus affect the interpretation and analysis of DOAS - observations Wagner et al. [2014].

Clouds can be identified by several measurement quantities that they influence. Since Mie scattering is dominant in clouds, the radiation scattered on a cloud has a different colour than the Rayleigh sky as can be easily observed by the white colour of clouds. Therefore clouds can, for example, be identified by looking at the ratio of the measured intensity at two wavelengths, a so-called colour index. For a zenith-looking instrument clouds usually enhance the measured radiation intensity. Wagner et al. [2014].

If clouds are present during the measurements could this cause large errors of the retrieved gas column density and the corresponding uncertainties. Cloud effects could especially be important if either the plume ore reference is recorded with a cloudy sky while the corresponding reference ore plume was recorded under not cloudy conditions. This effect could also occur if broken clouds are present. Then, measurements at some elevation angles might "see" clouds while others do not.
The Colour Index (CI) in this work was calculated between 320nm and 360 nm. The two wavelengths were chosen as they are as far apart as the filter used for stray-light prevention in the spectrometers allows. On the other hand, the lower wavelength avoids the deep UV range where SO2 and O3 absorption plays a dominant role. When clouds are present more radiation from larger wavelengths arrives due to Mie scattering in the cloud. Therefore, the CI decreases when clouds are present. Lübcke [2014]

We evaluated the CI at the zenith, to increase the stability of the fit we added in each cases 10 intensitys. Using always the zenith to evaluate the colour index makes the colour index more comparable, but if broken clouds occur, the CI of the reference and the plume could differ from the calculated CI of the zenith. This could be a reason for the large deviations of the mean BrO error as function of the colour index (see fig. 4.7)

- The BrO Error increases with the Colorindex differences as

$$\rightarrow BrO_{Error} = f(ext.P) + 1.01 \cdot 10^{13} \cdot \frac{\Delta Cidx}{0.1} + \mathcal{O}() \qquad Tungurahua$$

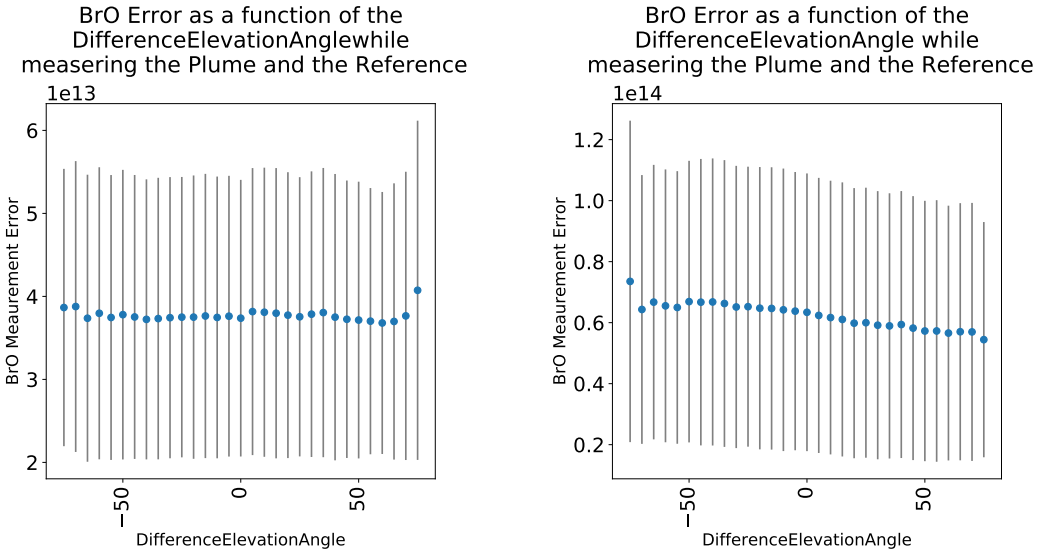
$$\rightarrow BrO_{Error} = f(ext.P) + 4 \cdot 10^{13} \cdot \frac{\Delta Cidx}{0.1} + \mathcal{O}() \qquad NevadoDelRuiz$$

4.1.5 Elevation Angle

The elevation angle describes the angle between the horizon and the zenith. When using the plume spectrum and the reference spectrum of the same time, the difference in elevation angle cannot be zero, since the plume is always somewhere else than the reference located.
The BrO error doesn't depend significantly on the difference between the Elevation Angles. This could have several reasons. One problem is, that the Elevation Angle of Plume and Reference spectrum is not the same. This could also be a reason of uncertainty of the evaluations of the plume spectrum.

