Retrieval Advances of BrO/SO2 Molar Ratios from NOVAC

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Optimierte Bestimmung des Molaren BrO/SO_2 Verhältnisses aus NOVAC Daten

Die Messung der absoluten Menge und des Verhältnisses von Vulkanischen gas Emissionen geben Einsicht in magmatische Prozesse. Das Network for Observation of Volcanic and Atmospheric Change (NOVAC) verfügt über ein System an automatisierten UV-Spektrometern, welche die Gas Emissionen der Vulkane aufzeichnen. Der Ausstoß von BrO und SO_2 kann mithilfe von Differenzieller optischer Absorptionsspektroskopie (DOAS) aus den aufgenommen Spekren bestimmt werden wobei die optische Absorption in der Fahne mit einem Hintergrundspektrum verglichen wird. Dies setzt voraus, dass das Hintergrund Spektrum nicht durch Vulkanische Gase beeinträchtigt ist. Typischerweise wird das Hintergrund Spektrum für einen Scan ein Höhenwinkel gewählt welcher als außerhalb der Fahne liegend identifiziert wird. Es hat sich jedoch gezeigt, dass auch diese Spektren noch durch Vulkanische Emissionen verunreinigt sein können. Als alternative Referenzspektren könnten 1) ein theoretisches Solar Atlas Spektrum oder 2) ein nicht verunreinigtes referenz Spektrum des selben Messgeräts dienen. Option 1) hat den Nachteil einer verringerten Messgenauigkeit, da Instrumenteneffekte hier modelliert werden müssen. Option 2) setzt vorraus, dass das Referenzspektrum unter ähnlichen Wetter- und Strahlungsbedingungen aufgenommen wurde. Wir verwenden die erste Methode um Kontaminierung zu identifizieren und greifen für die Bestimmung der Gas Konzentration auf die zweite Methode zurück um eine hohe fit Qualität sicher zu stellen. Stellen unsere Methode für NOVAC Daten von den Vulkanen Tungurahua und Nevado Del Ruiz vor.

Retrieval advances of BrO/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 an elevation angle which has been identified to be outside of the volcanic plume. However, experience shows those background spectra can still be contaminated by volcanic gases. Alternatively reference spectra can be derived from 1) a theoretical solar atlas spectrum or 2) a volcanic-gas-free reference spectrum recorded by the same instrument. 1) comes with a drawback of reduced precision, as the instrumental effects have to be modeled and added to the retrieval. For 2), the alternative reference spectrum should be recorded at similar conditions with respect to meteorology and radiation. We use the first option to check for contamination and the second to evaluate the spectra to maintain a god fit quality. We present our approach and its results when applied on NOVAC data from Tungurahua and Nevado Del Ruiz.

Contents

6 BrO evaluation and its limitations

This chapter discusses the evaluation of the BrO Column densities, calculated from the spectra recorded by the spectroscopic instruments of NOVAC. The quality of the BrO retrieval hereby is defined by the BrO retrieval error.
Figure 6.1 shows the BrO "Multi Add" retrieval error distribution, which is centered around $1.1e^{13}$ to $1.4e^{13}$. The instruments of Nevado del Ruiz are coloured blue, while the the instruments of Tungurahua are coloured in yellow to red.

The evaluation of the data from NOVAC are parted into the evaluation of SO_2 and the evaluation of BrO. While the retrieving of SO_2 is relatively easy due to the high amount of SO_2 in the plume (magnitude of SO_2 at Tungurahua $\approx 1e^{18}$), the BrO evaluation is much more problematic (as it can be seen in Figure 5.1). The magnitude of BrO SCD is around $\approx 1e^{14}$.
This results in a larger uncertainty of the BrO SCD. Most of the BrO data (98.3% of the data) are below the detection limit of $BrO_{err}/BrO_{value} < 1/4$. In comparison SCD's of SO_2 in almost all cases (99.5% of the data) are above the detection limit. Choosing a different reference than the reference measured at the same time as the plume in 99% of the cases results in an increasing of the absolute error. Thus a BrO error which is smaller than the "Same Time Error" is often not possible to retrieve. However, for a contaminated same-time-reference the relative error might decrease due to the underestimation of the gas amount.
Due to the large uncertainty of BrO relative to SO_2 the optimization of the BrO error is of particular importance. Therefore, the reference is chosen with respect to the BrO error to maximize the quality of the BrO/SO_2 ratio.

The amount of gas free alternative references is around 1500 per year. To make an optimal choice, it is necessary to examine the conditions which influence the BrO retrieval.
Every spectrum is measured under certain conditions. These measuring conditions generally are not equal for the plume and the reference. References for which the surrounding conditions e.g temperature or cloudiness are equivalent with the surrounding conditions of the plume measuring lead to a small error.
In the following, we take a closer look at the dependence of the BrO error on external parameters.

Data used for the analysis

For this analysis, every plume reference pair of the observed time span is used. Thus 1000 recorded "multi add" spectra result in 1000^2 possible plume reference pairs and

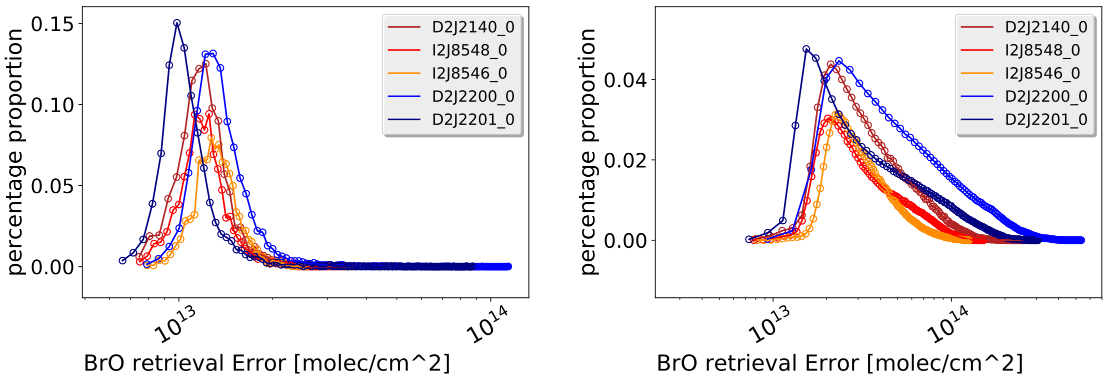


Figure 6.1: BrO error distribution shown for all instruments considered in this thesis. The left plot shows the BrO distribution for the "same time retrieval", the left plot shows the BrO error distribution for the evaluation with a reference from another time, where the temporal difference between plume and reference is not longer that two weeks. The peaks for the single instrument are located at: D2J2140: 1.2e+13; I2J8548: 1.3e+13$\frac{molec}{cm^2}$; I2J8546: 1.4e+13$\frac{molec}{cm^2}$; D2J2200: 1.4e+13$\frac{molec}{cm^2}$; D2J2201: 1.1e+13$\frac{molec}{cm^2}$

the corresponding differences in the external parameter and their associated BrO error.

6.1 BrO error dependence on external parameters

The measurement and evaluation of the spectra monitored with NOVAC depends on the surrounding conditions like temperature or cloudiness (Lübcke, 2014) Thus, the surrounding conditions need to be taken into account for choosing a new reference.

The better the surrounding conditions for the reference coincide with the conditions for the plume measurement, the lower is the BrO error.

The surrounding conditions that are considered in this thesis are:

- Temporal difference between measuring the plume and the reference.
- Temperature,
- Colorindex,
- Exposure time,
- Elevation angle,
- Daytime

The analysis of these external parameters are performed for spectra recorded at Tungurahua and Nevado del Ruiz. At Tungurahua three instruments with data recorded in the time span from July in 2008 to August in 2009 are used. Nevado del Ruiz contributes with two instruments in the time from the end of 2009 to the end of 2011.

6.1.1 Temporal difference

Due to instrument drifts the fit quality decreases with the time difference between recording the plume and the reference. This could be a result of a wavelength shift over time observed by Warnach (2015). As a result of the observed wavelength shift, the instrument function of the plume, does not match with the instrument function of the reference, thus the retrieving errors increase. Warnach (2015) suggests that the drift is caused by a hysteresis effect. Figure 6.2 shows the wavelength shift as a function of the time for six NOVAC instruments located at Tungurahua in the time between 2008 to 2014. In this thesis for the analysis data of Tungurahua between 2008 to the mid of 2009 are used. Figure 6.2 shows a rather steep drift in this time interval. Warnach (2015) observed a decrease of the shift after initial negative drift after the first two years at Pillate. Thus, it is observed that the temporal difference becomes less important for old instruments.
When using reference and plume spectra of the same time, these effects are cut out since the shift is equal for the plume and reference spectrum. For an increasing temporal different between reference and plume measurement time the fit quality decreases and so does the BrO error.
To examine the effect of the temporal difference on the retrieved BrO error, for all reference-plume pairs the corresponding BrO error is calculated. Due to the large amount of reference plume pairs within one year, it takes more than a month (Hardware details: Intel(R) Core(TM) i5-4570 CPU @ 3.20Ghz 64 Bit operating system, amount of kernels: 4) to evaluate the corresponding BrO error for every possible reference-plume pair of one instrument. We did this for the D2J2140 instrument installed at Tungurahua:
In Figure 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 plotted with a black line.
In Figure 6.3 (a) it can be seen that a large temporal difference results in an increase of the BrO error of up to 600%. BrO errors of such magnitudes are too large for our purposes. Therefore, it is useful to set a maximal temporal difference, to prevent too large BrO error and to reduce the calculation time. In Figure 6.3 (a) it can be seen that the evolution of the BrO error with the temporal difference is symmetric around zero. Thus it is not necessary to distinguish between positive or negative temporal differences. Figure 6.3 (b) shows the evolution of the BrO error for a maximal absolute temporal difference of 120 hours. It is only possible to record data during daytime. This causes the lack of data in the night time. A periodic decrease of the BrO error can be seen. This is a result of a decrease of the BrO

