

Department of Physics and Astronomy

University of Heidelberg

Master thesis

in Physics

submitted by

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born in Hamburg

2018

**Retrieval advances of BrO/SO₂ molar ratios from
NOVAC**

This Master thesis has been carried out by Elsa Wilken
at the
Institute for Environmental Physics, University of Heidelberg,
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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.

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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 SO_2 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

2 Volcanism and volcanic chemistry

2.1 Volcanism

The high thermal energy in the deep interior of the earth is mostly well separated from the earth's surface by the earth's crust. A volcano is geological structure that allows magma to reach the earth's surface. Such a phenomenon can occur in various ways. In the following paragraphs the different types of volcanoes are described.

Mid-ocean ridge volcanism The mid-ocean ridge volcanism can be traced back to tectonic processes of oceanic plates. The spreading of two plates, that are pulled apart, leads to a thinning of the oceanic earth crust. This way solid material from the upper mantel (lower than 100 km) can ascend to depths of approximately 50 km. As the pressure at this depth is much lower, the mantle material starts to melt to basaltic magma that fills the gap between the two plates.

Continental rift zone volcanism Similar to mid-ocean ridge volcanism continental rift zone volcanism results from two continental plate are pulled apart.

Subduction zone volcanoes Subduction zone volcanoes occur if an oceanic plate converges under another plate (oceanic or continental). This way the descending plate penetrate into the lower mantle. At a depth of 80-150 km the water of this plate evaporates and rises and causes the mantle material above to melt. The resulting water-rich magma mainly consists of andesite. Subduction zone volcanoes are known for their violent eruptions caused by the low viscosity magma.

Hot-spot volcanoes Hot-spot volcanoes occur on continental or oceanic plates. This type of volcanoes arises from a hot spot at the coremantle boundary inside Earth that leads to a plume in the mantle where solid material can rise. This material melts to basaltic magma at a depth of 100-150 km. Through a futher rise also other types of magma (e.g. rhyolitic, more-viscous magma) can arise.

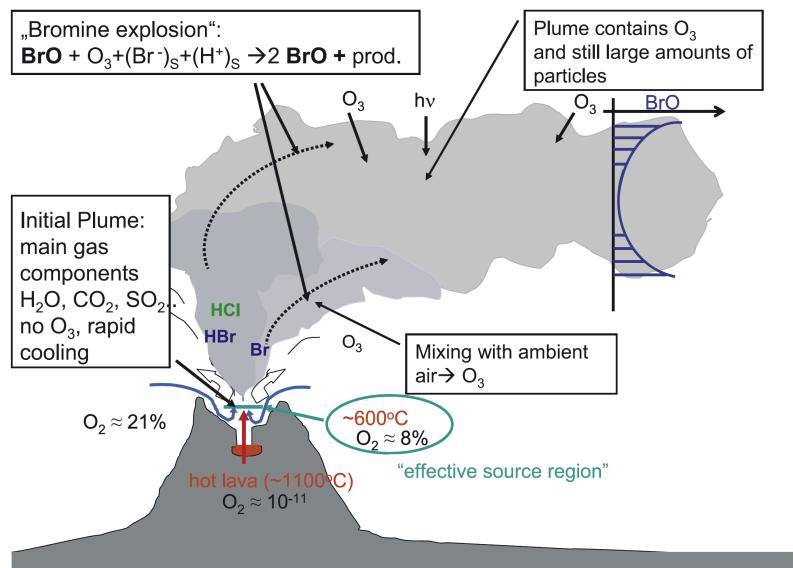


Figure 2.1: schematic sketch of a Bromine Explosion. Release of HBr at the volcanic vent. Mixing with ambient air in the effective source region leads to Br formation. This resulting Bromine species react to BrO with ozone from the plume. Adapted from Bobrowski et al. [2007]

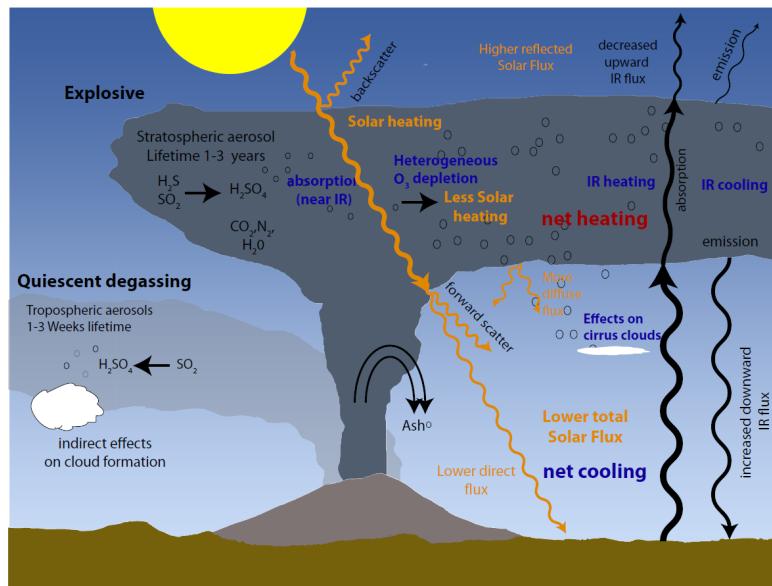


Figure 2.2: Influence of volcanic eruptions and quiet degassing on earth climate. Redrawn on the basis of Robock [2000]

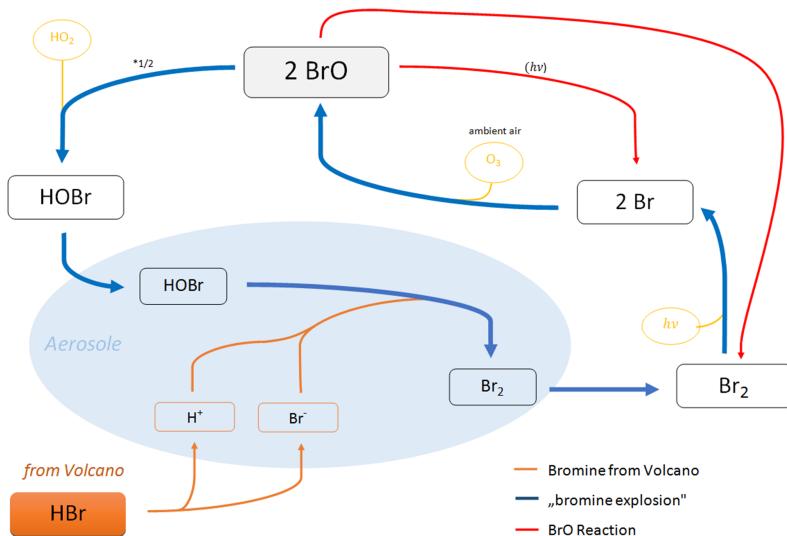


Figure 2.3:

2.1.1 Volcanic degassing

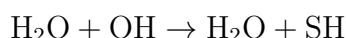
2.1.2 Volcanic gases and their impact on the climate

2.1.3 Volcanic plume chemistry

2.1.4 Sulphur species

Sulphur species are the third most abundant gases in volcanic plumes, hereby contributes SO₂ with about 25% and H₂S with 1 to 10%. Only H₂O and CO₂ have a larger share on the volcanic gases in the plume ??.

Outside of the volcanic plume the SO₂ amount is with approximately 1ppb negligible, in contrast the SO₂ amount inside the plume can easily reach 1ppm ? When H₂S escapes from the volcano vent, it enters the oxidizing conditions in the atmosphere. The conversion of H₂S into SO₂ starts with:



The SH radical goes through a series of reactions, leading to the SO₂ formation ? SO₂ is removed from the atmosphere by dry or wet deposition. At homogeneous reactions the lifetime is from 1-3 weeks Robock [2000]. Heterogeneous reactions such as take place on particles or liquid phases leads to much faster depletions.

Further discussions of the stability of SO₂ in the atmosphere can be found at Lübecke [2014].

In this thesis it is assumed that SO₂ is stable on timescales occurring with ground based remote sensing measuring of about 20 minutes.

The SO₂ amount in the atmosphere outside of the volcanic plume is with approximately 1ppb negligible. In contrast the SO₂ amount in the plume can easily reach

1ppm ?.

The fact that the SO₂ amount in the atmospheric background compared to the SO₂ amount in the plume is negligible alongside

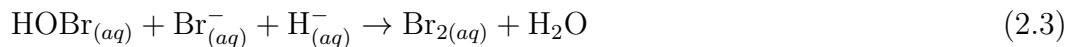
2.1.5 Bromine oxide

The amount of Bromine in volcanic plumes is rather low compared to SO₂ ?. The first time Bromine monoxid (BrO) was observed at a volcano was 2013 at the soufriere hills by ?. Since then many others were able to detect BrO using ground based remote sensing measurement techiques (DOAS: see section 3.1)

examples

The main Bromine formation which is released from the volcano is HBr. BrO is formed due to mixing with the ozone rich atmosphere at ambient temperatures Bo-browski et al. [2007].

Due to the raising of hot air in the volcano vent , ambient air is pulled into the vent. There temperatures of 600°C to 1200°C prevent the formation of BrO. Only Br id formed. BrO occures after further cooling and mixing while rising. When the temperature cooles down to ambient conditions the so called "Bromine Explosion" causes a non linear formation of BrO. The "Bromine Explosion" is illustrated in fig. 2.3 and can be described with the following reaction cycle:



The exponential BrO formation is slightly diminished by

2.1.6 Using volcanic gases to study volcanic activity

Tungurahua

Tungurahua is a subduction zone volcano located in the Ecuadorian Andes (Lat: 01°,28'S; Long:78°,27'W). 2014 Tungurahua was one of the most active volcanoes in southern America, since then the activity was decreasing. Tungurahua is 5023m high and is one of the defining volcanoes of the eastern volcanic rows in Ecuador. Hall et al. [1999]

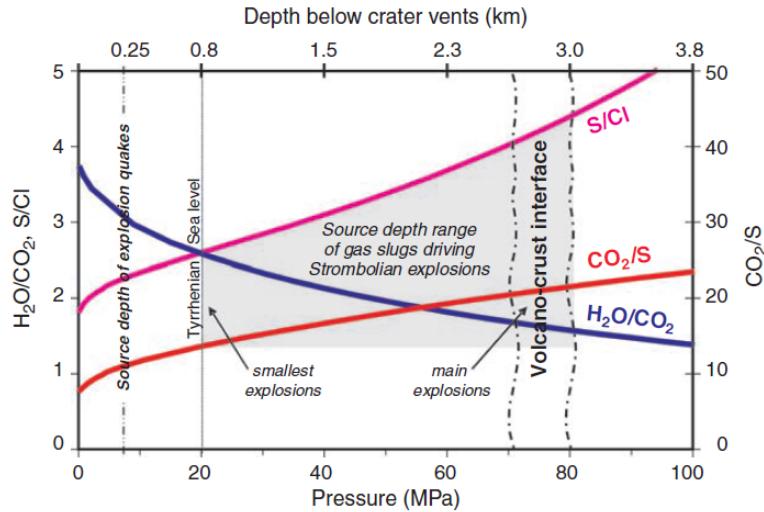


Figure 2.4: Dependency of the ratios of different volcanic trace gases on depth. Data originate from Stromboli volcano. From Lübecke [2014] reproduced from Burton et al. (2007)

Nevado Del Ruiz

Nevado Del Ruiz is also a subduction zone volcano. Nevado Del Ruiz is located in the Central Cordillera of Colombia, 140 km west of Bogota. (Lat: $04^{\circ},53'S$; Long: $75^{\circ},19'W$) The hight of Nevado Del Ruiz is 5389 m.

3 Remote sensing of volcanic gases

In this thesis we are interested in the volcanic trace gases SO₂ and BrO, both measured with the Differential Optical Absorption Spectroscopy (DOAS) a remote sensing technique proposed by [Platt and Stutz \[2008\]](#)

This chapter will give a short overview about the measuring technique.

Beer-Lambert Law

This section will give an overview about the reasons for decreasing light intensity when going through a medium.

The Lambert-Beer law describes the attenuation of light when traveling through a material.

Atoms and Molecules exists in several energy states, depending on the different electron configuration. Moreover Molecules have additionally rotation and vibration states, also enclose to the energy states. If a photon matches the energy gap between two possible energy states, this includes, that the lower energy state is occupied and the selection rules are fulfilled, the molecule could absorb the photon, remaining in a higher energy state.

The additional photon energy could be loosed by collision with another molecule or by emission. But since the direction of the emitted photon is mostly not the same direction of the absorbed photon the intensity I₀ of the light before passing the medium is higher than the intensity I after traveling the distance L through the medium.

This can be described as:

$$I(L, \lambda) = I_0(\lambda) \cdot \exp \left(- \int_0^L \sigma(\lambda, p, T) \cdot c(l) dl \right) \quad (3.1)$$

where $c(l)$ is the location-dependent concentration of the trace gas of interest. $\sigma(\lambda, p, T)$ is the absorption cross section, $\sigma(\lambda, p, T)$ is unique for each molecule and depends on pressure p and on the temperature T.