4.1.6 Exposure Time

The Exposure Time is a degree of sky lightness.The exposure time is the length of time the sensor of the NOVAC instrument is exposed to light. The amount of light



(a) Data of Tungurahua

(b) Data of Nevado Del Riz

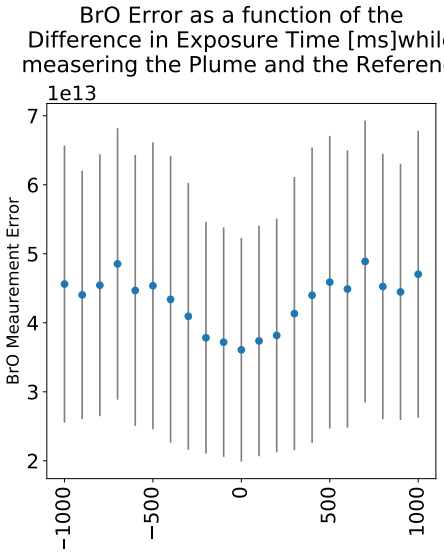
Figure 4.8: Titel unterm gesamten Bild

that reaches the film or image sensor is proportional to the exposure time. The exposure time is adjusted in the way that the maximum intensity does not overly the capacity of the sensor.
We can observe an small dependency of the BrO error on the Exposure time at Tungurahua and Nevado Del Ruiz as it is shown in fig. 4.9

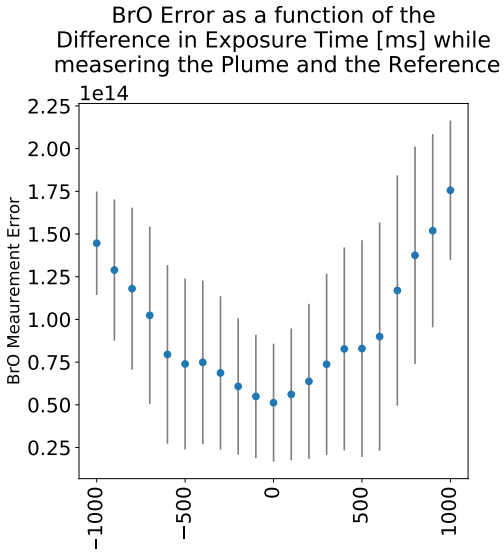
- The BrO Error increases with the exposure time differences as

$$\rightarrow BrO_{Error} = f(ext.P) + 1.92 \cdot 10^{12} \cdot \frac{\Delta ET}{10^{-2}s} + \mathcal{O}() \qquad Tungurahua$$

$$\rightarrow BrO_{Error} = f(ext.P) + 1.0 \cdot 10^{13} \cdot \frac{\Delta T}{10^{-2}s} + \mathcal{O}() \qquad NevadoDelRuiz$$



(a) Data of Tungurahua



(b) Data of Nevado Del Riz

Figure 4.9: Titel unterm gesamten Bild

5 Method

5.1 Fit data

- A Spectrum is treated as contaminated if the SO2 column density of the reference (evaluated with a solar atlas spectrum) is larger as $2{\cdot}10^{17}\frac{molec}{cm^2}$.
- Plume data are reliable if the SO2 column density is larger as $7\cdot10^{17}\frac{molec}{cm^2}$
- Data are above the detection limit if the column density as two times larger than the fit error.
- If the reference is contaminated:
  - We have a list of possible references where all references are not contaminated and the temporal distance to the plume date is no longer than 14 days.
  - we calculate of all possible references the differences in the external parameters
  - We use the analyse of external parameters described above to estimate the BrO error of all references
  - We choose the reference with the smallest estimated BrO error as new reference
  - We evaluate the plume spectra with the new reference.

5.2 Other approaches

- We also tried other possibilities than fitting to find the reference where the BrO error is minimal. In the following we present two additional possibilities but compared to fitting the results are not as good.