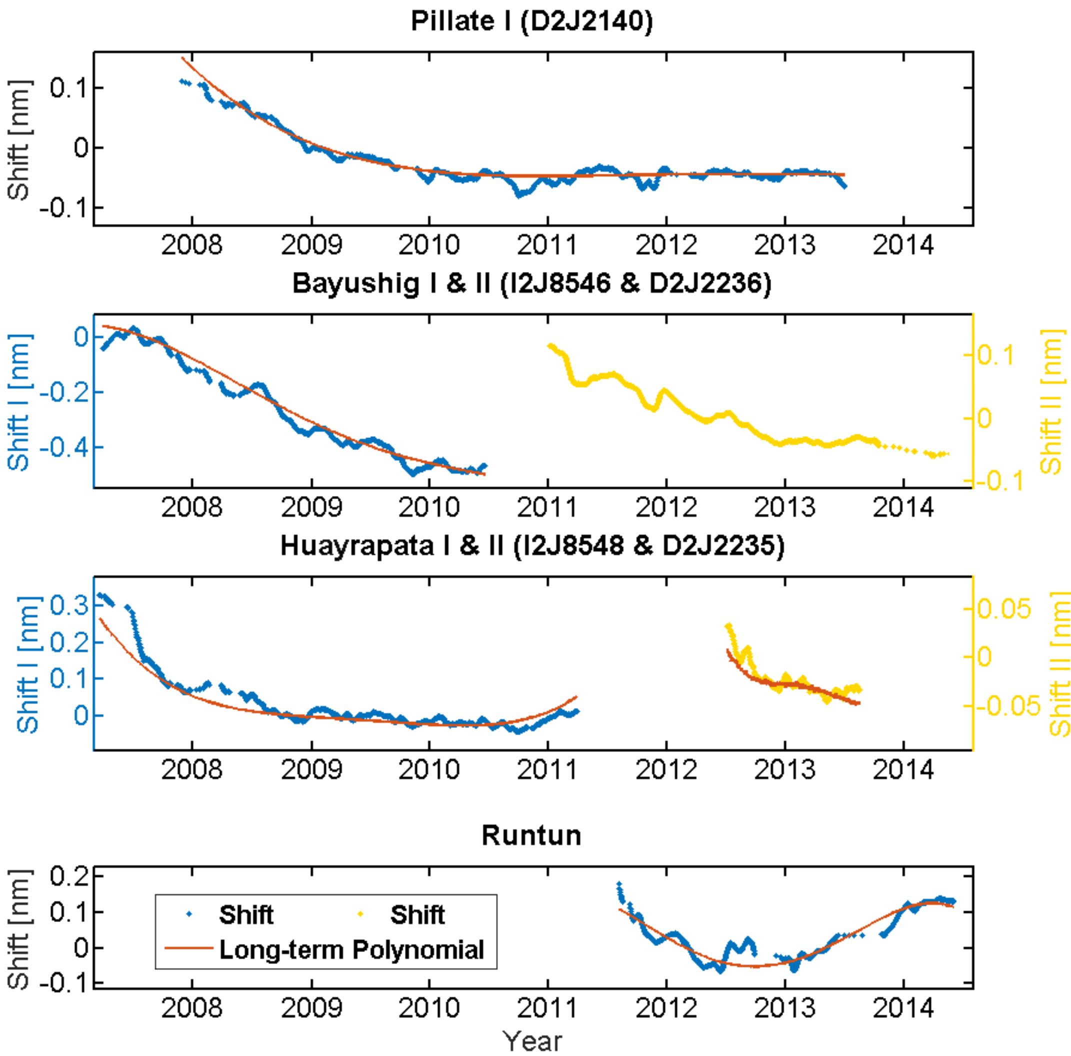
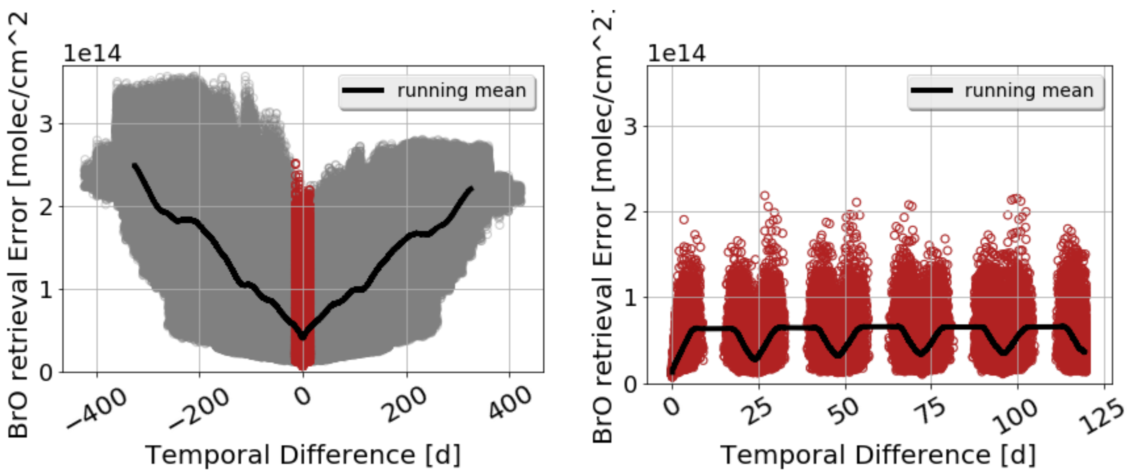


Figure 6.2: Wavelength shift over the time. The shift is shown for six NOVAC- instruments from Tungurahua. The red and yellow dots show the running mean over 20 days. Red line indicates a temperature independent long term polynomial. Source: Warnach (2015)



(a) (b)

Figure 6.3: The BrO error as a function of the temporal difference shown for the Pillate instrument from Tungurahua (2008-2009). (a) Temporal differences up to 400 days. (b) Temporal differences up to 120h. The periodical BrO error evolution indicates the impact of the daytime

error when the surrounding conditions coincidence. In this case the daytime coincidence causes the BrO error decrease. This effect is analysed in detail in Section 6.1.3.

The maximal temporal difference should be large enough to ensure a sufficient amount of references to be able to pick a reference with similar conditions. However, the maximal temporal difference should be small enough to prevent too large BrO errors due to long term shifts.

To evaluate the maximal time difference, for which we still get reliable results for every plume, where the "same time reference" is contaminated, the alternative reference is chosen, which leads to the minimal BrO error.
In Figure 6.4 a histogram with the probability of picking the best reference as a function of the time difference is plotted. Obviously, the best results are achieved, if the day of measuring the plume is the same day as measuring the reference. A Gaussian fit is used to fit the data of the histogram We allow all time differences within two sigma area. Thus, the maximal time difference is 14 days
By restricting the temporal difference to 14 days, the amount of possible gas free references decreases to an average of 195 alternative references per contaminated plume (see table 6.1). Hereby every plume has potential alternative reference spectra. The minimum amount of references is 8.
If a continuously evaluation is required, this means the spectra are evaluated directly after the recording, the number of suitable gas free references halves since only references recorded before the plume are available.

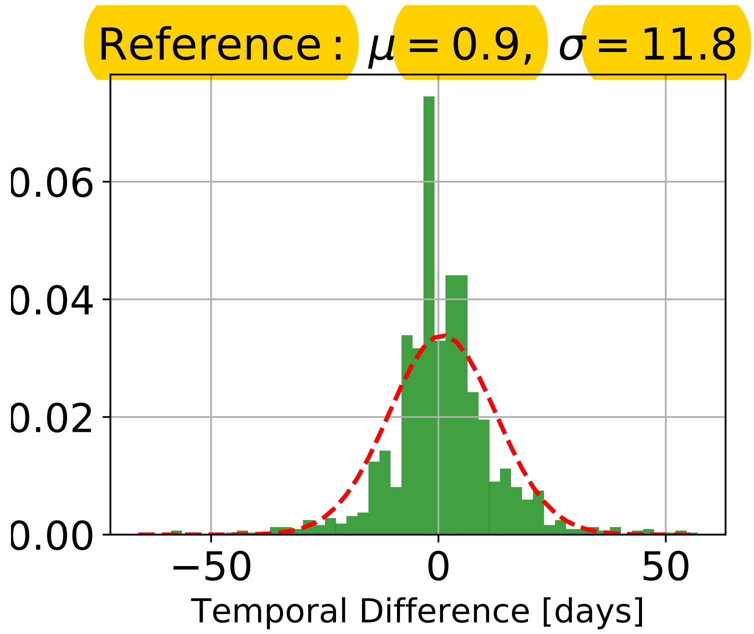


Figure 6.4: Histogram showing the frequency of getting the best reference as function of the temporal difference between plume and reference measuring. A Gaussian-like distribution is retrieved. The red dotted line visualizes a Gaussian fit for the shown histogram.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Mean	84.6	163.7	217.1	284.0	225.6
Std	35.8	29.9	64.8	69.5	41.2
Min	8	113	97	64	63
Max	169	214	399	433	297

Table 6.1: Amount of possible references when restricting the time span between plume and reference to two weeks. Here in the ”Mean” and “Std” row for each instrument the average restriction is shown with the corresponding standard deviation. The “Min” and “Max” rows show the extend of restriction in the extreme cases (minimum and maximum amount of available references / restriction ratio).

For the following analysis of the remaining external parameters all temporal differences are below 14 days.

6.1.2 Temperature

The instrument design of the NOVAC instruments compromises between accuracy and robustness as explained in Chapter 4. In particular, there are no internal thermal stabilizations installed as an attempt to reduce the instruments power consumption. 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 6.7).
The above discussed temperature dependence of the WMP causes a reduction of the fit quality with increasing instrument temperature difference between plume and reference. Thus, the BrO error also increases with the temperature difference. Compared to the other external parameters the temperate difference has the largest impact on the BrO error.