An important quantity used in many optical remote sensing techniques is the optical density τ . The optical density is a measure for the weakening of radiation when going through a material. τ can be calculated using the lambert beer law:

$$\tau = -\ln \left(\frac{I(\lambda)}{I_0(\lambda)} \right) = \sigma \cdot S \quad (3.2)$$

Hereby is S the column density. The column density is the concentration of the trace when integrating along the light path, the dimension of S is therefore the number of molecules divided by an area: $\frac{\text{molec}}{\text{cm}^2}$.

$$S = \int_0^L c(l) dl \quad (3.3)$$

When measuring at a volcano, that means measuring in the atmosphere the situations gets more complex, since we need to deal with several absorbers and scattering processes have to be taken into account. One possibility is to treat scattering effects as pseudo absorbers with the respective extinction coefficients for Rayleigh (ϵ_R) and Mie (ϵ_M) scattering

$$I(L, \lambda) = I_0(\lambda) \cdot \exp \left(- \int_0^L \sum_j \sigma_j(\lambda, p, T) \cdot c_j(l) + \epsilon_R(\lambda, l) + \epsilon_M(\lambda, l) dl \right) \quad (3.4)$$

The first term of eq. (3.4) in the exponential function, multiple absorbers j are considered, the corresponding concentration depends on the position l of the light path. The last two terms in describe the extinction due to Rayleigh and Mie scattering in the atmosphere.

Inelastic scattering (for example the Ring effect) and effects due to turbulences in the atmosphere, are neglected here.

3.1 Differential Optical Absorption Spectroscopy(DOAS)

It is impossible to distinguish between various broad-band effects, like scattering in the atmosphere or instrument effects which influence the measured spectra [Lübcke \[2014\]](#). Therefore eq. (3.4) cannot be applied to real measurements.

Differential Optical Absorption Spectroscopy (DOAS) was invented in the late 1970s by [Perner and Platt \[1979\]](#). This section will give an overview about the DOAS technique. More detailed information can be found in the work of [Platt and Stutz \[2008\]](#)

Differential Optical Absorption Spectroscopy uses the fact, that absorption can be divided into broad-band parts and narrow-band parts. Broad band parts are effects that only changes weakly with the wavelength, i.e. scattering and instruments effects have a broad-band structure. The narrow band part includes effects that strongly depends on the wavelength. Within the DOAS-Method only narrow-band absorption features of molecules are used to obtain their column densities. The absorption cross section of trace gases j have broad-band ($\sigma_b(\lambda)$) and narrow band ($\sigma'(\lambda)$) features, only the narrow-band structures are used in DOAS.

$$\sigma(\lambda) = \sigma_b(\lambda) + \sigma'(\lambda) \quad (3.5)$$

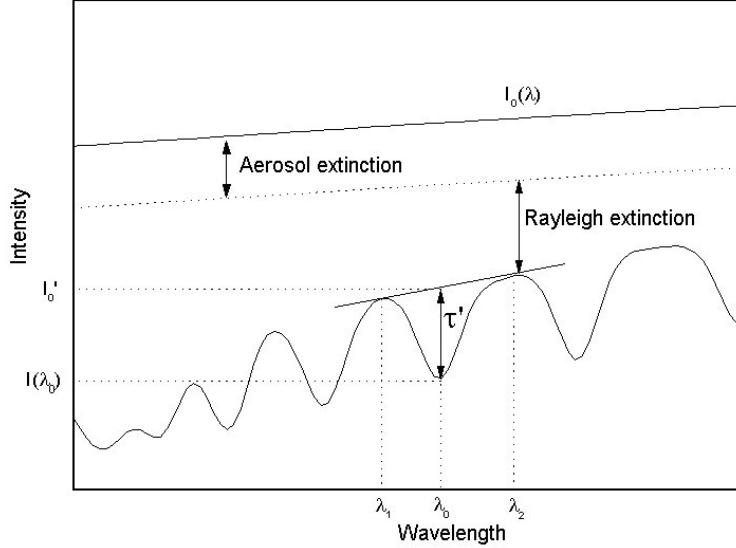


Figure 3.1: Basic idea of the DOAS principle: Light attenuate due to broad band and narrow band effects. The broad band extinction is caused by aerosols and Raylight scattering ($I_0 \rightarrow I'$). The measured intensity I is formed by narrow band effects due to differential absorption structures by trace gases with the optical density τ' . Adapted from Kern [2009]

With this considerations the Lambert-Beer law eq. (3.4) can be rewritten dividing the exponential part into a narrow-band part and a broad-band part:

$$I(\lambda, L) = \overbrace{I_0(\lambda) \cdot \exp \left(- \int_0^L \sum_j \sigma_{b,j}(\lambda, p, T) \cdot c_j(l) + \epsilon_R(\lambda, l) + \epsilon_M(\lambda, l) dl \right)}^{=I'_0(\lambda)} \cdot \exp \left(- \int_0^L \sum_j \sigma'_j(\lambda, p, T) \cdot c_j(l) dl \right) \quad (3.6)$$

The so defined $I'_0(\lambda)$ differs from $I_0(\lambda)$ only by broad band effects. With $I'_0(\lambda)$ a differential optical density τ' can be defined:

$$\tau' = \ln \left(\frac{I'_0(\lambda)}{I(\lambda)} \right) = \int_0^L \sum_j \sigma'_j(\lambda) \cdot c_j(l) dl = \sum_j \sigma'_j(\lambda) \cdot S_j \quad (3.7)$$

The optical density can now be calculated by using the difference of the column density S_M in the measurement spectrum to the column density S_R of a reference spectrum. From Equation (3.6) we know:

$$I_{P,R} = I'_0 \cdot \exp(-S_{P,R} \cdot \sigma(\lambda)) \quad (3.8)$$

In general the obtained column density S_M is called differential slant column density: "dSCD". If the reference spectrum does not contain the trace gas of interest (is not contaminated with trace gases) that means $S_R = 0$, S_M is called the slant column density (SCD). With Equation (3.8) the optical density can be derived by:

$$\tau(\lambda) = -\ln\left(\frac{I_M}{I_R}\right) = \sigma(\lambda) \cdot (S_M - S_R) \quad (3.9)$$

3.1.1 Technical Implementation of the DOAS Approach

The theory explained above only describes the ideally situation. In real measurements more problems occur due to instrument limitations inelastic scattering causing the Ring effect and due to impacts of external parameters like temperature. In the following a short overview about these problems and their consequences for our retrieval is given. Further information can be found in Lübecke [2014].

Optical and spectral resolution of the spectrometer

The resolution of the spectrometer is finite, thus, the detector receives a spectrum $I^*(\lambda)$ which can be retrieved with a convolution of the incident spectrum $I(\lambda)$ with the instrument function $H(\lambda)$:

$$I^*(\lambda) = I(\lambda) * H(\lambda) = \int I(\lambda - \lambda') \cdot H(\lambda - \lambda') d\lambda' \quad (3.10)$$

For the evaluation all σ_j of the trace gases of interest need to have the same spectral resolution as the instrument used for recording the spectra. In this work we will use high resolution cross sections and convolute them with the instrument function H :

$$\sigma * (\lambda) = \sigma(\lambda) * H(\lambda) \quad (3.11)$$

The instrument function H can be approximated by using the spectral lines of a mercury lamp since the width of those lines is only a few pm, they could be treated as delta peaks when comparing it to the resolution of the spectrometers.

Effects of the detector

The detector only has discrete pixels, therefore a wavelength interval is mapped to a pixel i .

$$I'(i) = \int_{\lambda(i)}^{\lambda(i+1)} I^*(\lambda'd) d\lambda' \quad (3.12)$$

For the retrieval the relationship between the detector channels and the wavelength of the spectrum need to be known. The wavelength to pixel mapping (WMP) for a detector with q channels can be calculated as:

$$\lambda(i) = \sum_{k=0}^{q-1} \gamma_k \cdot i^k \quad (3.13)$$

Hereby, is γ_0 a shift of the spectrum and γ_1 is a squeeze (respectively stretch) of the spectrum. The wavelength to pixel mapping can be discovered by using a mercury lamp again and compare pixel-position with the well known wavelength of the individual HG-lines of the mercury lamp.

The wavelength to pixel mapping depends on the instrument temperature as well as on the ambient pressure Lübcke et al. [2014].

Ring effect

As mentioned above inelastic scattering causes the Ring effect (named after Grainger and Ring, 1962). The Ring effect is observable through a filling of the Fraunhofer lines in spectra of scattered solar radiation, (e.g. if the sunlight travels through the earth atmosphere). When compared to direct sunlight measurements (e.g. outside of the earth atmosphere). (Bussemer [1993], Solomon et al. [1987]) proposes that the Ring effect is a result of rotational Raman scattering mainly of O_2 and N_2 in the atmosphere. Solomon et al. [1987] suggested to treat the Ring effect as a pseudo-absorber.

Part II

Evaluation of the Data of Tungurahua and Nevado Del Ruiz

4 Network for Observation of Volcanic and Atmospheric Change

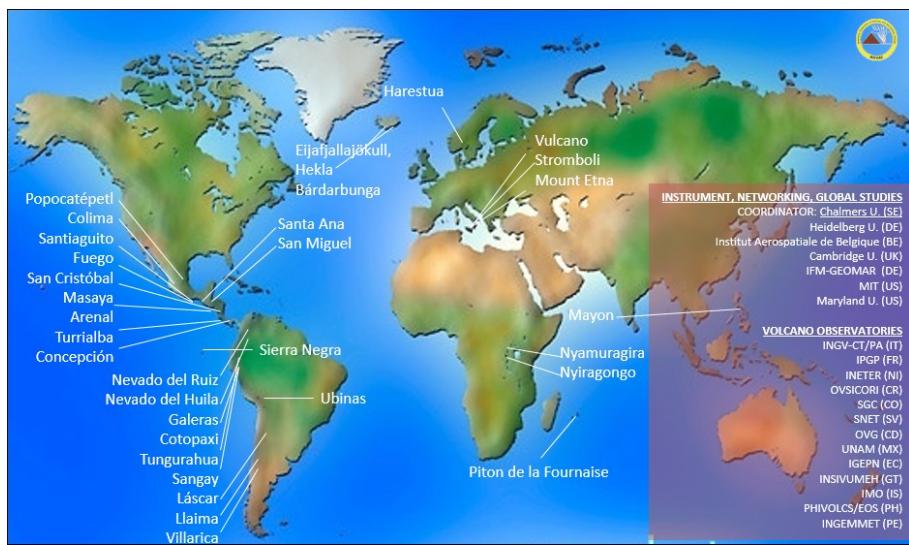


Figure 4.1: Global map of the volcanoes monitored by NOVAC. Used with friendly permission of Santiago Arellano.

Network for Observation of Volcanic and Atmospheric Change (NOVAC) is a network of instruments monitoring volcanoes over the whole world. NOVAC was installed to gain another tool for risk assessment, for gas emissions and geophysical researches.

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. Figure 4.1 shows a map, with all volcanoes of the Network for Observation of Volcanic and Atmospheric Change.

The great advantage of the data monitored in NOVAC is the fact that NOVAC provides continuous gas emission data over many years. This ensures statistically meaningful results for the data evaluation.

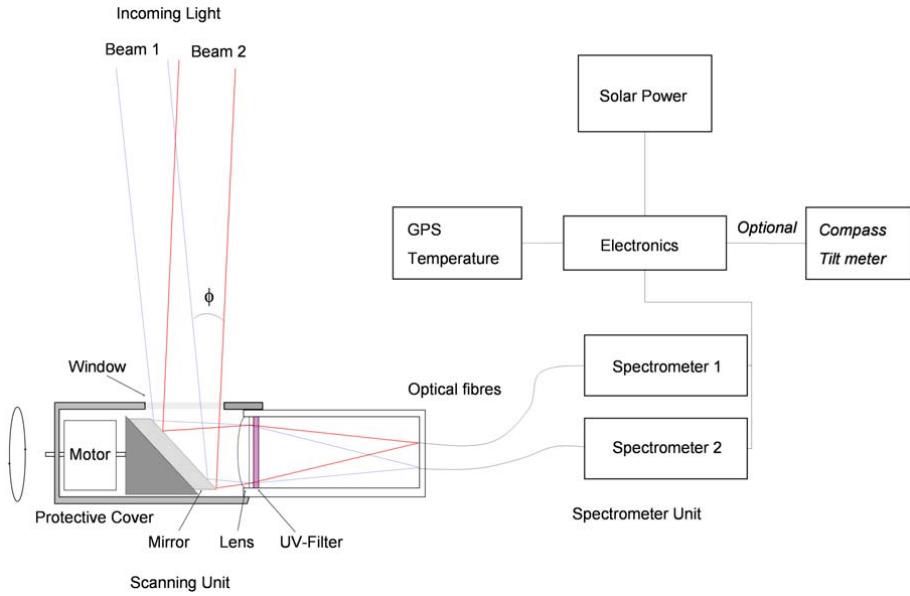


Figure 4.2: shematic sketch of a NOVAC instrument. From Galle et al. [2010]

The instruments used in NOVAC are scanning UV-spectrometer named 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 in this case means that the measurement is only possible during daytime and if the Sunlight is sufficient.

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. NOV

The spectrometers measure in the UV region in a wavelength range of 280 to 420 nm. In this range the differential structures of SO₂ and BrO are 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.

This comes with a reduced precision of the data, but the huge amount of data produced by NOVAC compensates for this limitation.