5.2.1 Nearest neighbours

- Description of the Nearest Neighbours Method

5.2.2 Iterative

- Description of the iterative Method

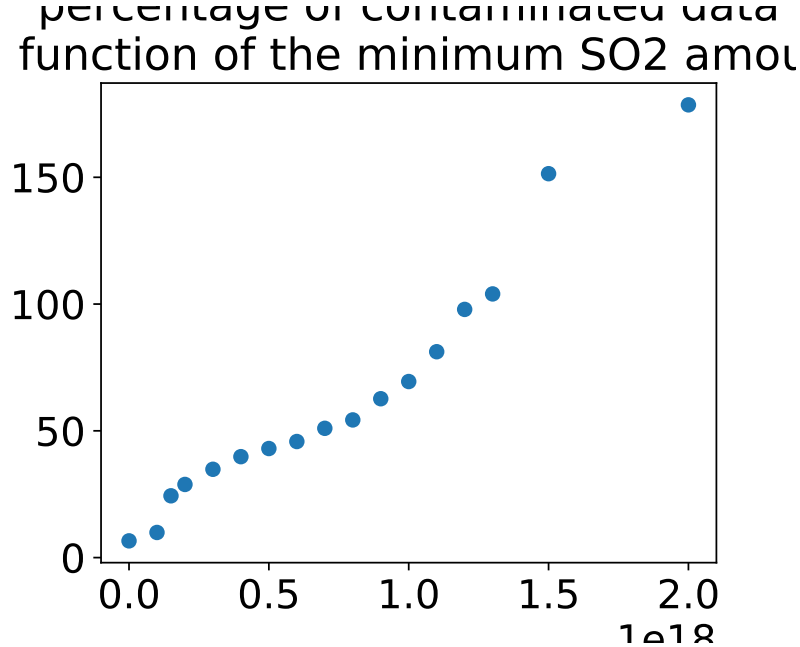


Figure 5.1:

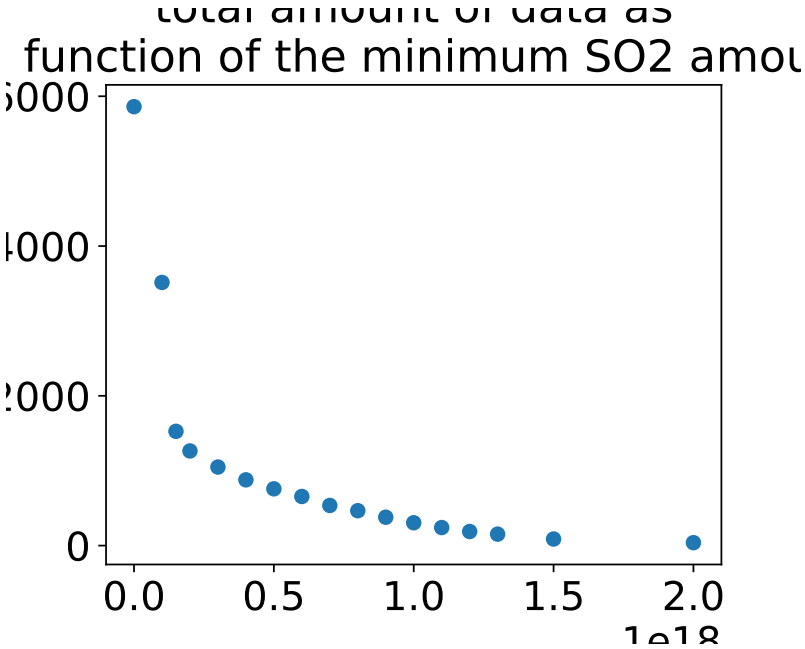


Figure 5.2:

6 Comparison with NOVAC Evaluation

- Results only for contaminated data
  - Difference in SO2 data evaluated with NOVAC-method and contamination-based evaluation
  - Difference in BrO data evaluated with NOVAC-method and contamination-based evaluation
  - Difference in BrO/So2 Ratio data evaluated with NOVAC-method and contamination-based evaluation
- More BrO data: 51%
- More valid BrO data: 38%

7 Results

Interpretation of the BrO/SO2 ratio time-series

7.1 Tungurahua

$MengeanDateninsgesamt:$	$5883 \equiv$	1
$Davon:(NOVACAuswertung)berplumelimit$	$712 \equiv$	0.121
$Davon:MengeanDaten, dienichtKontaminiertsind:$	$5504 \equiv$	0.936
$DavonimPlume-limit:$	$599 \equiv$	0.102
$DavonberdemDetectionLimit:$	$36 \equiv$	0.006
$Davonsindkontaminiert:$	$379 \equiv$	0.064
$Davon(mitNOVacausgewertet)berplumelimit:$	$114 \equiv$	0.301
$Davon(NeueAuswertung)berplumelimit$	$185 \equiv$	0.488