In Figure 6.6 the BrO error is plotted against the temperature difference between the plume and the reference spectrum. The blue dots show the mean BrO error at the specific temperature difference, the standard deviation is illustrated with gray error bars. The mean BrO deviation for the sametime evaluation is additionally marked with a red point. The plots reveal a symmetry around axis with zero temperature

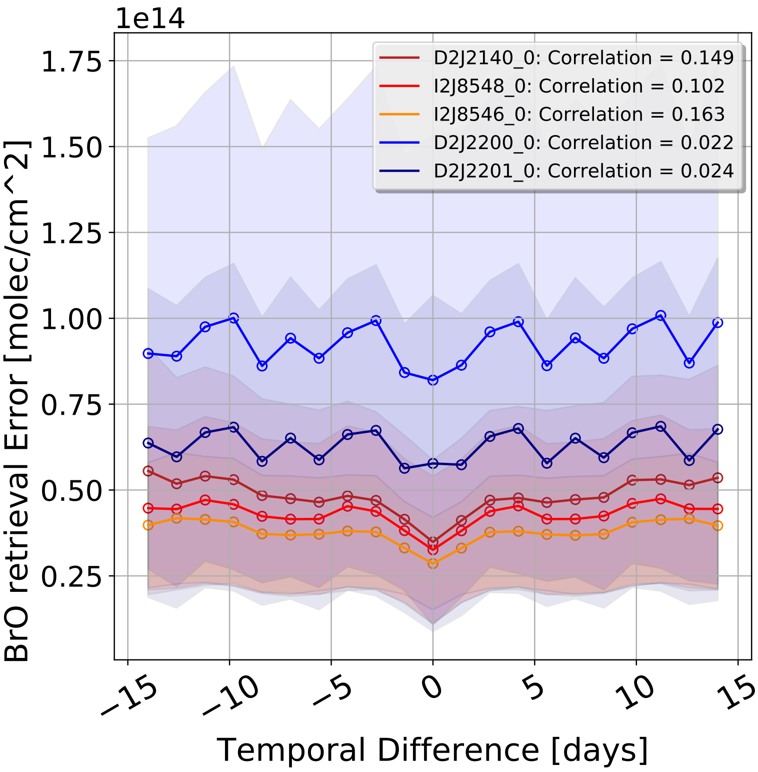


Figure 6.5: The BrO measurement error as a function of the temporal difference in days between the reference and the plume is shown for each of the individual instruments at Tungurahua and Nevado del Ruiz. The instruments at Nevado del Ruiz are coloured in blue, while the instruments at Tungurahua are coloured in red colour tones. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. An increase of the BrO error with the absolute difference in temperature is observable. This is quantified by a correlation between the BrO retrieval error and the absolute temporal difference. The plots reveal a symmetry around the axis with zero temperature difference.

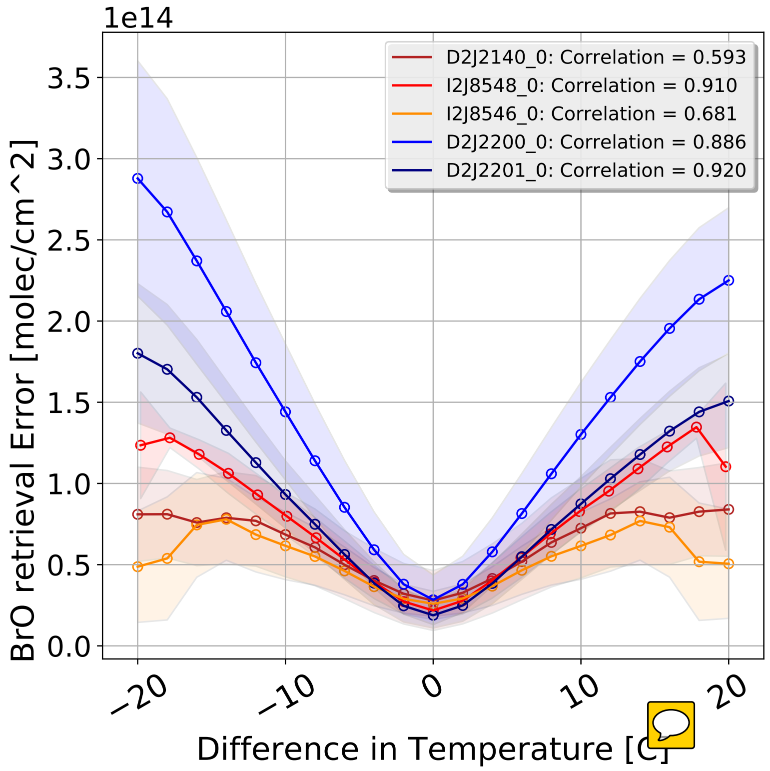
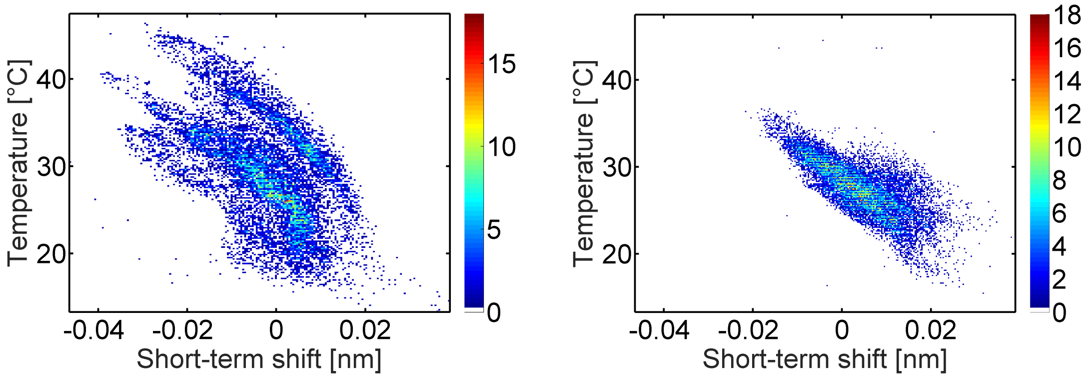


Figure 6.6: The BrO measurement error as a function of the difference of temperature between the reference and the plume is shown for each of the individual instruments at Tungurahua and Nevado del Ruiz. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. An increase of the BrO error with the absolute difference in temperature is observable. This is quantified by a correlation between the BrO retrieval error and the absolute difference in temperature. The plots reveal a symmetry around the axis with zero temperature difference.



(a) (b)

Figure 6.7: Short term wavelength as a function of the instrument temperature for Pillate 1. The coloring of the scatter points indicate the temporal evolvement. (a) initial period prior to January 2010 (b) after 2010. Source: Warnach (2015).

difference. To quantify the dependency between the BrO error and the difference in temperature the data are fitted with a polynom of the first order. Because of the observed symmetry around zero the absolute temperature difference is used for the fit. The computed fitting parameters slope and zero point for each instrument are shown in Section 6.1.2.

The zero points at Tungurahua vary from $1.6 \cdot 10^{13} \frac{molec}{cm^2}$ to $2.58 \cdot 10^{13} \frac{molec}{cm^2}$. The variation at Nevado del Ruiz ranges from $9.07 \cdot 10^{12} \frac{molec}{cm^2}$ to $1.38 \cdot 10^{13} \frac{molec}{cm^2}$.

Also the correlation between the BrO error and the absolute temperature difference is shown. Here the correlation is calculated using the python library Numpy. The correlation ranges from 0.593 for the instrument D2J2140 to 0.92 for D2J2201 and exhibits a large variation between the instruments.

The ΔT_2 row in the table shows the temperature difference for which the error doubles compared to a temperature difference of zero. If restricting the temperature difference to the mean ΔT_2 over all instruments ($Mean(\Delta T_2) = 3.3$) the amount of possible references decrease as shown in Table 6.3. Excluding references with temperature differences above $Mean(\Delta T_2) = 3.3$ restricts the amount of potential references to 46.8% for D2J2140 to 82.3% for D2J2200.

The advantage of restricting the accepted temperature difference is a better control of the choice of the best reference. The disadvantage is that the amount of possible references decreases. Thus, it could occur that a reference is dismissed, which has a large temperature difference but is very similar in the remaining parameters.

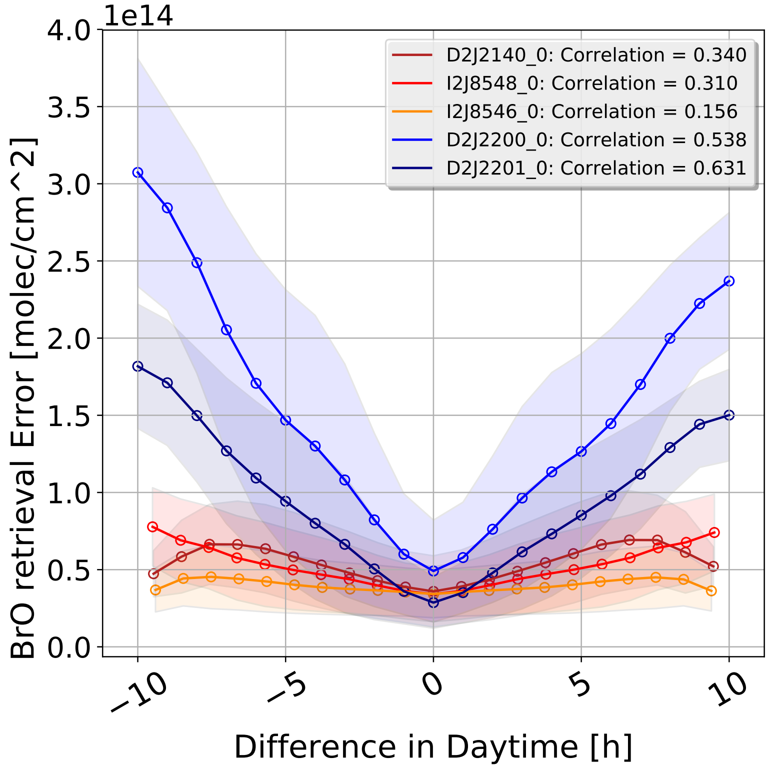


Figure 6.8: The BrO measurement error as a function of the difference of daytime between the reference and the plume is shown for each of the individual instruments at Tungurahua and Nevado del Ruiz. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. An increase of the BrO error with the absolute difference in daytime is observable. This is quantified by a correlation between the BrO retrieval error and the absolute difference in daytime. The plots reveal a symmetry around axis with zero daytime difference.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Slope	4.10e+12	3.93e+12	6.50e+12	1.24e+13	8.17e+12
Correlation	0.593	0.681	0.910	0.886	0.920
Zero point	2.58e+13	2.23e+13	1.60e+13	1.38e+13	9.07e+12
ΔT_2	6.3	5.7	2.5	1.1	1.1

Table 6.2: The BrO measurement error as a function of the difference of temperature between the reference and the plume is fitted with a first order polynomial for each of the individual instruments at Tungurahua and Nevado del Ruiz. This table shows the fitting parameters slope and zero point. Moreover, the correlation between the BrO error and the absolute temperature difference is shown. For the temperature difference this correlation with an average of 0.797 is the highest compared to the other external parameters. In the ΔT_2 row the temperature difference for which the error doubles compared to a temperature difference of zero is shown. This is already the case for a difference of 3.3°C

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 in the morning or evening compared to the noon. Therefore, the scattering effects and the Fraunehofer structures are different for both spectra.