4.1 Measurement Routine

The instruments are set up five to ten km downwind of the volcano. To cover most of the occurring wind directions two to five instruments are installed at each vol-

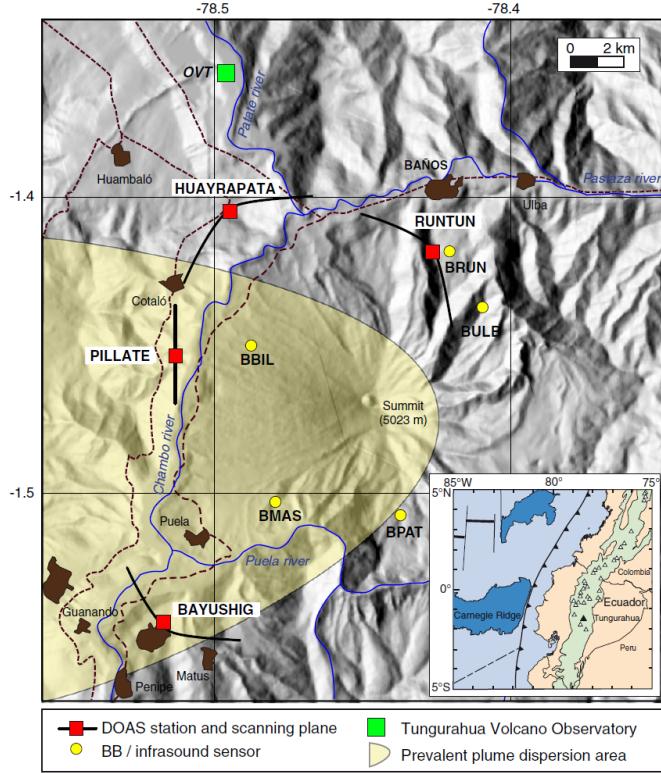


Figure 4.3: Topographic Map of the Tungurahua Volcano. The predominant plume direction is shaded in yellow. Four NOVAC stations are shown as red squares, the corresponding scanning geometry is sketched with black lines. From Hidalgo et al. [2015].

cano. Ideally, the measurement plane is orthogonal to the plume, to get the best measurement results. In reality, the measurement plane might be rotated.

For the calculations of gas data from the DOAS retrieval a scan of the Plume and a scan without any volcanic trace gases (reference spectrum) is needed. This is done without any knowledge of the plume location by scanning the whole sky. The measurement routine starts with a spectrum in zenith direction: the pre-reference. The exposure time of the pre-reference will be used for the whole scan. Afterwards, the dark current spectrum is recorded for the correction of the dark current and offset.

Then the instrument turns automatically to the side, recording spectra at the elevation angle from -90° to 90° with steps of 3.6° .

The instruments records 53 spectra per Scan. One hole measurement takes 6 to 15 minutes.

5 Evaluation Routine

Section 3.1 gives an overview about the theory of the DOAS Method. This chapter will go through the algorithm which is used for the evaluation of the spectroscopic data recorded in NOVAC. The occurring problem of contamination of the reference will be explained and possible solutions will be presented.

5.1 NOVAC-Evaluation

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

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

The term $P(\lambda)$ is a polynomial that accounts for all broad-band effects that differ between the background spectrum $I_0(\lambda)$ and the measurement spectrum $I(\lambda)$. All Gases j with relevant structures in the wavelength range used for the evaluation of SO₂ (BrO) and the additional pseudo absorbers are listed in section 5.1. The remaining task of the DOAS routing is to find a model function $F(\lambda)$ that minimizes χ^2 :

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

While $F(\lambda)$ can be expressed on the basis of eq. (5.1):

$$F(\lambda) = \ln(I_0) + P(\lambda) - \sum_j \sigma_j(\lambda) \cdot S_j \quad (5.3)$$

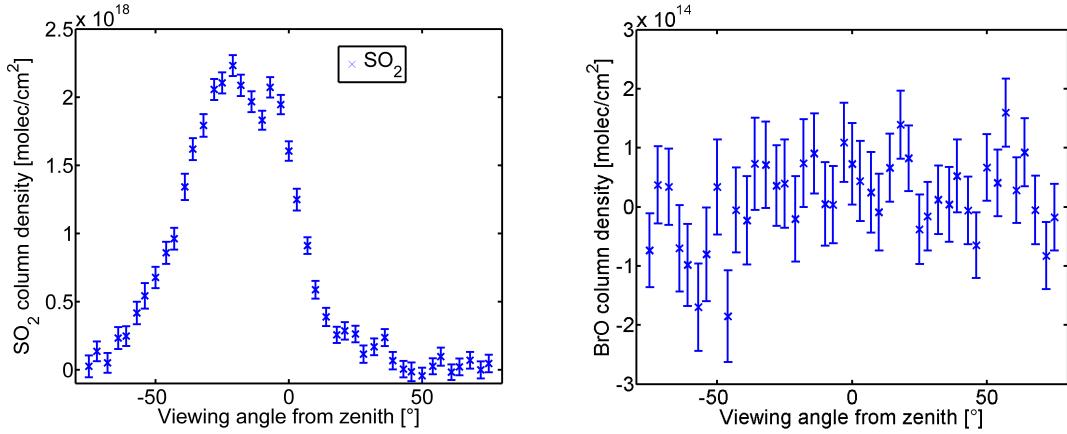
The DOAS fitting routine uses a combination of a standard least-squares fit and a Levenberg-Marquardt algorithm to minimize χ^2

The Network for Observation of Volcanic and Atmospheric Change provides Spectral Data for 50 different elevation angles. For the DOAS evaluation we need a

BrO Evaluation SO₂ Evaluation

SO ₂
O ₂
O ₃
O ₄

Table 5.1: All Gases used in NOVAC- Evaluation when retrieving the column densities of BrO and SO₂



(a) SO₂ SCD as a function of the elevation angle with error bars resulting from the DOAS fitting routine (b) BrO SCD as a function of the elevation angle with error bars resulting from the DOAS fitting routine

Figure 5.1: SCD's as a function of viewing angles. Adapted from [Warnach \[2015\]](#)

reference and a measurement spectrum. To get the SCD's we need to get references without any amount of the volcanic trace gas of interest (This will be discussed more detailed in section 5.2). With the so found $F(\lambda)$ the column density of BrO and SO₂ from the measurement spectrum relatively to the reference spectrum can be calculated using the calculations made above.

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 the measurement spectrum in the volcano plume and the reference region which need to be outside of the plume. 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 3.1, that means we divide each recorded spectra by the pre-reference and take the logarithm to get rid of the Fraunhofer structures and to be able to just look at the important structures of the plume. The result is SO₂ dSCD's as a function of the elevation angle. So we can localize the maximum and the minimum of SO₂ amount, but not the SCD's. To get the gas dSCD's of the evaluated spectra, one fits the absorption cross section of

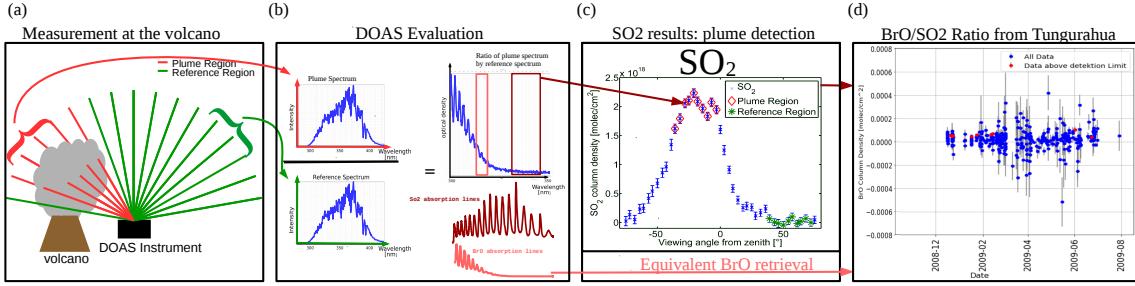


Figure 5.2: NOVAC Evaluation: (a) Measurement at the volcanoe (b) Evaluation of the spectral data with the DOAS routine using the absorption cross sections of BrO and SO₂. (c) finding the location of the plume and reference (d) the ratios BrO/SO₂ at Tungurahua

all important gases on the recorded spectrum. In our case we take all gases written in tab. ?? into account. Inside the plume the SO₂ amount is much higher than outside the plume. 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 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 In fig. 5.1 (a) the SO₂ SCD as a function of the elevation angle is shown. The SO₂ curve show a clear 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°. (b): The extrema of the BrO curve are not as distinct as at the SO₂ curve.

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. 5.1 (b). 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.

Taking the BrO/SO₂ ratio if the column densities are close to zero yields unpre-

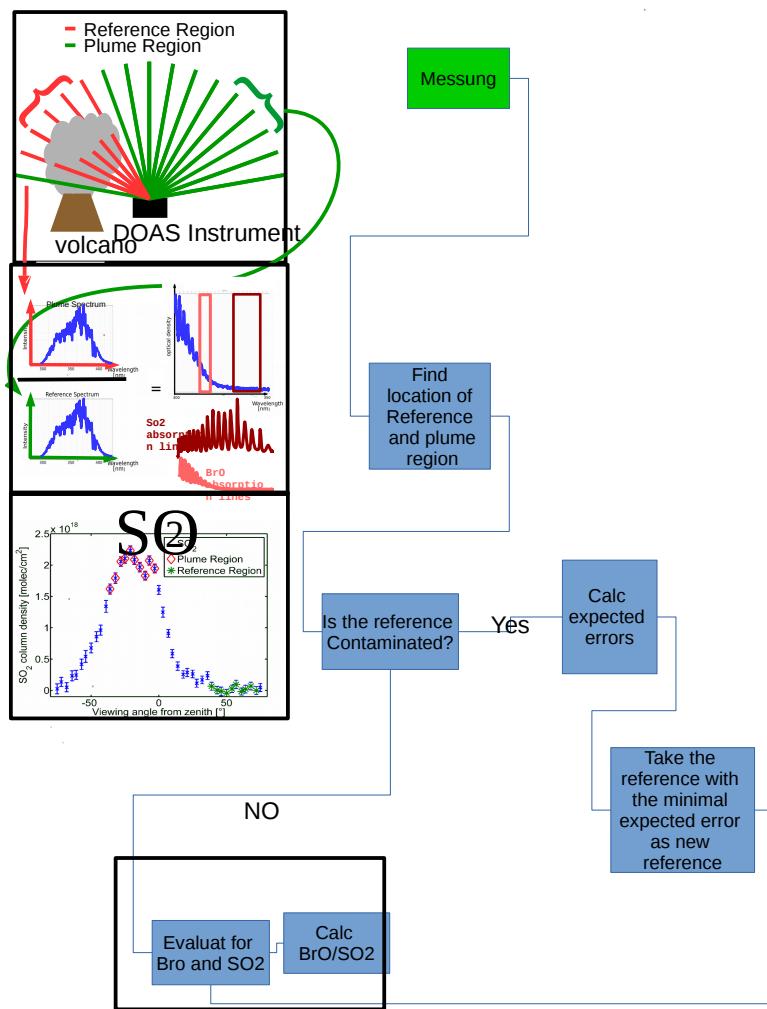


Figure 5.3: Sketch of the DOAS Routine

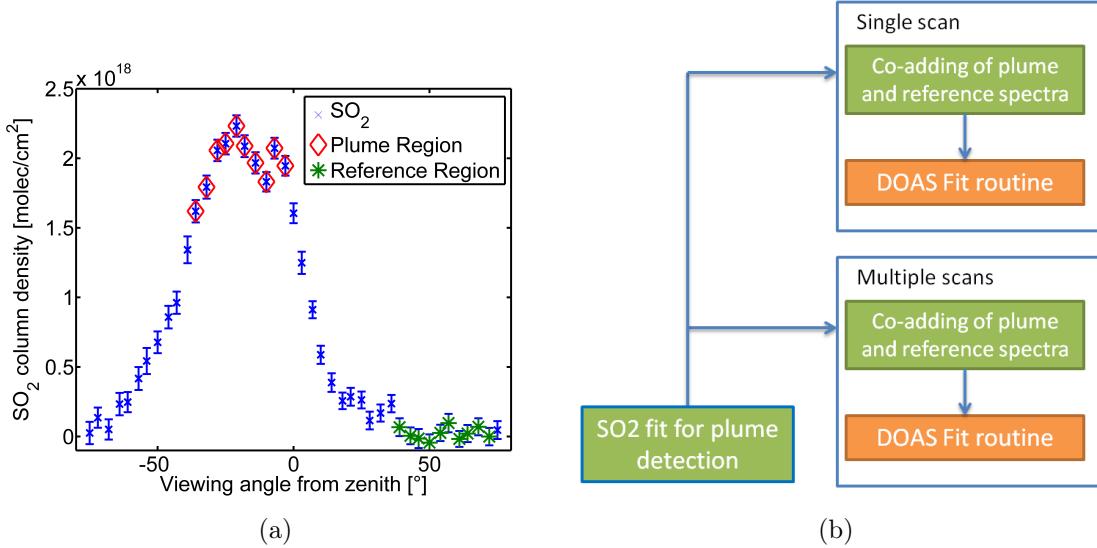


Figure 5.4: (a) SO₂ SCD as a function of the elevation angle. The co-added Plume region is marked with red diamonds, and the co added reference region with green stars. From Warnach [2015]. (b) Flow chart of the BrO and SO₂ evaluation. From Lübcke [2014].

dictable 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 a SO₂ threshold. A reasonable BrO threshold need to be at least in the order of the DOAS fit error. But this could lead to elevated BrO/SO₂ ratios, since the BrO error is often close to the detection limit, and thus exclude all low BrO column densities from the evaluation. The other possibility is to set a SO₂ threshold. In this thesis an SO₂ threshold of $7 \cdot 10^{17} \frac{\text{molec}}{\text{cm}^2}$ was used for the selection of spectra for the evaluation of the BrO/SO₂ ratio. $7 \cdot 10^{17} \frac{\text{molec}}{\text{cm}^2}$ is relatively high column density. However this approach assures that no significant amount of gases will be filtered out, therefore the BrO/So2 will not be significantly influenced Lübcke et al., 2014 and that all accepted measurement spectra will be inside of the volcano plume.