Dh in den kontaminierten daten sind mit NOVAC ausgewerteten daten 2.485 häufiger über dem plume limit

7.2 Nevado Del Ruiz

$MengeanDateninsgesamt:$	$8962 \equiv$	1
$Davon:(NOVACAuswertung)berplumelimit$	$142 \equiv$	0.016
$Davon:nichtkontaminiertedaten:$	$8596 \equiv$	0.959
$DavonimPlume-limit:$	$123 \equiv$	0.014
$DavonberdemDetectionLimit:$	$53 \equiv$	0.006
$Davonsindkontaminiert:$	$366 \equiv$	0.041
$Davon(mitNOVacausgewertet)berplumelimit:$	$20 \equiv$	0.055
$Davon(NeueAuswertung)berplumelimit$	$179 \equiv$	0.489

Dh in den kontaminierten daten sind mit NOVAC ausgewerteten daten 3.449 häufiger über dem plume limit

8 Issues of our method

8.1 Contamination of the plume

- 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 is also contaminated. This might be the case if the volcanic gas of the volcano is not taken away by the wind, but accumulates in the plume. If this is the case, using an other reference would lead to an overestimation of the column density of gases.

9 Conclusion

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Part III

Appendix

A Lists

A.1 List of Figures

A.2 List of Tables

B Bibliography

K Chance and RL Kurucz. An improved high-resolution solar reference spectrum for earth's atmosphere measurements in the ultraviolet, visible, and near infrared. *Journal of quantitative spectroscopy and radiative transfer*, 111(9):1289–1295, 2010.

Peter Lübcke. *Optical remote sensing measurements of bromine and sulphur emissions: Investigating their potential as tracers of volcanic activity.* PhD thesis, 2014.

Peter Lübcke, Nicole Bobrowski, S Arellano, Bo Galle, G Garzón, Leif Vogel, and U Platt. Bro/so 2 molar ratios from scanning doas measurements in the novac network. *Solid Earth*, 5(1):409, 2014.

G Pinardi, MV Roozendael, and C Fayt. The influence of spectrometer temperature variability on the data retrieval of so2. *NOVAC second annual activity report, NOVAC consortium*, 44:48, 2007.

U Platt and N Bobrowski. Quantification of volcanic reactive halogen emissions. *Volcanism and Global Change, eds A. Schmidt, K. Fristad, L. Elkins-Tanton, Cambridge University Press, Cambridge, UK, ISBN*, 1466525386, 2015.

Ulrich Platt and Jochen Stutz. Differential absorption spectroscopy. *Differential Optical Absorption Spectroscopy*, pages 135–174, 2008.

A Schmidt and A Robock. Volcanism, the atmosphere and climate through time. *Volcanism Glob. Environ. Chang*, pages 195–207, 2015.

Anja Schmidt, Kirsten Fristad, and Linda T Elkins-Tanton. Volcanism and global environmental change, 2015.

Hans-Ulrich Schmincke. *Vulkanismus*. Wissenschaftliche Buchgesellschaft, 3 edition, 2000.

S Solomon, RW Portmann, RR Garcia, W Randel, F Wu, R Nagatani, J Gleason, L Thomason, LR Poole, and MP McCormick. Ozone depletion at mid-latitudes: Coupling of volcanic aerosols and temperature variability to anthropogenic chlorine. *Geophysical research letters*, 25(11):1871–1874, 1998.

Thorvaldur Thordarson and Stephen Self. Atmospheric and environmental effects of the 1783–1784 laki eruption: A review and reassessment. *Journal of Geophysical Research: Atmospheres*, 108(D1), 2003.

T Wagner, A Apituley, S Beirle, S Dörner, U Friess, J Remmers, and R Shaiganfar. Cloud detection and classification based on max-doas observations. *Atmospheric Measurement Techniques*, 7(5):1289–1320, 2014.

Simon Warnach. Improvements of bro and so2 retrievals of novac data - tungurahua volcano as a case study. Master's thesis, 2015.

Erklärung:

Ich versichere, dass ich diese Arbeit selbstständig verfasst habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Heidelberg, den (Datum) .....