In Figure 6.8 the BrO error is plotted against the daytime difference between the plume and the reference spectrum. The plots are similar to the plots for the temperature: The blue dots show the mean BrO error at the specific daytime difference, the standard deviation is illustrated with gray error bars. The mean BrO deviation for the sametime evaluation is additionally marked with a red point.
As for the temperature the plots reveal a symmetry around the axis of zero daytime difference.
To quantify the dependency between the BrO error and the difference in daytime the data are fitted with a polynom of the first order. Because of the observed symmetry around zero the absolute daytime difference is used for the fit. The computed fitting parameters slope and zero point for each instrument are shown in Section 6.1.3.
As it can be seen in Section 6.1.3, the zero points at Tungurahua vary from $3.28{\cdot}10^{13}\frac{molec}{cm^2}$ to $3.43{\cdot}10^{13}\frac{molec}{cm^2}$. The variation at Nevado del Ruiz ranges from $2.24{\cdot}10^{13}\frac{molec}{cm^2}$ to $4.01{\cdot}10^{13}\frac{molec}{cm^2}$.
The correlations ranges from 0.156 for the instrument I2J8546 to 0.631 for D2J2201 and exhibits a large variation between the instruments.
The ΔDT_2 row in the table shows the daytime difference for which the error doubles

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Mean	39.6/46.8%	119.3/72.9%	158.2/72.9%	233.6/82.3%	151.6/67.2%
Std	24.7/68.9%	50.4/168.6%	76.0/117.2%	84.5/121.6%	72.6/176.2%
Min	1/12.5%	8/7.1%	12/12.4%	3/4.7%	6/9.5%
Max	130 /76.9%	213 /99.5%	386/96.7%	414 /95.6%	296 /99.7%

Table 6.3: This table shows the absolute amount and the ratio (to Table 6.1) of remaining references if restricting the temperature difference to the mean ΔT_2 over all instruments ($Mean(\Delta T_2) = 3.3°C$). Here in the "Mean" and "Std" row for each instrument the average restriction is shown with the corresponding standard deviation. The "Min" and "Max" rows show the extend of restriction in the extreme cases (minimum and maximum amount of available references / restriction ratio).

compared to a daytime difference of zero.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Slope	5.07e+12	1.40e+12	3.77e+12	2.04e+13	1.38e+13
Correlation	0.340	0.156	0.310	0.538	0.631
Zero point	3.43e+13	3.39e+13	3.28e+13	4.01e+13	2.24e+13
ΔDT_2	6.8	24.2	8.7	1.9	1.62

Table 6.4: The BrO measurement error as a function of the difference of daytime between the reference and the plume is fitted with a first order polynomial for each of the individual instruments at Tungurahua and Nevado del Ruiz. This table shows the fitting parameters slope and zero point. Moreover, the correlation between the BrO error and the absolute daytime difference is shown. In the ΔDT_2 row the daytime difference for which the error doubles compared to a daytime difference of zero is shown.

If restricting the daytime difference to the mean ΔT_2 over all instruments with significant impact of the daytime, ($Mean(\Delta DT_2) = 4.75h$) the amount of possible references decrease as shown in Table 6.5.The mean ($Mean(\Delta DT_2)$) is calculated without taking the I2J8546 into account due to the low correlation of 0.156. Using the I2J8546 instrument as well would lead to an $Mean(\Delta DT_2)$ of $8.6h$, thus, the restriction would not have any influence, since the maximal time difference is limited to the time where the sun is shining.
Excluding references with daytime differences above $4.75h$ restricts the amount of potential references to 85.1% for D2J2140 to 96.8% for $D2J2200$. In extreme cases a restriction down to 51.3% of the entire set of references can occur.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Mean	72.0/85.1%	147.4/90.0%	198.4/91.4%	275.0/96.8%	205.8/91.2%
Std	31.87/89.0%	32.0/107.0%	71.0/109.5%	70.8/101.8%	50.1/121.6%
Min	6/75.0%	58/51.3%	91/93.8%	54/84.4%	45/71.4%
Max	160/94.7%	214/100%	399/100%	433/100%	297/100%

Table 6.5: This table shows the absolute amount and the ratio (to Table 6.1) of remaining references if restricting the daytime difference to the mean ΔDT_2 over all instruments except I2J8546 due to the large uncertainty ($Mean(\Delta DT_2) = 4.75h$). Here in the "Mean" and "Std" row for each instrument the average restriction is shown with the corresponding standard deviation. The "Min" and "Max" rows show the extend of restriction in the extreme cases (minimum and maximum amount of available references / restriction ratio).

6.1.4 Colorindex

Clouds have a strong influence on the atmospheric radiative transfer and thus affect the interpretation and analysis of DOAS (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 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 SO_2 and O_3 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 add 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 Figure 6.9)

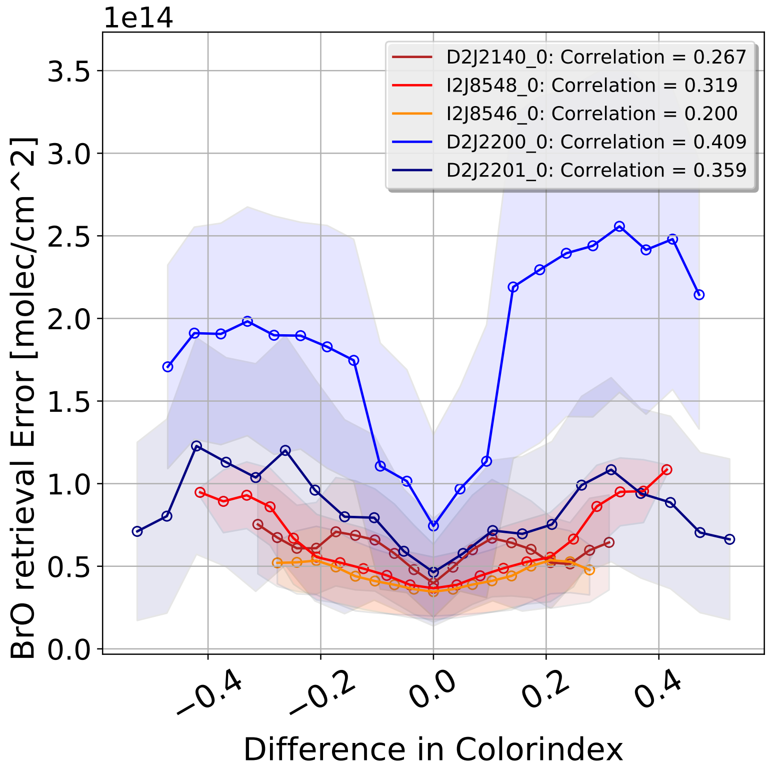


Figure 6.9: The BrO measurement error as a function of the difference of colorindex between the reference and the plume is shown for each of the individual instruments at Tungurahua and Nevado del Ruiz. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. An increase of the BrO error with the absolute difference in colorindex is observable. This is quantified by a correlation between the BrO retrieval error and the absolute difference in colorindex. The plots reveal a symmetry around axis with zero colorindex difference.

In Figure 6.9 the BrO error is plotted against the colorindex difference between the plume and the reference spectrum. The plot is done similar to the plots for the temperature. The plots mostly reveal a symmetry around the zero colorindex difference-axis. Thus, the absolute colorindex can be used for the fitting which is done equivalently to the analysis of the temperature and the daytime. The computed fitting parameters slope and zero point for each instrument are shown in table 6.6. The zero points at Tungurahua vary from $3.36{\cdot}10^{13}\frac{molec}{cm^2}$ to $4.01{\cdot}10^{13}\frac{molec}{cm^2}$. The variation at Nevado del Ruiz ranges from $4.74{\cdot}10^{13}\frac{molec}{cm^2}$ to $7.21{\cdot}10^{13}\frac{molec}{cm^2}$.
The correlation is as well calculated and ranges from 0.2 for the instrument I2J8546 to 0.409 for D2J2200.
The ΔCI_2 row in the table shows the colorindex difference for which the error doubles compared to a colorindex difference of zero.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Slope	2.30e+14	7.92e+13	1.17e+14	5.42e+14	1.91e+14
Correlation	0.267	0.200	0.319	0.409	0.359
Zero point	4.01e+13	3.36e+13	3.47e+13	7.21e+13	4.74e+13
ΔCI_2	0.174	0.424	0.297	0.133	0.248

Table 6.6: The BrO measurement error as a function of the difference of colorindex between the reference and the plume is fitted with a first order polynomial for each of the individual instruments at Tungurahua and Nevado del Ruiz. This table shows the fitting parameters slope and zero point. Moreover, the correlation between the BrO error and the absolute colorindex difference is shown. In the ΔCI_2 row the colorindex difference for which the error doubles compared to a colorindex difference of zero is shown.