5.2 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. Thus the gas amount is underestimated by the NOVAC-Evaluation: In fig. 5.5 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

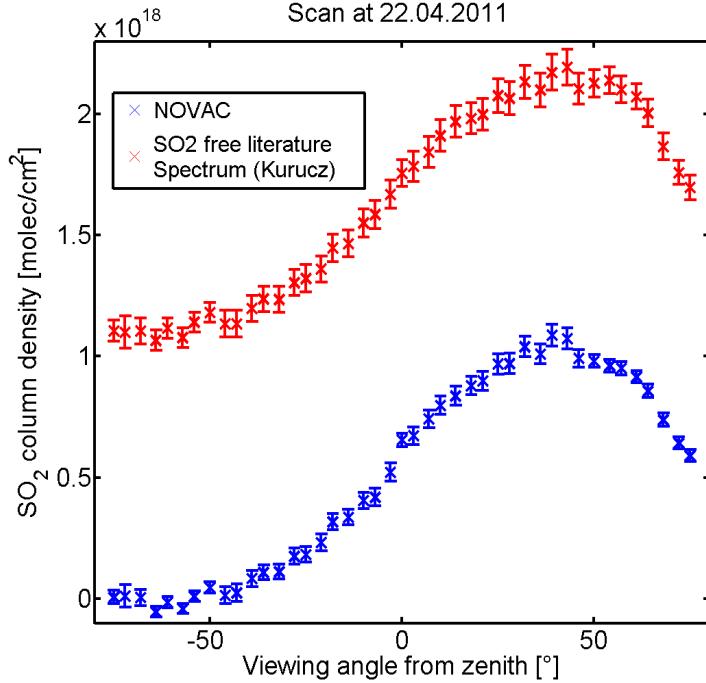


Figure 5.5: Scan with a contaminated reference spectrum from April 2011. From Warnach [2015]

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 5.2) or 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

Figure 5.6:

Figure 5.7:

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 could be a volcanic-gas-free reference spectrum recorded by the same instrument. When using such a reference several problems occur:

As described in chapter 4 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.

Figure 5.8:

6 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.

6.1 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 the plume spectrum. So we won't be able to get an BrO Error which is smaller than the "Same Time Error".

6.1.1 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 a reference in temporal proximity.

Figure 6.1 shows the instrumental drift as a function of time, to create fig. 6.1 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

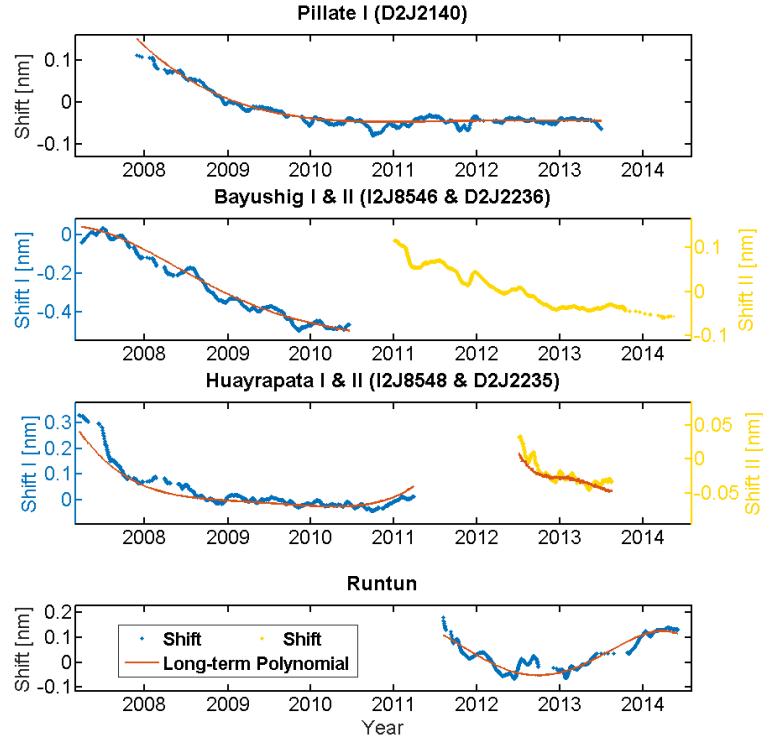


Figure 6.1:

difference.

In fig. 6.3 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, where 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.

6.1.2 Temperature

The instrument design of the NOVAC instruments compromise between accuracy and longevity as explained in chapter 4. In particular there are no internal thermal stabilizations installed as an attempt to reduce the need for power. This can influence the recorded spectra.

Each pixel of the spectrometer, which is used for the DOAS experiment, collects photons of a certain wavelength range.

The calibration for the wavelength to pixel mapping (WMP) is commonly done with a Mercury lamp or by the comparison with the high defined Kuruz spectrum. As the WMP depends on the optical alignment of the spectrometer, which itself depends on the temperature, it is not constant. Changes in the spectrometers temperature can cause changes in the instrument line function and shifts in the WMP (Pinardi et al. [2007]). Moreover, Warnach [2015] show that, short term shifts are related to the instrument temperature (see Figure 6.4).

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. 6.5. 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 $3.53 \cdot 10^{12}$ per degree.

$$\begin{aligned} \rightarrow BrO_{Error} &= f(ext.P) + 3.53 \cdot 10^{12} \cdot \frac{\Delta T}{1C^\circ} + \mathcal{O}() && Tungurahua \\ \rightarrow BrO_{Error} &= f(ext.P) + 7.56 \cdot 10^{12} \cdot \frac{\Delta T}{1C^\circ} + \mathcal{O}() && NevadoDelRuiz \end{aligned}$$

between monitoring the plume
and reference region

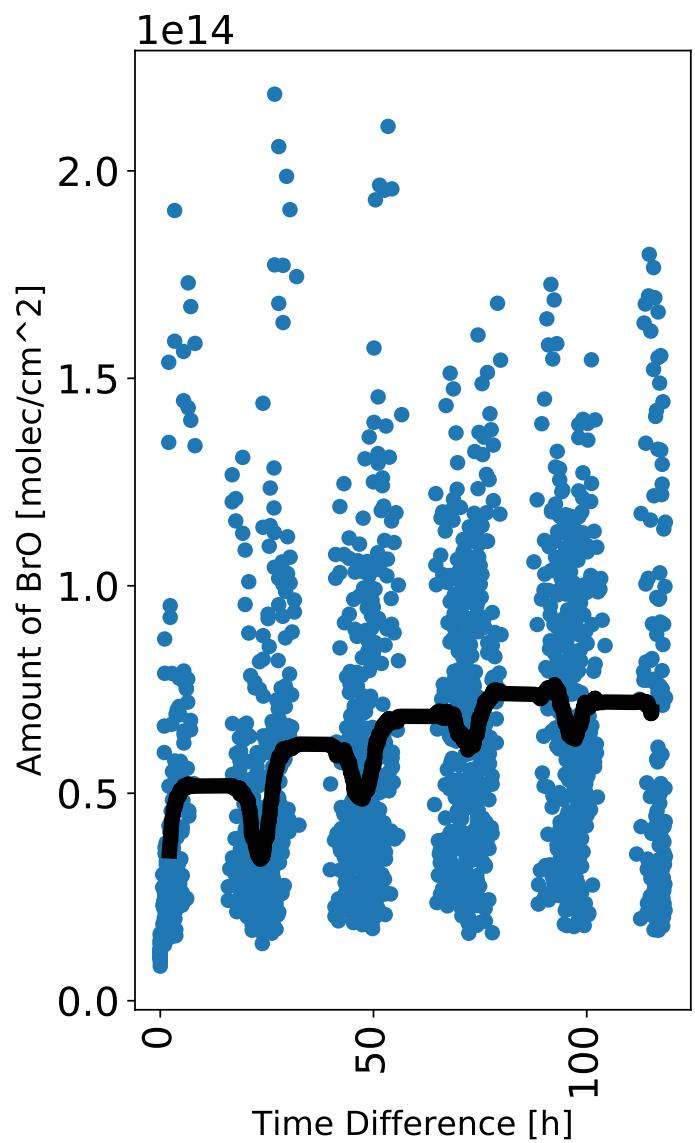


Figure 6.2:

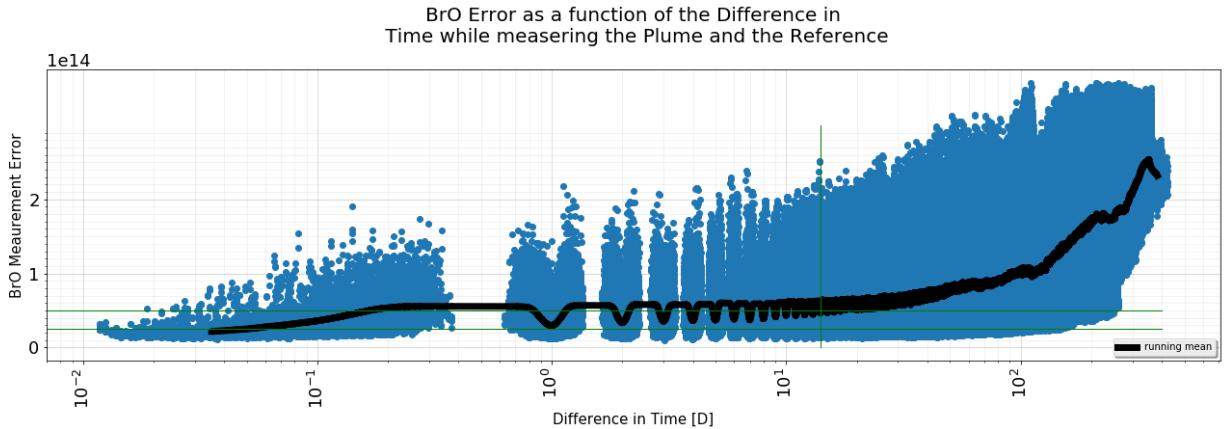


Figure 6.3:

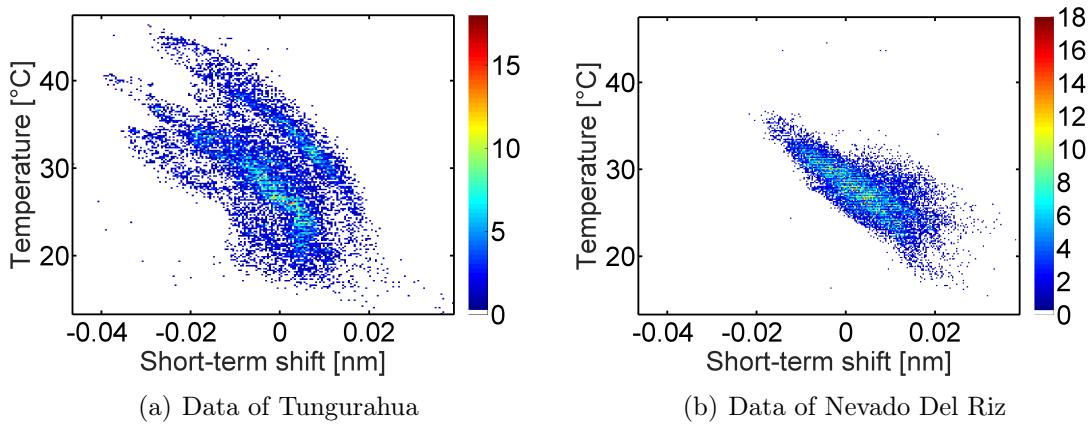


Figure 6.4: Titel unterm gesamten Bild

6.1.3 Daytime

During the day a 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 6.6 shows the dependency of the BrO error on the daytime. The data are calculated as 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

- 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:

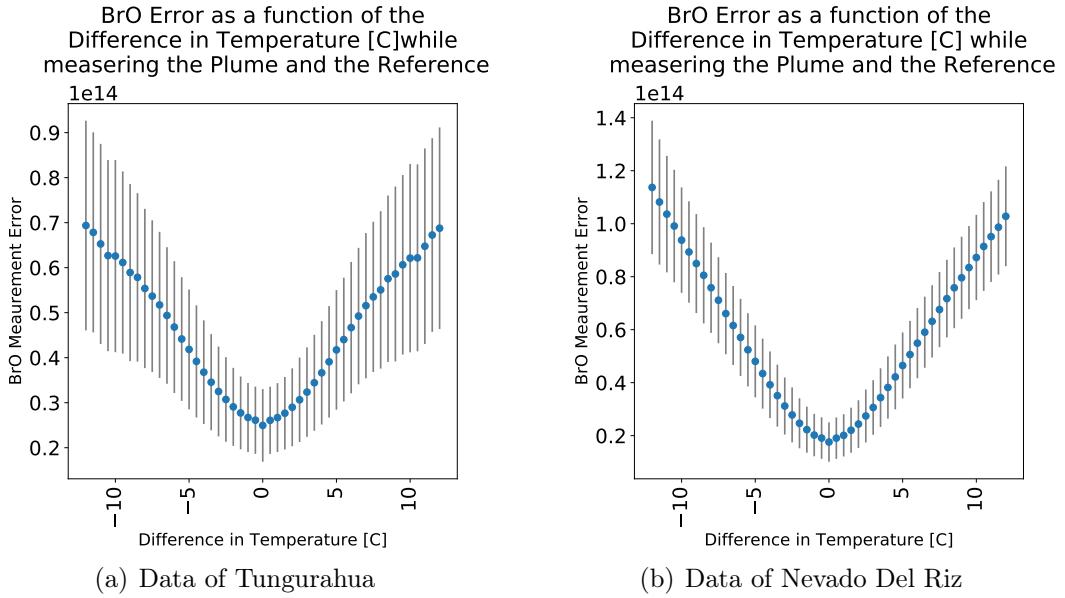


Figure 6.5: The BrO Measurement Error as a function of the difference of temperature between measuring the reference and the plume are shown. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. A increase of the BrO Error with the distance in temperature is observable.

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

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

6.1.4 Colorindex

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. As Mie scattering is dominant in clouds the wavelength of the light that is scattered is different than the Rayleigh sky. Thus, clouds can be easily identified by their white color. Therefore, the cloudiness of the sky can be quantified in a scalar measure defined by the ratio of the measured intensity at two wavelengths, the so-called colour index. Wagner et al. [2014] showed that for a zenith-looking instrument the measured radiation intensity is enhanced by clouds. Thus, clouds can cause large errors for the retrieved gas column density and the corresponding uncertainties. Cloud effects are especially severe if the cloudiness for the recorded plume and

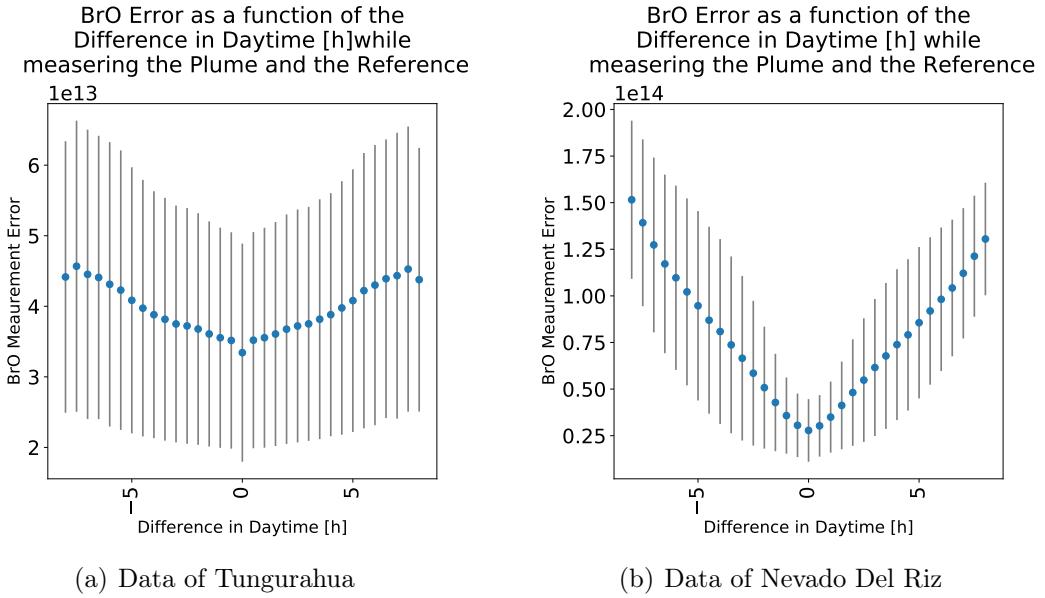


Figure 6.6: The BrO Measurement Error as a function of the difference of the day time between measuring the reference and the plume are shown. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. A increase of the BrO Error with the distance in day time is observable.

reference spectra strongly defer. Also for broken clouds the described effect can be observed as measurements at some elevation angles might be influenced by clouds while others are not. In this work the Colour Index (CI) is the ratio between the intensities at 320nm and 360 nm. These two wavelengths 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. The Mie scattering in the clouds is responsible for the higher amount of radiation from larger wavelengths. This results in a decrease of the CI ([Lübcke \[2014\]](#)).

We evaluated the CI at the zenith, to increase the stability of the fit we added in each cases 10 intensities. 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. 6.7)

- The BrO Error increases with the Colorindex differences as

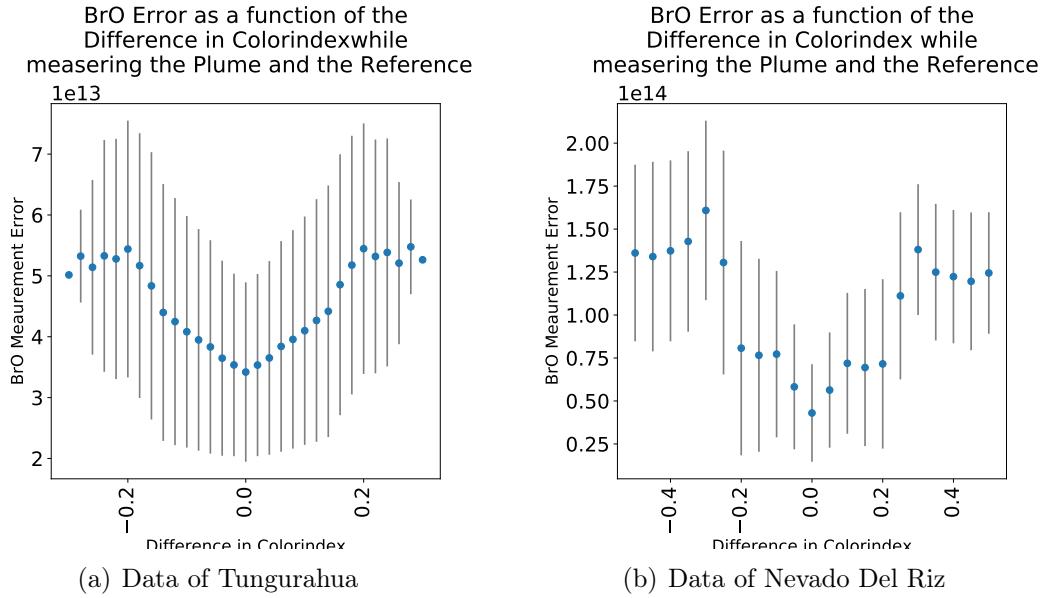


Figure 6.7: The BrO Measurement Error as a function of the difference of colorindex between measuring the reference and the plume are shown. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. A increase of the BrO Error with the distance in colorindex is observably.

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

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

6.1.5 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.

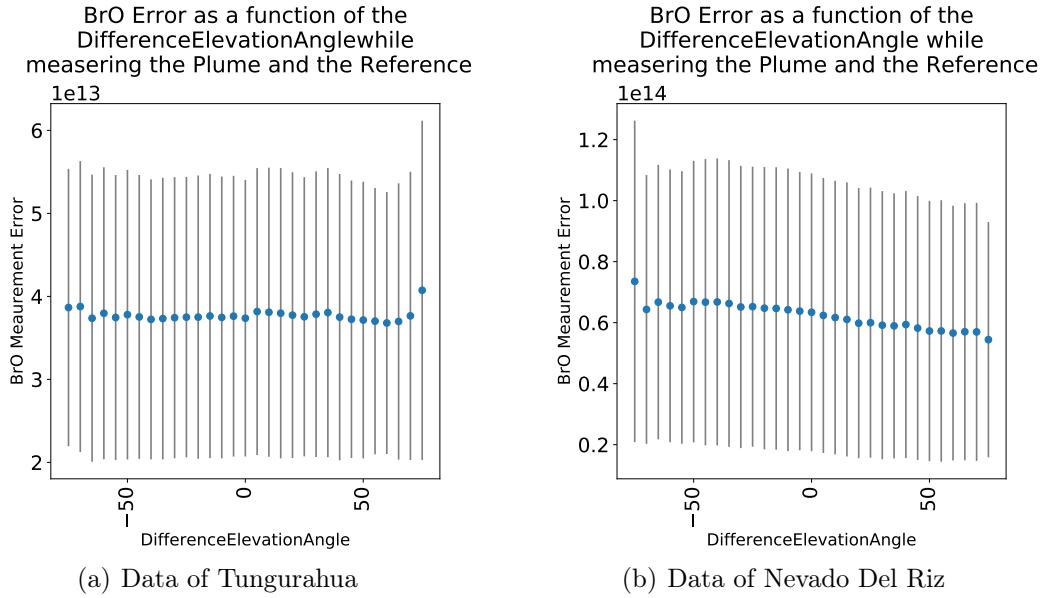


Figure 6.8: The BrO Measurement Error as a function of the Elevation Angle. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. We can't see any significant correlation.

6.1.6 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 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 a small dependency of the BrO error on the Exposure time at Tungurahua and Nevado Del Ruiz as it is shown in fig. 6.9

- The BrO Error increases with the exposure time differences as

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

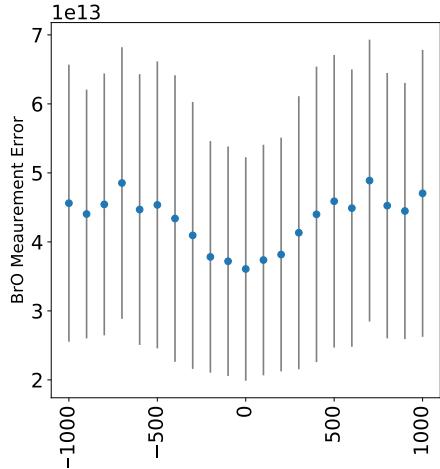
$$\rightarrow BrO_{Error} = f(ext.P) + 1.0 \cdot 10^{13} \cdot \frac{\Delta T}{10^{-2}s} + \mathcal{O}() \quad NevadoDelRuiz$$

Dependency of external parameters on each other

Difference of Temperature on Difference of Exposure Time

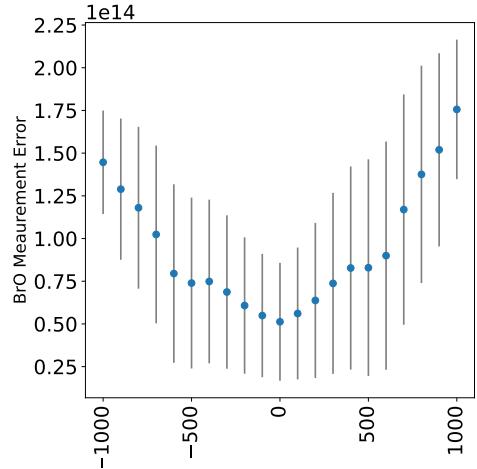
$$\Delta T = -26.32 \cdot \Delta ExpTime + 2 \cdot 10^{-15} \quad (6.1)$$

BrO Error as a function of the Difference in Exposure Time [ms] while measuring the Plume and the Reference



(a) Data of Tungurahua

BrO Error as a function of the Difference in Exposure Time [ms] while measuring the Plume and the Reference



(b) Data of Nevado Del Riz

Figure 6.9: The BrO Measurement Error as a function of the difference of exposure time between measuring the reference and the plume are shown. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. A increase of the BrO Error with the distance in exposure time is observably.