If restricting the colorindex difference to the mean $Mean(\Delta CI_2) = 0.255$ over all instruments the amount of possible references decrease very little as can be seen in Table 6.7.

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 location of the plume does not coincidence with the location of the reference.
In fig. 6.10 the BrO error is plotted as a function of the elevation angle. Obviously no significant correlation between the two parameters can be identified. This is not surprising because other than the previously discussed parameters we do not expect

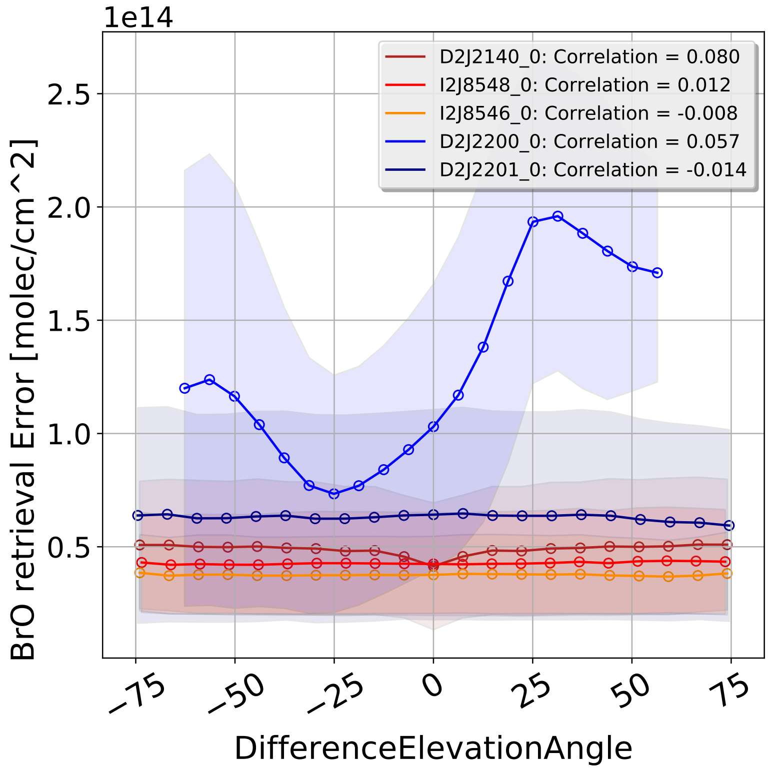


Figure 6.10: The BrO measurement error as a function of the difference of elevation angle between the reference and the plume is shown for each of the individual instruments at Tungurahua and Nevado del Ruiz. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. The plots do not reveal a symmetry around axis with zero elevation angle difference for all instruments. The D2J2200 instrument at Nevado del Ruiz is not symmetric around zero.

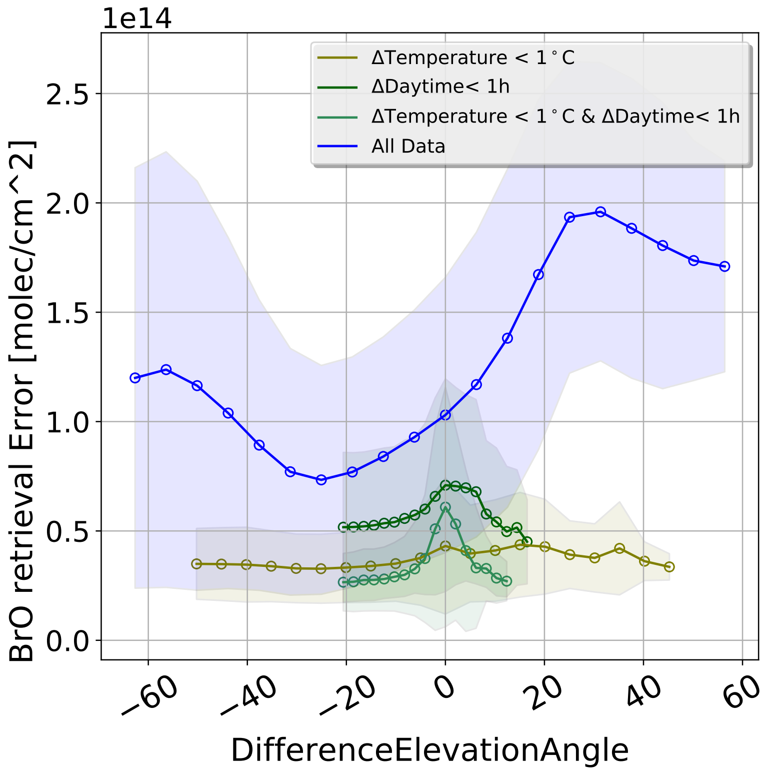


Figure 6.11: The BrO measurement error as a function of the difference of elevation angle between the reference and the plume for the D2J2200 instrument. To evaluate the origin of the behavior of the BrO retrieval error of the D2J2200 instrument as a function of the difference in elevation angle, the data are analysed on its temperature and daytime dependence. The same dependence is shown with restriction to an difference in temperature (ΔTemperature) of below $1°C$ or restriction on a daytime difference of below 1h ($\Delta Daytime \pm 1h$). The curves are marked with different green color tones, as it is shown in the legend. The blue line shows the BrO error as function of the elevation angle, when using all data for comprehension.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Mean	84.6/100%	163.7/100%	215.6/99.3%	275.4/97.0%	219.4/97.3%
Std	35.8/100%	29.9/100%	65.4/101%	67.8/97.6%	49.86/121%
Min	8/100%	113/100%	97/100%	61/95.3%	28 /44.4%
Max	169/100%	214/100%	399/100%	421/97.2%	297/100%

Table 6.7: This table shows the absolute amount and the ratio (to Table 6.1) of remaining references if restricting the colorindex difference to the mean ΔCI_2 over all instruments ($Mean(\Delta CI_2) = 0.2553.$). Here in the "Mean" and "Std" row for each instrument the average restriction is shown with the corresponding standard deviation. The "Min" and "Max" rows show the extend of restriction in the extreme cases (minimum and maximum amount of available references / restriction ratio).

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Slope	1.73e+8	1.55e+10	-9.00e+9	2.92e+11	-3.96e+10
Correlation	0.000	-0.010	0.012	0.065	-0.034
Zero point	4.77e+13	4.23e+13	3.78e+13	8.37e+13	6.44e+13

Table 6.8: The BrO measurement error as a function of the difference of elevation angle between the reference and the plume is fitted with a first order polynomial for each of the individual instruments at Tungurahua and Nevado del Ruiz. This table shows the fitting parameters slope and zero point. Moreover, the correlation between the BrO error and the absolute elevation angle difference is shown.

a more precise measurements for a difference of zero. Only the data of the D2J2200 instrument significantly varys with the elevation angle. The observable variation of the BrO error with the elevation angle differs from the symmetric dependence of all other external parameter, the minimum BrO error can be found at a difference in elevation angle of -20°. This curve is a result of the solar altitude over the day which can be obtained if only using data of the same day time. Such a plot can be seen in Figure 6.11. Figure 6.11 shows the BrO retrieval error as function of the difference elevation angle for the D2J2200 instrument at the Nevado del Ruiz volcano. The blue line is equivalent to the results which are shown in Figure 6.10 for comparison. The green lines show data, with a maximal difference in temperature of $1°C$ or maximal difference in daytime of $1h$. If restricting the data to just small differences in temperature or/and daytime, the dependency between the BrO retrieval and elevation angle appears to be not significant. Whereas the maximum of the BrO error can be found at an difference in elevation angle of zero.

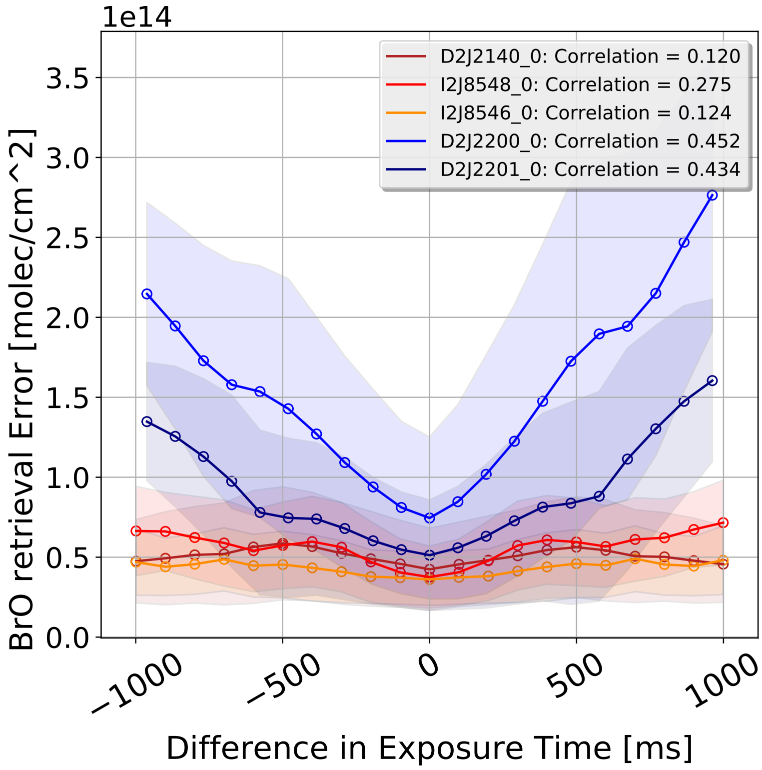


Figure 6.12: The BrO measurement error as a function of the difference of exposure time between measuring the reference and the plume are shown. To evaluate the plume spectra all reference spectra with a temporal distance of no longer than two weeks are used. An increase of the BrO error with the distance in exposure time is observable.

Since the BrO error does not depend significantly on the elevation angle no restriction on difference of the elevation angle is needed.

6.1.6 Exposure time

The exposure time is the length of time the sensor of the NOVAC instrument is exposed to light. In one scan the exposure time is set constant to the exposure time of the first scan, the pre reference. 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. Thus, the exposure time can be used as a degree of sky lightness.
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 Figure 6.12. The BrO error as a function of the difference in exposure time is also symmetric around zero for all instruments. Thus the absolute difference in the exposure time is sufficient for the evaluation.