Figure 6.10:

Difference of Temperature on Difference of colorindex

$$\Delta T = 0.0022 \cdot \Delta ColIdX + 2 \cdot 10^{-19} \quad (6.2)$$

Difference of Temperature on Difference of Day time

$$\Delta T = 0.262 \cdot \Delta daytime - 4 \cdot 10^{-17} \quad (6.3)$$

Difference of Temperature on Difference of Elevation angle

$$\Delta T = 1.08 \cdot \Delta ElevAngle - 1 \cdot 10^{-16} \quad (6.4)$$

Difference of Exposure on Difference of Col Idx

$$\Delta Exposure = -6.22 \cdot 10^{-5} \Delta ColIdX + 1 \cdot 10^{-18} \quad (6.5)$$

Difference of Exposure on Difference of Day time

$$\Delta Exposure = -0.004 \cdot \Delta daytime - 1 \cdot 10^{-17} \quad (6.6)$$

Difference of Exposure on Difference ofElevation angle

$$\Delta Exposure = -0.047 \cdot \Delta ElevAngle + 3 \cdot 10^{-16} \quad (6.7)$$

Difference of Colorindex on Difference of Day time

$$\Delta ColIdX = 4.51 \cdot \Delta daytime - 1.2 \cdot 10^{-15} \quad (6.8)$$

Difference of Colorindex on Difference of Elevation angle

$$\Delta ColIdX = -52 \cdot \Delta ElevAngle + 1.45 \cdot 10^{-14} \quad (6.9)$$

Difference of Colorindex on Difference of Elevation angle

$$\Delta ColIdX = 3.5 \cdot \Delta ElevAngle - 6 \cdot 10^{-16} \quad (6.10)$$

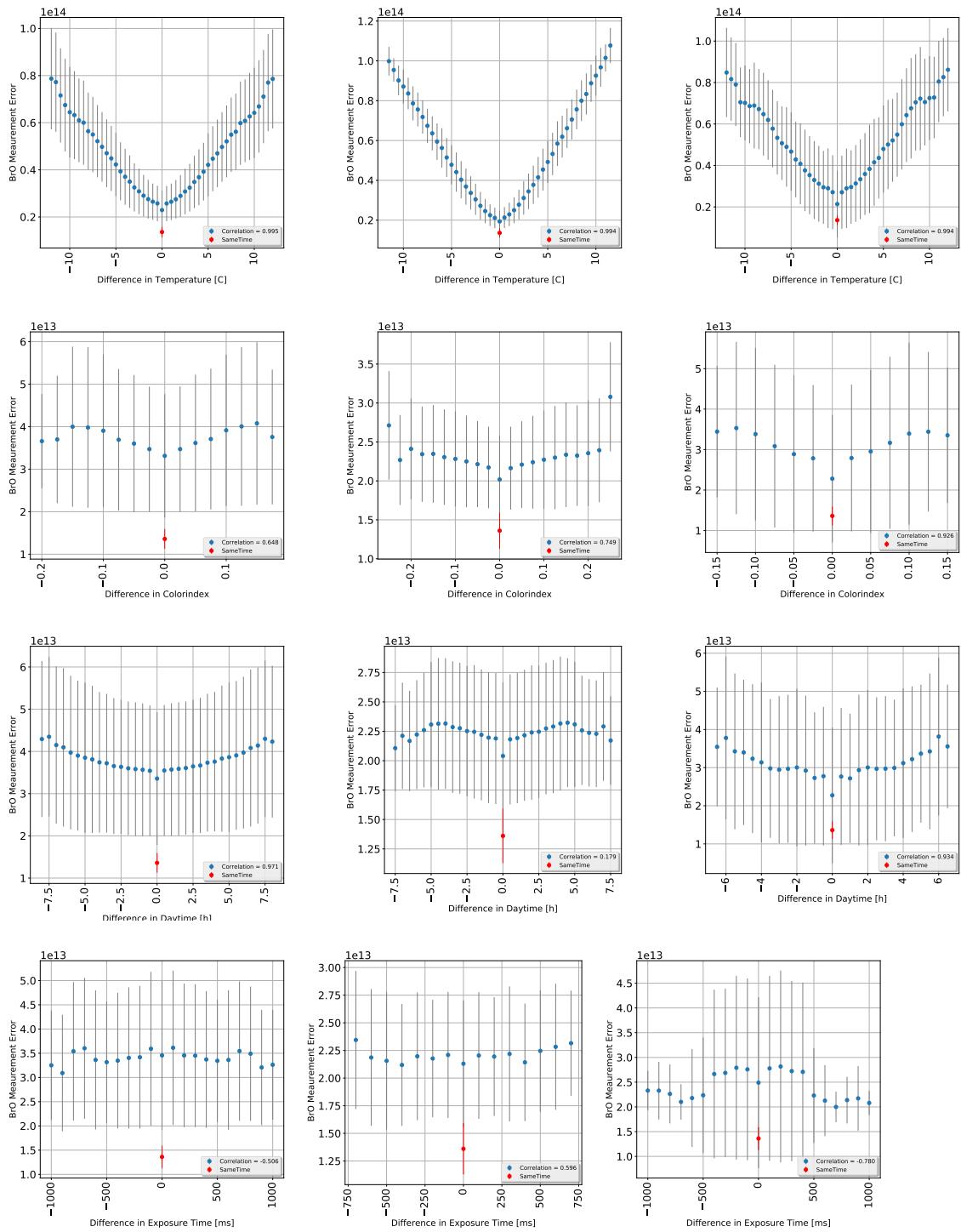
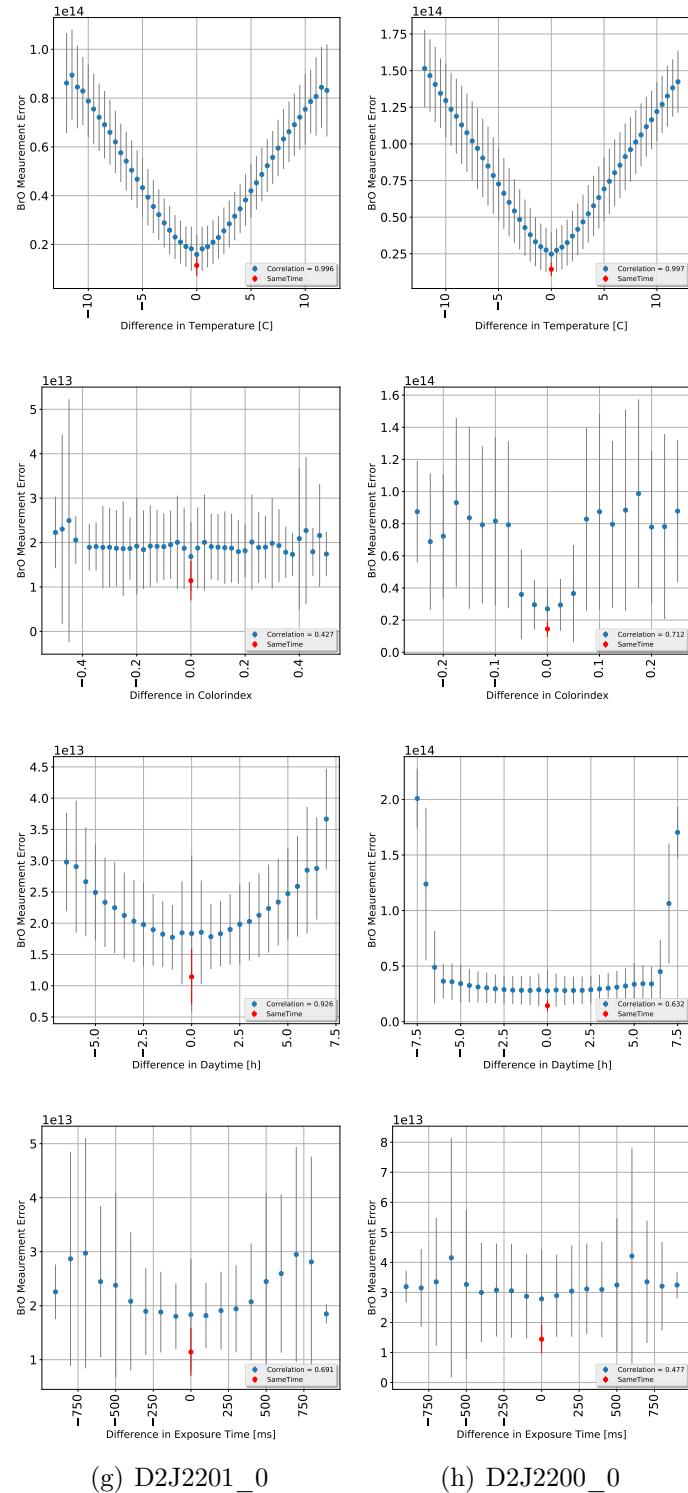


Figure 6.11: DiffExpTime at Tungurahua

Figure 6.12: BrO Error as a function of the external while measering the Plume and the Reference at Nevado del ruiz



7 Method

Based on the findings about the influence of external parameters on the BrO error we developed an algorithm which is able to pick an appropriate volcanic-trace-gas free reference.

The first step is, to evaluate every reference with solar atlas spectrum, to check for contamination. A Spectrum is treated as contaminated if the SO₂ column density of the reference (evaluated with a solar atlas spectrum) is larger as $2 \cdot 10^{17} \frac{\text{molec}}{\text{cm}^2}$.

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 analysis 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.

The assumption is, that the BrO error ϵ_{BrO} can be described as the sum of ϵ_0 and the deviation of ϵ_{BrO} with respect to all external parameters. ϵ_0 is the BrO error when evalute the plume spectrum with the "same-time-reference", it is determined due to the accurateness of the NOVAC-instruments.

$$\epsilon_{BrO} = \epsilon_0 + \frac{d\epsilon}{dt} + \frac{d\epsilon}{d^\circ} + \frac{d\epsilon}{dT} + \frac{d\epsilon}{ddt} + \frac{d\epsilon}{dc} + \mathcal{O}(OE) \quad (7.1)$$

$$\rightarrow \Delta\epsilon_{BrO} = \epsilon_{BrO} - \epsilon_0 = \frac{d\epsilon}{dt} + \frac{d\epsilon}{d^\circ} + \frac{d\epsilon}{dT} + \frac{d\epsilon}{ddt} + \frac{d\epsilon}{dc} + \mathcal{O}(OP) \quad (7.2)$$

With ϵ_{BrO} describes the BrO Error, t: time between plume time and referencetime, T, temperaure; dt: daytime, c: colorindex, OP: other excluded external parameters
The task occurring at this stage is to find the best representation for the deviations.
An then find the reference which minimize $\Delta\epsilon_{BrO}$

The easiest way is to just calculate the BrO error of all possible references for every plume. Using this method we would be able to just choose the reference where the BrO error is minimal. But this takes to much time since the evaluation would be proportional to the number of possible references because the evaluation need to be

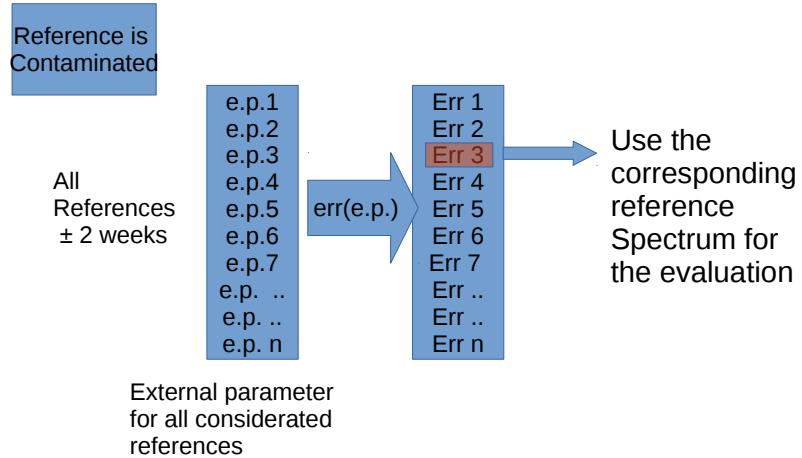


Figure 7.1:

done for every plume-reference pair. Doing the evaluation for every plume-reference pair would make it impossible to do the evaluation in real, or near real time. But we use this optimal evaluation to rate our model and compare them among each other. The optimal evaluation always choose the reference with the smallest absolute error. We don't use the relative error due to his vulnerability. Using the relative error could lead to a less precision.

Hier ein Bild, das eine Plume gegen viele referenzen auswertet und hier die Abweichungen zeigt

The results of the algorithm which chooses the reference automatically are described relative to an optimal evaluation. If the relative error is larger than 5 we don't use the data.

We tried several methods for choosing the best reference based on the analysis of external parameters. Fitting the data with a first order polynomial brought the best results.

7.1 Fit data

When looking at the analysis of the external parameters (see fig. 6.5-6.9) we can observe curves which are symmetric to the zero position. Therefore we conclude that it makes no difference whether the difference of a specific external parameter is positiv or negativ. Thus we take the absolute values for our calculations.

If we assume that all differentiations are linear, than we can write eq. (7.2) as:

$$\Delta\epsilon_{BrO} = a_t \cdot \Delta t + a^\circ \cdot \Delta^\circ + a_T \cdot \Delta T + a_{dt} \cdot \Delta dt + a_c \cdot \Delta c + \mathcal{O}(OP) \quad (7.3)$$

We used the same data as in fig. 6.5-6.9 to get the coefficients a_x of eq. (7.3). We used on ordinary least square linear regression to get the coefficients a_x . In particular we used the python function `LinearRegression` from the library `sklearn SKI`.

In section 6.1 the dependency of the BrO error on external parameters are discussed. The question occurring here is, which parameters should we use for the algorithm which choose the reference automatic? To answer this question for the fitting routine we evaluated data of Tungurahua and Nevado Del Ruiz with different combinations of the external parameter described in section 6.1. Since we could not observe any correlation between the BrO Error and the Elevation angle the external parameter elevation angle was neglected in this analysis. To rate the results for the single instruments (three at Tungurahua and two at Nevado Del Ruiz) the difference to the "optimal evaluation" (explained in ??) was used. Hereby the factor x, a quantity which describes the distinction between the optimal-Method and the contamination based method serves as indicator:

$$X = \frac{1}{n} \sum_k^n \frac{EContBased_k}{EOpt_k} \quad (7.4)$$

n is the total amount of contaminated spectra, $EOpt$ is the BrO error, in the optimal-evaluation, $EContBased$ is the BrO error, in the contamination based-evaluation. Figure 7.2 shows the calculations of the x factor for the Tungurahua and the Nevado Del Ruiz volcano. The x-axis shows the external parameter used for the factor X. The y-axis shows the added factors x for every instrument at the volcanoes. The x factors were weighted with the percentage amount of data. We can see, that for both volcanoes the x factor is minimal for the combination of the following external parameters:

- *Temperature* • *Daytime* • *Exposure Time* • *Temporal Difference* The factors X change from instrument to instrument. The results for every instrument can be seen in the appendix (fig. .1). The factors X range from xxxxxxxx to xxxxxxxxxxxxx.