The instruments at Tungurahua do not show a significant dependence (correlation coefficient between 0.067 and 0.251) on the exposure time, even though there is always a minimum of the BrO error at a difference of the Exposure Time of 0ms. Nevado del Ruiz shows a stronger correlation between the BrO error and the exposure time.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Slope	5.54e+9	1.54e+10	3.04e+10	1.72e+11	9.37e+10
Correlation	0.067	0.121	0.251	0.452	0.434
Zero point	4.63e+13	3.58e+13	3.87e+13	6.88e+13	4.68e+13
ΔT_2	8357	662	1273	95	499

Table 6.9: The BrO measurement error as a function of the difference of exposure time between the reference and the plume is fitted with a first order polynomial for each of the individual instruments at Tungurahua and Nevado del Ruiz. This table shows the fitting parameters slope and zero point. Moreover, the correlation between the BrO error and the absolute exposure time difference is shown.

Table 6.9 shows the slope, correlation, zero point and the ΔET_2s. The differences in exposure time where the BrO error increases by a factor of two compared to the difference of exposure time of zero. Restrictions of the exposure time to the mean of the ΔET_2s of all instruments which is 632.25 ms leads to an average decrease compared to table 6.1 of data of 98.78%. The results for each instrument can be found in table 6.10.

Section 6.1.6 shows the amount of possible references if the only data are considered which do not exceed the thresholds in each external parameter. The average amount of available references per plume decreases to 64%. While the performance is as good as without the restriction, this means the averaged BrO error is almost the same (deviations are below 0.1%).

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Mean	81.7/96.5%	162.8/99.4%	212.8/98.0%	284.0/100%	225.6/100%
Std	35.3/98.6%	30.1/101%	64.5/99.5%	69.5/100%	41.2/100%
Min	8/100%	113/100%	95/97.9%	64/100%	63/100%
Max	167/98.8%	214/100%	395/99.0%	433/100%	297/100%

Table 6.10: Amount of possible references when restricting the difference in exposure time between plume and reference to differences below 632.25 ms.

Instrument	D2J2140	I2J8546	I2J8548	D2J2200	D2J2201
Mean	36.0/42.6%	112.9/69.0%	148.9/68.6%	217.0/76.4%	140.4/62.2%
Std	22.35/62.4%	50.6/169.2%	75.9/117.1%	82.1/118.1%	71.0/172.3%
Min	1/12.5%	8/7.1%	12/12.4%	3/4.7%	6/9.5%
Max	127/75.1%	212/99.1%	382/95.7%	398/91.9%	283/95.3%

Table 6.11: Amount of possible references while restricting the difference in colorindex between plume and reference to differences above 0.255. maximal Time difference is $3.358°C$, maximal daytime difference is 4.75h without Exposure Time between plume and reference to differences below 632.25 ms.

Dependency of external parameters on each other

In all discussions on the impact of the external parameter on the retrieved BrO error the dependency of the external parameter on each other are neglected. It is plausible that the temperature correlates with the cloudiness or the lightness due to sunlight. Therefore the correlation of the exposure time with the BrO error could be a result of the correlation of the temperature with the BrO error. Figure 6.13 shows an example of the dependency of external parameters on each other. The difference in temperature as a function of the difference in exposure time. The BrO error is color-coded.

All correlations between the external parameters are shown in Figure 6.14. Figure 6.14 shows discrete correlation values from 0.3 to 1. Correlations below 0.3 are ignored. Small plus and minus signs indicate whether the correlation is negative or positive. The temperature depends on the daytime, due to the dependence of the temperature on the sun, thus a correlation between the difference in temperature and the difference in daytime (Correlation of ≈ 0.5) can be observed. Since the temperature depends on the intensity of the sun, it also correlates with the difference in exposure time (Correlation of ≈ 0.4). The difference in temperature also slightly correlates with the difference in colorindex, due to the dependency of temperature on the cloudiness (Correlation of ≈ 0.3). The low correlations could appear due to the uniform cloudiness near to the equator. The correlation between the temperature difference to the temporal difference (Correlation of ≈ 0.3) probably occurs due to long term changes in temperature. Furthermore the difference in exposure time correlates with the daytime and the colorindex (Correlation of ≈ 0.4) as a result of the dependency on the sun intensity.

To eliminate the correlation between the external parameters the BrO error dependency on one external parameter where calculated by keeping the differences in the other external parameters constant. Hereby only parameters were kept constant, where the correlation is above 0.3. Thus, when looking at the temperature, only the difference in temperature need to be constant, since the temporal distance does not

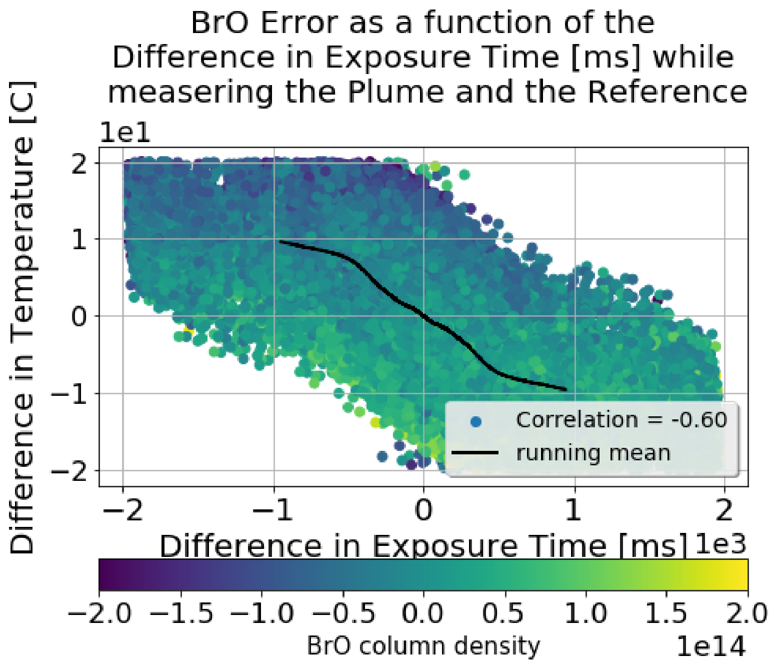


Figure 6.13: An example of the dependency of external parameters on each other. The difference in temperature as a function of the exposure time. data from Tungurahua.

correlate wit the other considered external parameter. The results can be seen in Figure 6.15 to Figure 6.18.

Figure 6.15 shows the BrO retrieval error as a function of the temporal difference between the reference and the plume spectrum. All differences in temperature are below one degree. Compared to the correlations, calculated without eliminating the dependence on the temperature, the correlations increase. The dependence of the instruments installed at Tungurahua are still significant higher. From the results can be interpreted that the temporal difference between the time when measuring the plume and the reference has a impact on the fit quality, but this impact is smaller as the impact of the instrument temperature.
Figure 6.16 shows the dependency of the BrO retrieval error on the difference in exposure time for all considered instruments. Hereby, only data are used, where the difference in temperature is below 1 degree, the difference in colorindex is below 0.05 and the difference in daytime is below one hour. The temporal difference and the difference in elevation angle are not kept constant, since we could not observe a relation between the exposure time and the temporal difference or the elevation angle. The correlations between the BrO error and the difference in exposure time decrease for each instrument if the temperature, daytime and colorindex are kept constant. Even though, the correlations at Nevado Del Ruiz are still higher as the correlations at Tungurahua.

Figure 6.17 shows the BrO retrieval error as a function of the difference in colorindex for all instruments. The temperature and the exposure time shows a dependency on the colorindex as it can be seen in Figure 6.14. Both are kept constant, the difference in temperature is below 1 degree and the difference in exposure time is below 100 ms. The correlations decrease compared to Figure 6.9. Especially the correlation of the D2J2201_0 instrument decreases.
Figure 6.18 shows the BrO retrieval error as a function of the difference in daytime for all considered instruments. As it can be seen in fig. 6.14 the exposure time and the temperature need to be kept constant. The difference in temperature is below 1 degree, the difference in exposure time belwo 100 ms. A general decrease of the correlations compared to Figure 6.8 is observable.
Restricting the data, to where the temperature difference is kept below one degree, leads to an distortion of the data. Thus the results plotted in Figure 6.15 to Figure 6.18 could also have systematic errors.
When comparing the correlations of the data from **??** and **??** to the correlations of Figure 6.6 to Figure 6.12 a large reduction of the correlation is obvious. Only the difference in temperature still shows a significant correlation to the BrO error. However, the minimal BrO error coincidence in almost all cases with a difference in external parameters of zero. A dependency of the BrO error on the external parameter can still be seen even tough the correlation is very small.
Excluding of the external parameters due to the rather low correlation leads to a worse quality of the results, since the effects of the single parameter add up to a not negligible amount. However, note that the added impact of all external parameter except for the temperature are less important than the temperature. The BrO error of contaminated spectra evaluated with the contamination based method (See Chapter 7) increases by 15% if the other external parameters are excluded. If all external paramter except for the temperature are used the calculated BrO error increases by 37%.

For the final evaluation of contaminated data we use the results of Figure 6.6 to Figure 6.9. Since the correlations between the external parameters are considered in the final 4 dimensional fit.

6.2 BrO dependence on external parameters

The external parameters not only influence the fit quality but also the evaluation of the gas amount. A high different in certain external parameter could distort the calculated BrO column density. Figure 6.19 shows the evaluation of one plume with respect to different references. The temporal difference between the references and the plume do not exceed two weeks. In theory we expect that the choice of the reference should not make a difference, therefore all BrO column densities resulting from the evaluation should be equivalent. But we can see a high variation if choosing

different references. The variability of the BrO column density depends as well on the external parameters, when looking at the temperature dependency a mean decrease of th BrO column density with an increasing temperature can be observed. Figure 6.19 is a result of an exemplary evaluation of one plume. An examination of all several plumes evaluated by different references is shown in Figure 6.20. The plots are equivalent to the plots for BrO error (for an example see fig. 6.6). The BrO SCDs vary strongly with the differences in external parameters. It is observable, that the BrO SCDs recorded by the instruments at Nevado Del Ruiz vary in a larger range than for the BrO SCDs recorded by instruments at Tungurahua. This can also be observed for the BrO retrieval errors. The absolute BrO SCDs increase with the difference in external parameters.
(a) Temporal difference: For the temporal difference no significant correlation can be observed. (b) Difference in color index: The correlations differ for every instrument even for instruments of the same volcano. The correlations vary from -0.368 to 0.446. (c) Difference in daytime: For the instruments at Nevado Del Ruiz the BrO SCD correlates strongly with the difference in daytime. This can be a result of the dependence on the temperature, since the correlations are very similiar, only the correlations are a little bit stronger for the difference in temperature. (d) The strange dependence which can be seen between the BrO error and the difference in elevation angle for the D2J2200 instrumnt can be seen in this plot as well. The other instruments do not show any correlation between the BrO SCD and the difference in elevation angle.(e) The correlations for the difference in exposure time are opposite to the correlations in daytime.

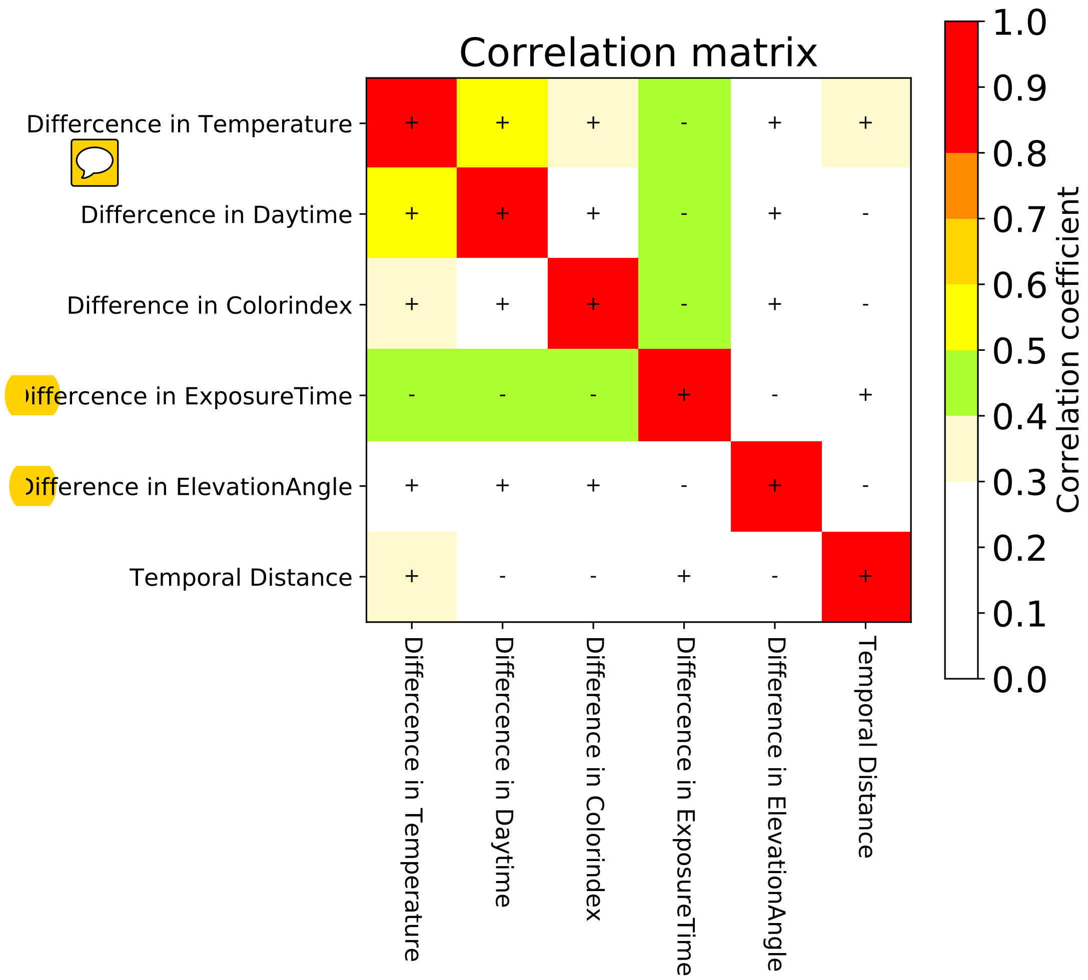


Figure 6.14: Correlation matrix of the external parameters. The correlation is discrete colour coded. Positive correlation is labeled with a plus whereas negative correlation is labeled with a minus. The correlation matrix is calculated using the data from D2J2140_0.

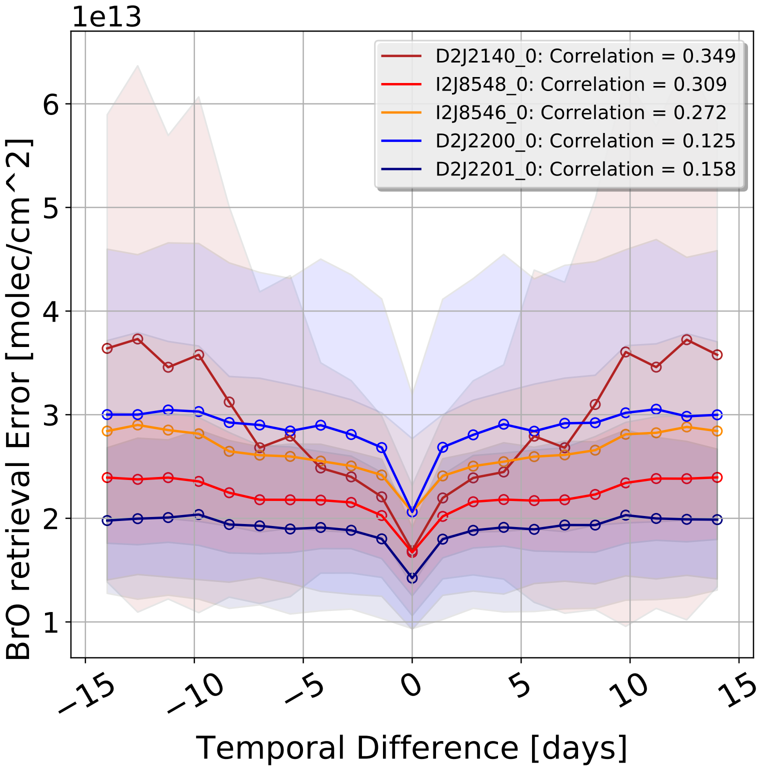


Figure 6.15: The BrO measurement error as a function of the temporal difference between measuring the reference and the plume are shown. Therefor, the reference spectra are restricted such that the maximal temperature difference between reference and plume is $1°C$.

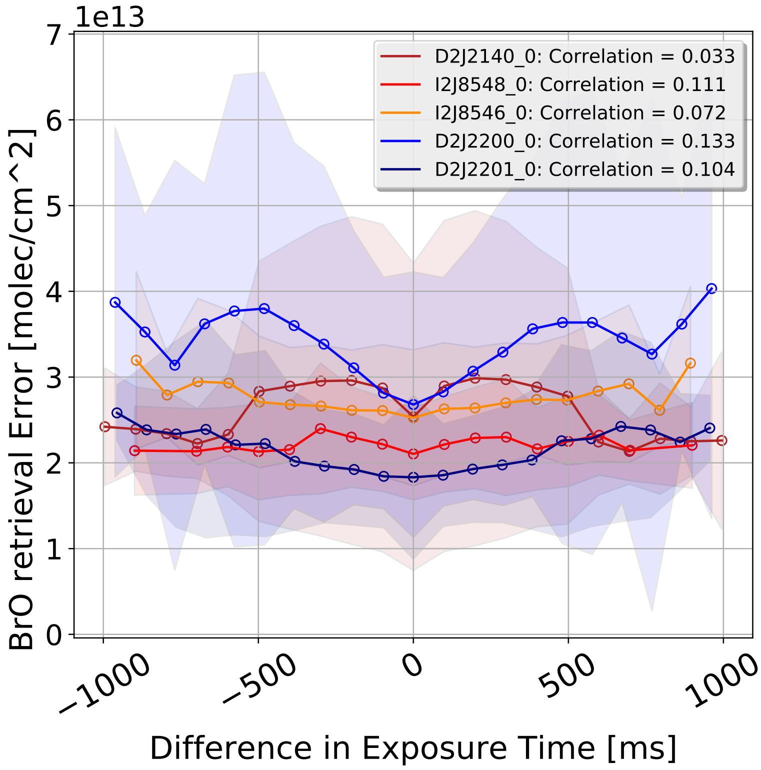


Figure 6.16: The BrO measurement error as a function of the exposure time difference between measuring the reference and the plume are shown. Therefor, the reference spectra are restricted such that the maximal color index difference between reference and plume is 0.05. The maximal daytime difference is $1h$.