The constants for Tungurahua and Nevado Del Ruiz are:

- Plume data are reliable if the SO₂ column density is larger as $7 \cdot 10^{17} \frac{molec}{cm^2}$
- Data are above the detection limit if the column density as two times larger than the fit error.
- If the reference is contaminated:

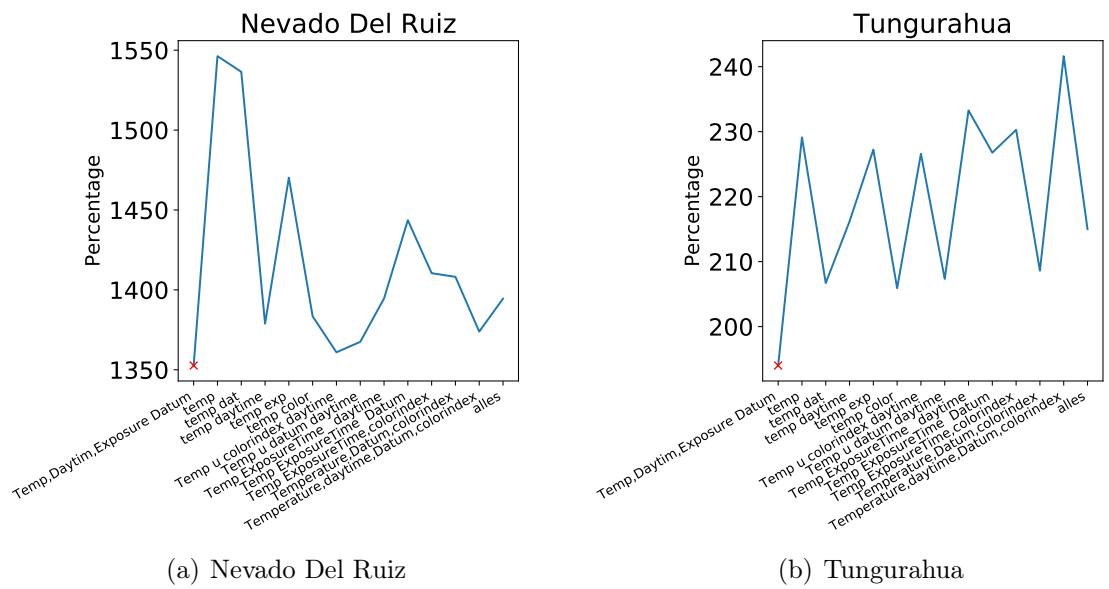


Figure 7.2:

Figure 7.3:

Figure 7.4:

(a) Data of Nevado Del Riz D2J2201_0		
Constant	value	importance
a_T	7.338e+12	0.840
a_{ET}	1.545e+10	0.045
a_t	-2.6e+09	0.0
a_{dt}	1.805e+12	0.091
a_c	2.301e+13	0.031

(b) Data of Nevado Del Riz D2J2200_0		
Constant	value	importance
a_T	1.162e+13	0.908
a_{ET}	2.811e+10	0.046
a_t	-1.7e+09	0.0
a_{dt}	1.076e+12	0.034
a_c	3.587e+13	0.016

(c) Data of Nevado Del Both Instruments		
Constant	value	importance
a_T	1.073e+13	0.973
a_{ET}	3.478e+10	0.070
a_t	-9.1e+08	0.0
a_{dt}	1.523e+11	0.006
a_c	-6.811e+13	-0.047

Table 7.1: (a)Data from Nevado Del Ruiz from the D2J2201_0 instrument. All external parameter where taken into account. $\epsilon_0 = 5.404e+12$ (b)Data from Nevado Del Ruiz from the D2J2200_0 instrument. All external parameter where taken into account. $\epsilon_0 = 1.105e+13$ (c) Data from Nevado Del Ruiz from both instrument. All external parameter where taken into account. $\epsilon_0 = 1.260e+13$

		Error	Amount of Data	valid data
All Variables	independent	1.51	95%	10,5%
	dependent	1.40	98%	8%
Exposure Time	independent	1.47	97%	10%
	All	1.39	98%	7%
Exp.Time u Coloridx	independent	1.40	98%	11
	All	1.35	98%	7%

Evaluation of all contaminated data from Nevado Del Ruiz

Instrument	Dev from opt eval. (mean/median)	valid data
D2J2201_0	1.14 / 0.82293	128/283 = 45.2%
D2J2200_0	1.5 / 0.89965	954/1109 = 86.0%
Both	1.26/0.847	1073/1392 = 77.1%

Table 7.2: Data from Nevado Del Ruiz from the D2J2201_0 instrument. All external parameter where taken into account. $\epsilon_0 == 5.404e + 12$

7.2 Other approaches

- In the optimal results are 15% valid data
- 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.

7.2.1 Nearest neighbours

- Description of the Nearest Neighbours Method

Nearest neighbor search (NNS), as a form of proximity search, is the optimization problem of finding the point in a given set that is closest (or most similar) to a given point. Closeness is typically expressed in terms of a dissimilarity function: the less similar the objects, the larger the function values. Formally, the nearest-neighbor (NN) search problem is defined as follows: given a set S of points in a space M and a query point $q \in M$, find the closest point in S to q. Donald Knuth in vol. 3 of *The Art of Computer Programming* (1973) called it the post-office problem, referring to an application of assigning to a residence the nearest post office. A direct generalization of this problem is a k-NN search, where we need to find the k closest points. Most

commonly M is a metric space and dissimilarity is expressed as a distance metric, which is symmetric and satisfies the triangle inequality. Even more common, M is taken to be the d -dimensional vector space where dissimilarity is measured using the Euclidean distance, Manhattan distance or other distance metric. However, the dissimilarity function can be arbitrary. One example are asymmetric Bregman divergences, for which the triangle inequality does not hold.

7.2.2 Iterative

- Description of the iterative Method

The idea of the iterative method was, that the importance of the individual external parameters are very different, that means if we have the list of possible references, we took all references where the temperature difference is minimal, so we get a new, much smaller list of possible references. From this list we choose all references where the next external parameter for example the daytime is minimal and get again a new list. We proceed this way with the following external parameters. We experiment with the sequence of the parameters, to increase the success of the method. The final sequence was:

Temperature •

8 Comparison with NOVAC Evaluation

This chapter shows and discuss the difference of the BrO, SO₂ and BrO/SO₂ 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.

The following external parameter where used for the evaluation:

- Temperature
- Daytime
- Colorindex
- check das noch mal

To obtain the reference with minimal expected BrO error the calculation of eq. (7.3) and the corresponding coefficients from table 7.1 were used. The maximal temporal difference between measuring the reference and the plume is two weeks. Figure 8.1 shows a comparison of the data when evaluating with the NOVAC-method and the contamination based method. The x axis shows the column density calculated with NOVAC-method, the y axis shows the column density calculated the the contamination based method. Only data are used where the corresponding SO₂ column density lies above the plume limit ($SO_2_SCD > 7 \cdot 10^{17}$). Meaning the column densities evaluated with the contamination based method. The corresponding SO₂ SCD's evaluated with NOVAC could be below $7 \cdot 10^{17}$. The plots at the left side show the results from the Tungurahua volcano while the plots at the right side 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. The BrO data are visualized in the plots at the top of fig. 8.1.

Beschreibung

In the middle of fig. 8.1 are the results of SO₂ visualized:

Beschreibung

The BrO/SO₂ ratio is visualized at the bottom of fig. 8.1:

Beschreibung

Another interesting question is, whether the change in the gas column density respectively the ratio depends on the amount evaluated with the NOVAC-method. To check this dependency ?? was plotted. The data used for this figure are the same as for fig. 8.1.

- 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
- Amount of BrO data more than before (valid and not valid and above detection limit)
- Amount of SO₂ data more than before (valid and not valid and above detection limit)
- Amount of BrO/SO₂ data more than before (valid and not valid and above detection limit)
- More BrO data: 51%
- More valid BrO data: 38%
- Compare the daily means: how many more data? due to higher S02 values
-

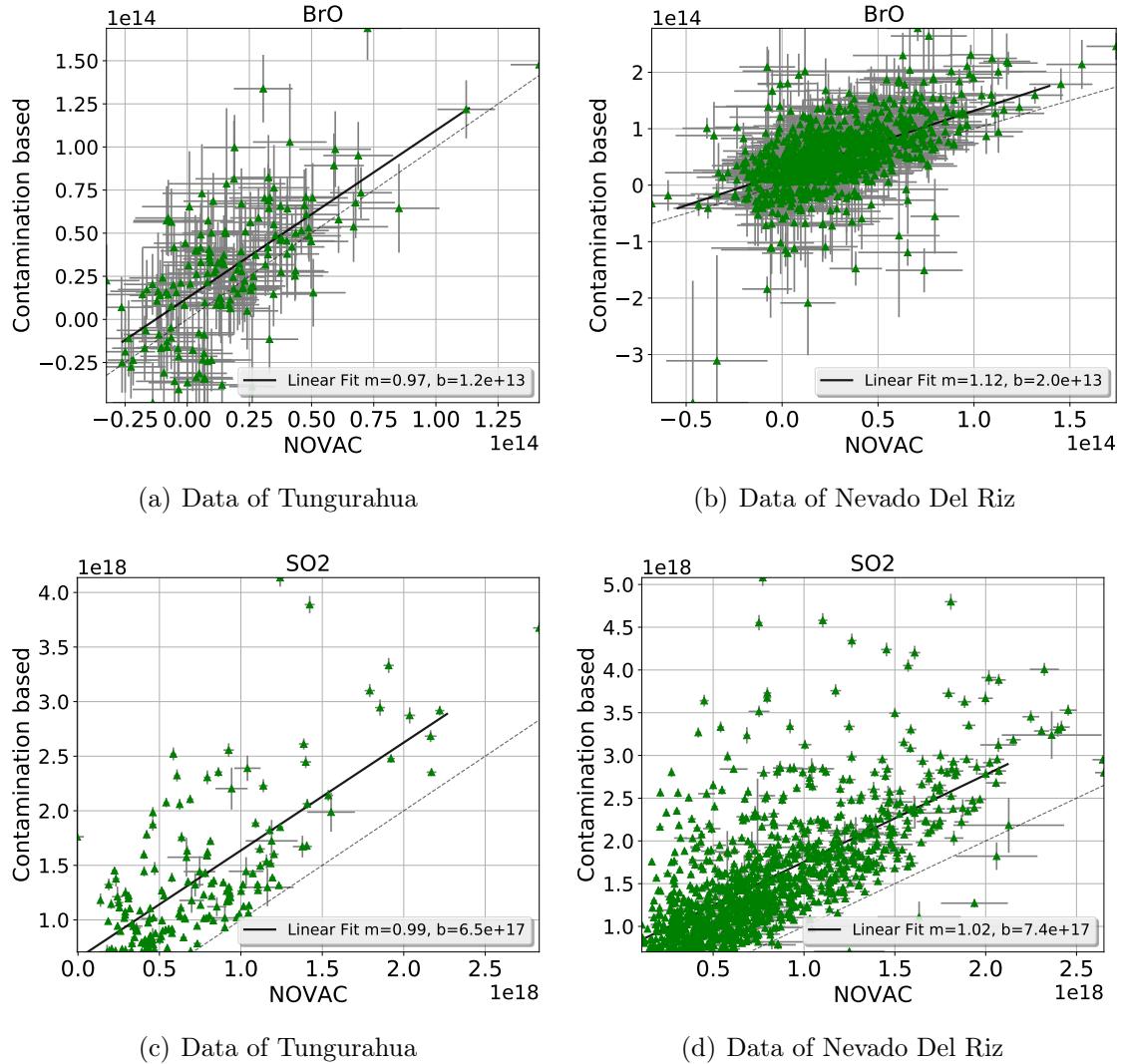
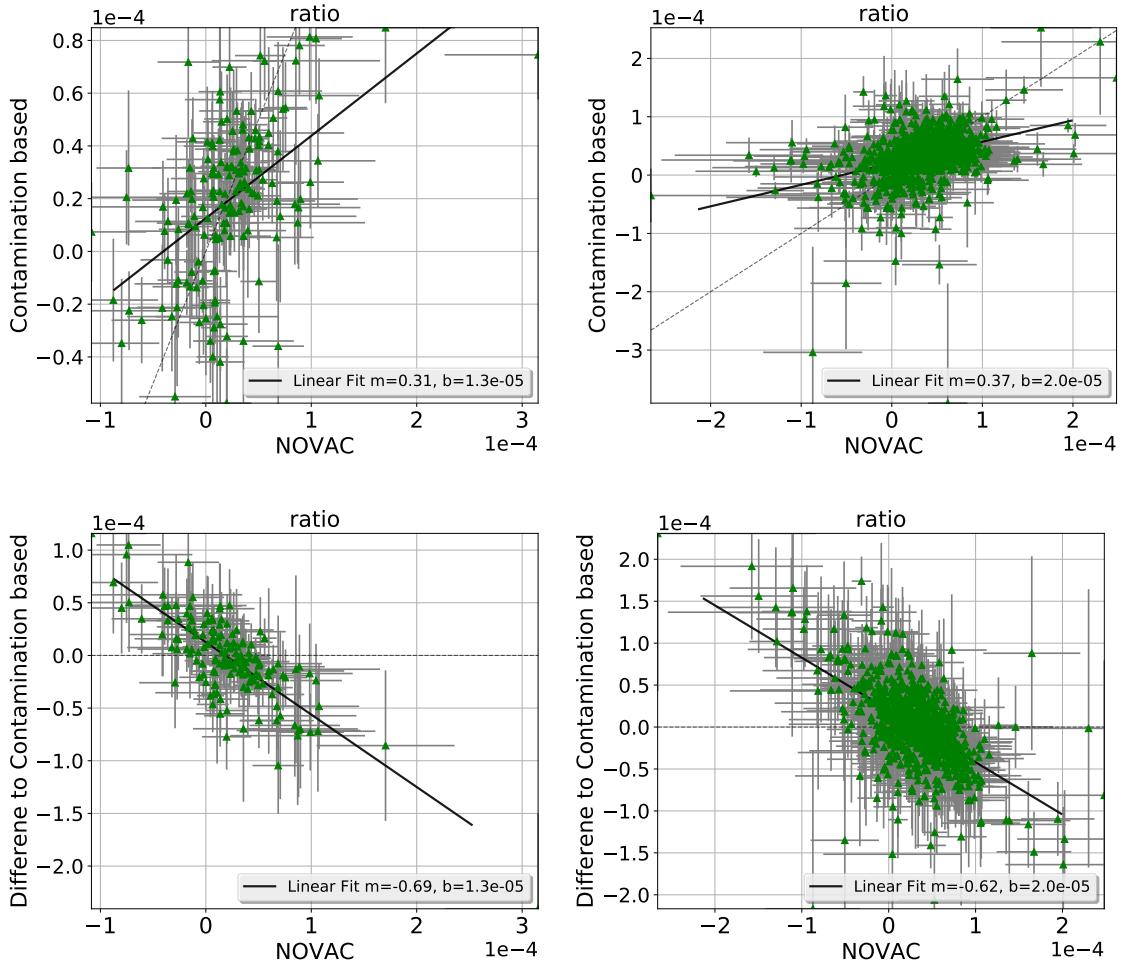


Figure 8.1: The dependency of the Difference between contamination based data and NOVAC to the data evaluated with the NOVAC data



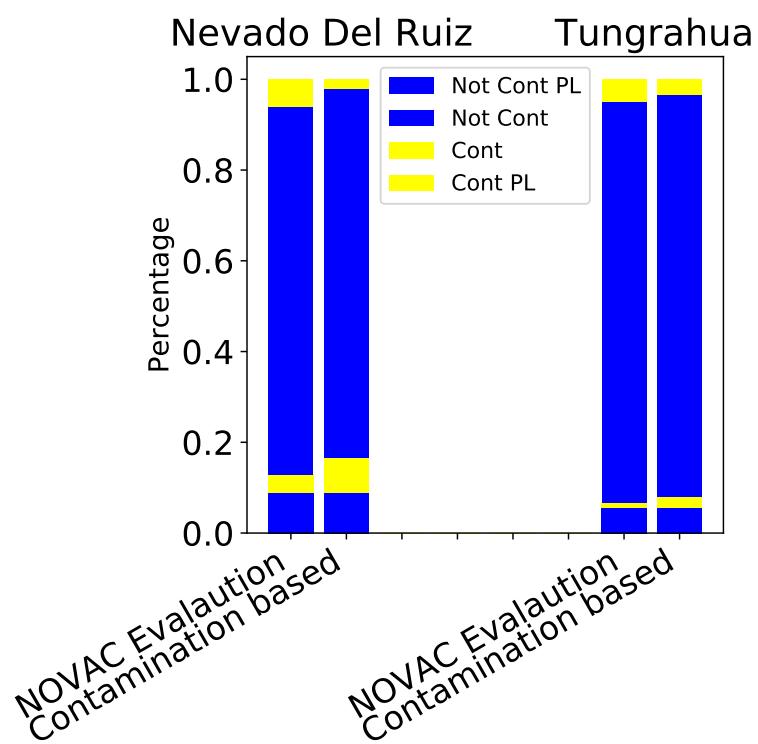


Figure 8.2:

9 Results

Interpretation of the BrO/SO₂ ratio time-series

9.1 Tungurahua

<i>Menge an Daten insgesamt :</i>	5883	≡	1
<i>Davon : (NOVAC Auswertung) berplume limit</i>	712	≡	0.121
<i>Davon : Menge an Daten, die nicht kontaminiert sind :</i>	5504	≡	0.936
<i>Davon im Plume – limit :</i>	599	≡	0.102
<i>Davon über dem Detection Limit :</i>	36	≡	0.006
<i>Davon sind kontaminiert :</i>	379	≡	0.064
<i>Davon (mit NOVAC ausgewertet) berplume limit :</i>	114	≡	0.301
<i>Davon (Neue Auswertung) berplume limit</i>	185	≡	0.488

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

9.2 Nevado Del Ruiz

<i>Menge an Daten insgesamt :</i>	8962	≡	1
<i>Davon : (NOVAC Auswertung) berplume limit</i>	142	≡	0.016
<i>Davon : nicht kontaminierte daten :</i>	8596	≡	0.959
<i>Davon im Plume – limit :</i>	123	≡	0.014
<i>Davon über dem Detection Limit :</i>	53	≡	0.006
<i>Davon sind kontaminiert :</i>	366	≡	0.041
<i>Davon (mit NOVAC ausgewertet) berplume limit :</i>	20	≡	0.055
<i>Davon (Neue Auswertung) berplume limit</i>	179	≡	0.489

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

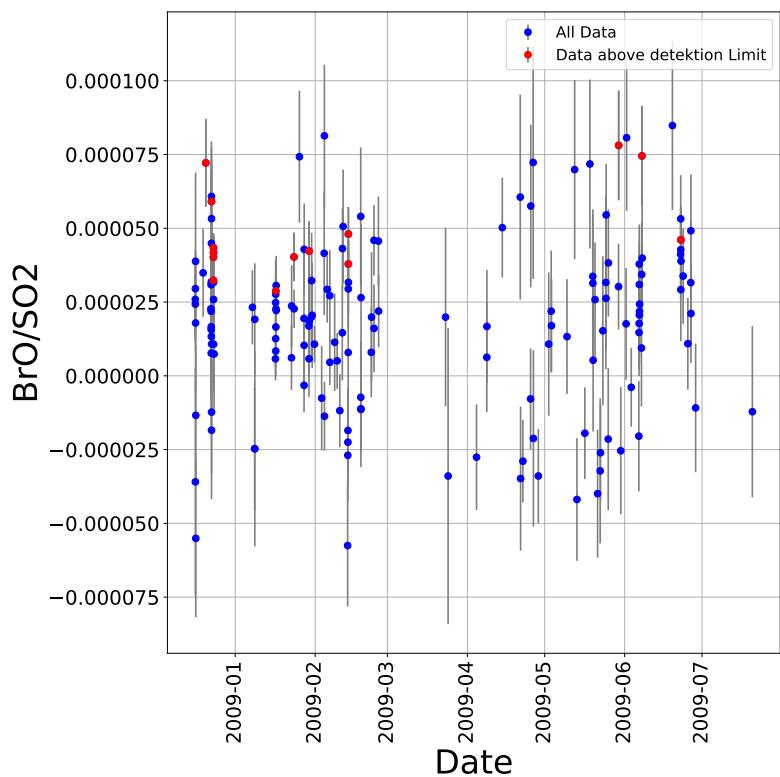


Figure 9.1:

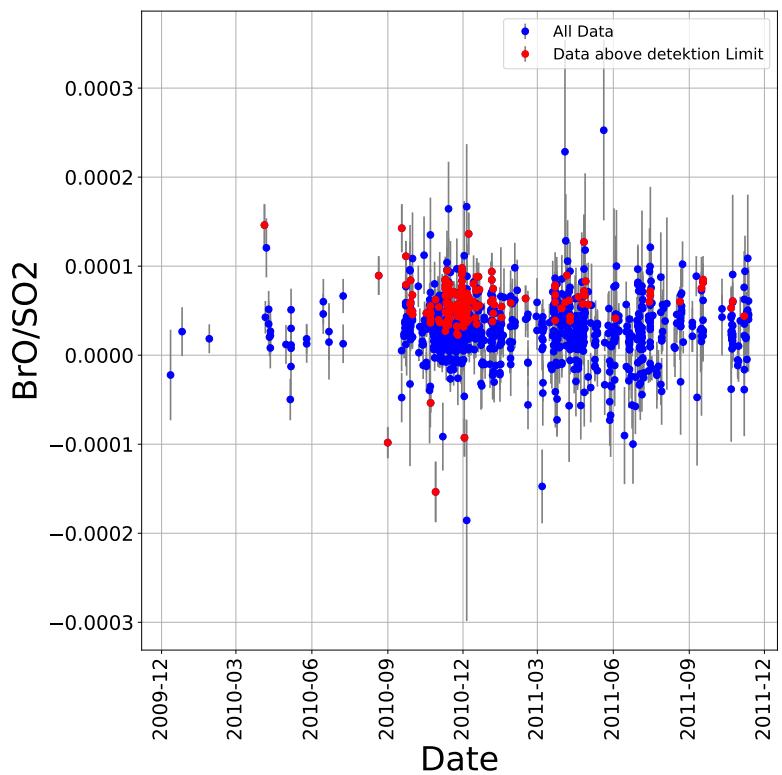


Figure 9.2:

10 Issues of our method

The presented method

10.1 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.

11 Conclusion

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Part III

Appendix

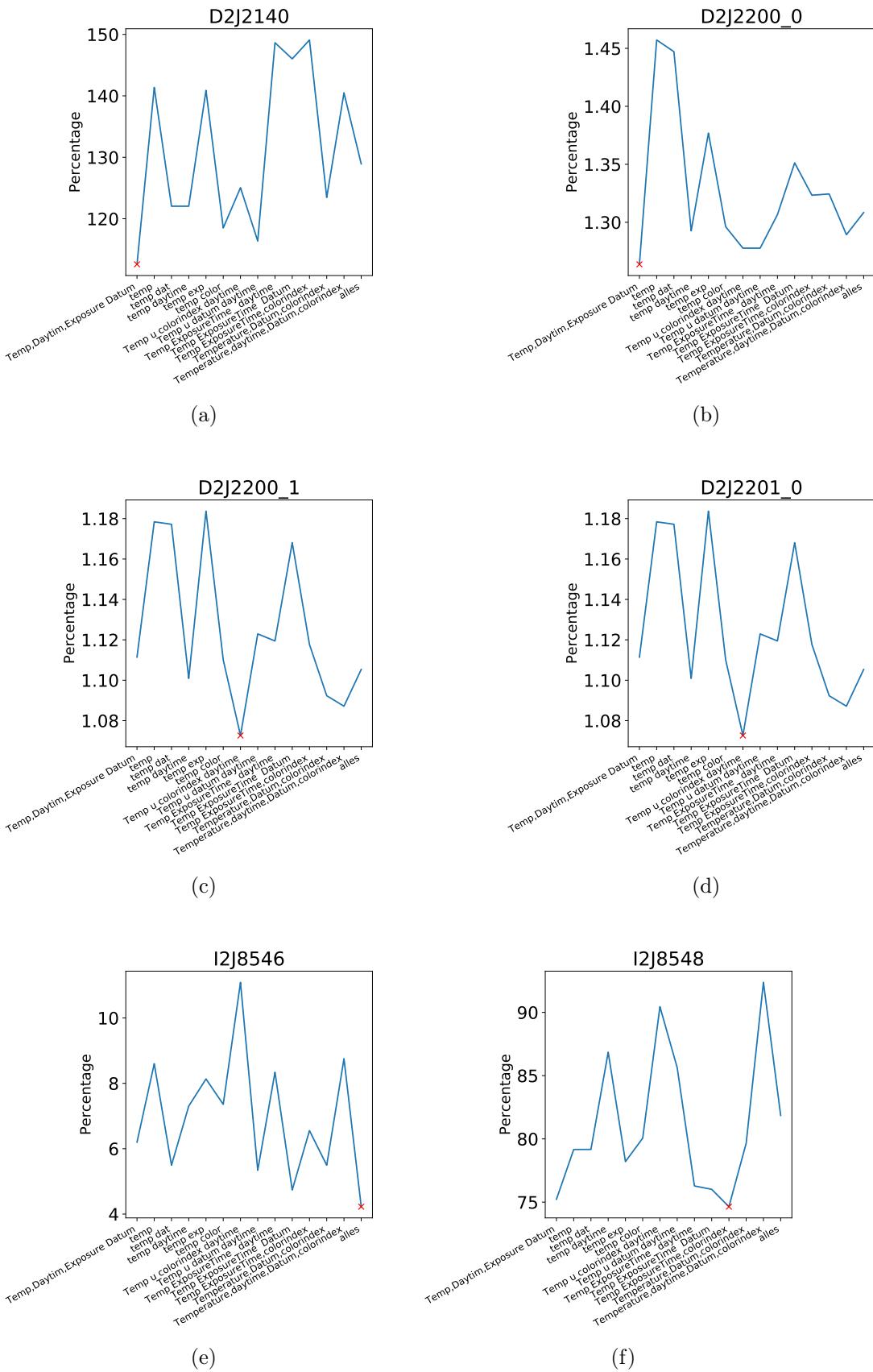


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Erklärung:

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

Heidelberg, den (Datum)