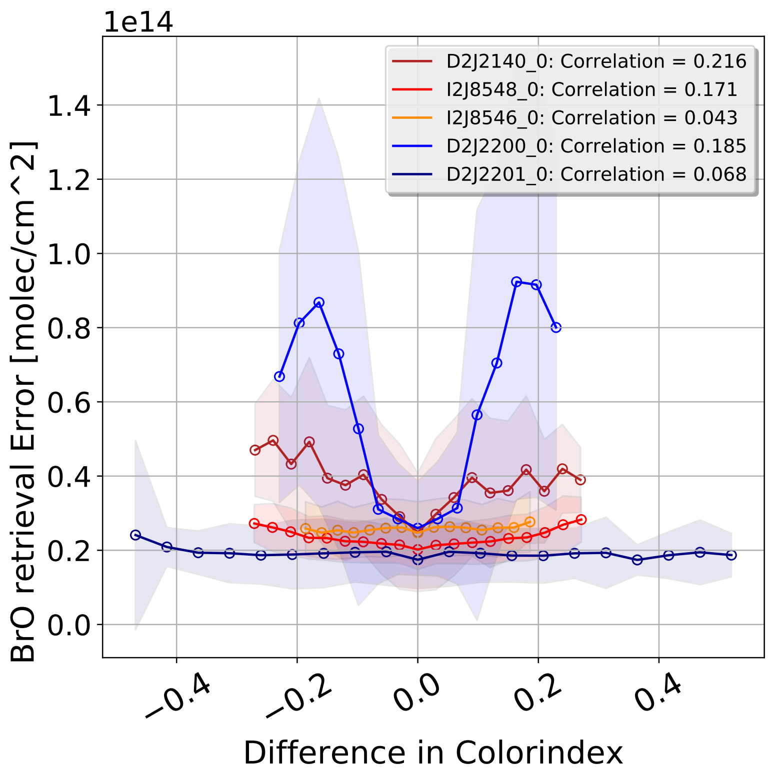


Figure 6.17: The BrO measurement error as a function of the color index difference between measuring the reference and the plume are shown. Therefor, the reference spectra are restricted such that the maximal temperature difference between reference and plume is $1°C$. The maximal exposure time difference is $100ms$.

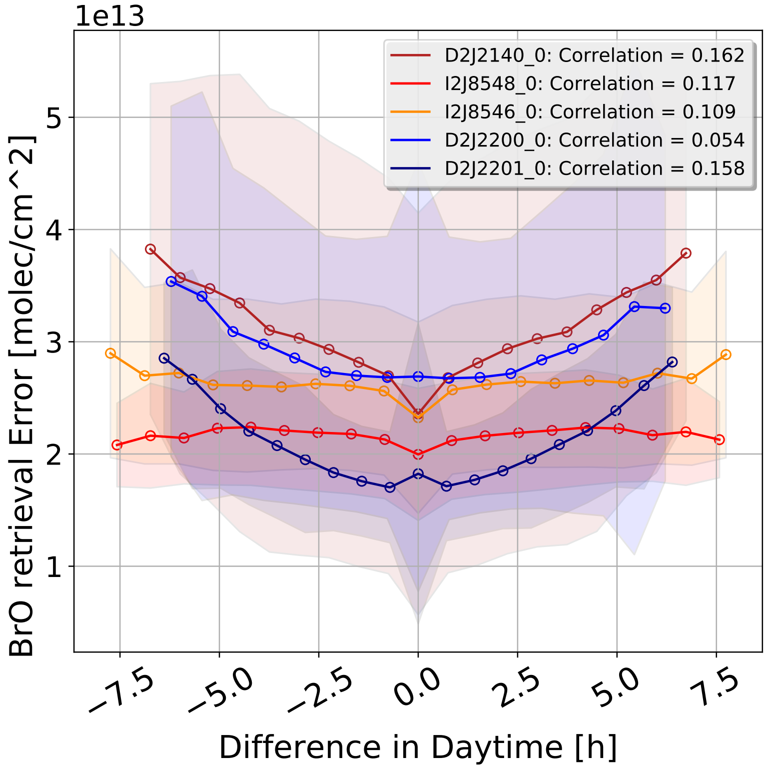
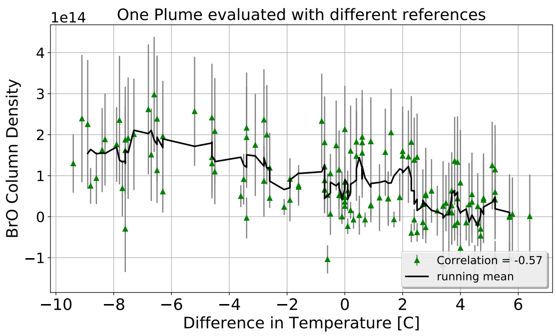
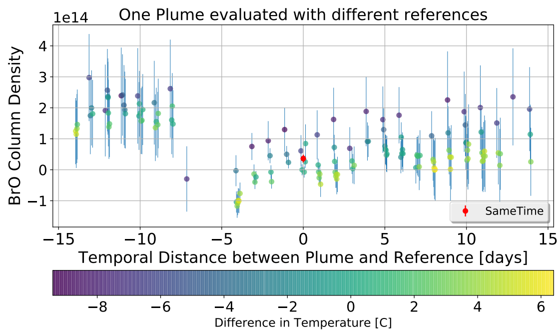


Figure 6.18: The BrO measurement error as a function of the daytime difference between measuring the reference and the plume are shown. Therefor, the reference spectra are restricted such that the maximal temperature difference between reference and plume is $1°C$. The maximal exposure time difference is $100ms$.



(a)



(b)

Figure 6.19: One plume is evaluated by using different references. The plume is recorded at Tungurahua volcano with the D2J2140_0 instrument. The recording time was the 03.12.2008 at 16:46 o clock. The y axis shows the BrO column density difference between the NOVAC method and contamination based method. (a) The difference in BrO is plotted as a function of the temperature difference between the plume and the references. Every data point indicates one reference. (b) The difference in BrO is plotted as a function of the temporal difference between the one plume and the different references.

(a)

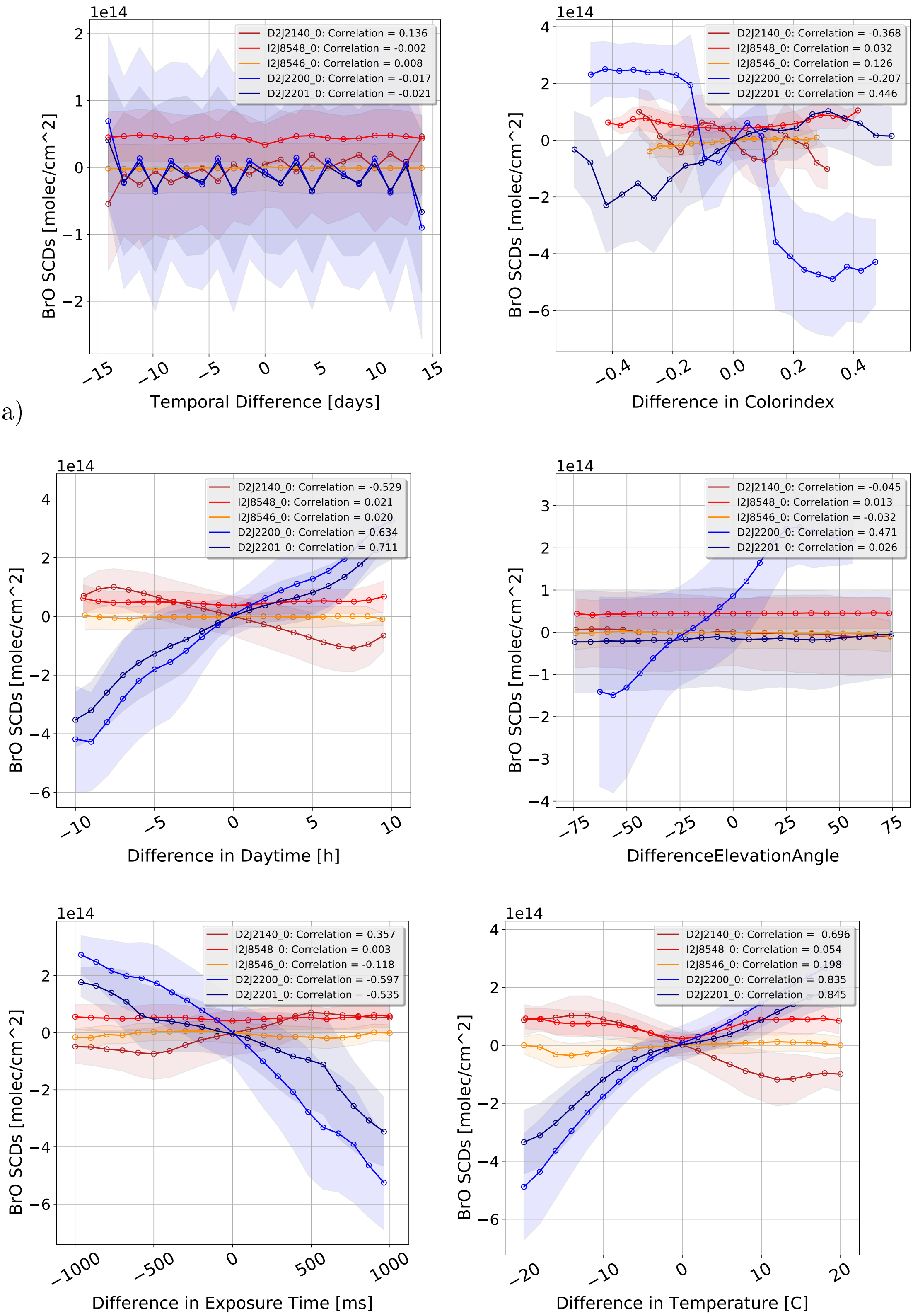


Figure 6.20: The BrO measurement value as a function of the difference of the external parameters between measuring the reference and the plume are shown.

Summary

This chapter examines the influence of external on the precision of the BrO evaluation. Herby the following parameter are considered: temporal difference, temperature, daytime, colorindex, elevation angle, exposure time. The findings are based on the data of three instruments installed at the Tungurahua volcano and two instruments at the Nevado Del Ruiz volcano. The maximal temporal difference between measuring the plume and the reference is set to 14 days to prevent large uncertainties in the BrO evaluation. Due to the mechanical influence on the wavelength to pixel mapping the temperature for all analysed instruments has the most significant impact on the BrO evaluation for all considered external parameters. The elevation angle does not seem to influence the evaluation for all examined instruments thus the elevation is excluded from the evaluation. The influence of the other external parameter change at every instrument. So a relatively strong impact of the exposure time can be seen at the D2J2201_0 instrument at Nevado Del Ruiz, while the exposure time does not seem to significantly influence the evaluation of the data from the I2J8548_0 at Tungurahua.