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BrO/SO₂ molar ratios from scanning DOAS measurements in the NOVAC network

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Abstract

The molar ratio of BrO to SO₂ is, like other halogen/sulphur ratios, a possible precursor for dynamic changes in the shallow part of a volcanic system. While the predictive significance of the BrO/SO₂ ratio has not been well constrained yet, it has the major advantage that this ratio can be readily measured using the remote-sensing technique Differential Optical Absorption Spectroscopy (DOAS) in the UV. While BrO/SO₂ ratios have been measured during several short-term field campaigns this article presents an algorithm that can be used to obtain long-term time series of BrO/SO₂ ratios from the scanning DOAS instruments of the Network for Observation of Volcanic and Atmospheric Change (NOVAC) or comparable networks. Parameters of the DOAS retrieval of both trace gases are given and the influence of co-adding spectra on the retrieval error will be investigated. Difficulties in the evaluation of spectroscopic data from monitoring instruments in volcanic environments and possible solutions are discussed. The new algorithm is demonstrated by evaluating data from the NOVAC scanning DOAS systems at Nevado del Ruiz, Colombia encompassing almost four years of measurements between November 2009 and end of June 2013. This dataset shows variations of the BrO/SO₂ ratio several weeks prior to the eruption on 30 June 2012.

1 Introduction

The molar ratio of halogen (mainly HCl, HF) to sulphur species (mainly SO₂) in volcanic plumes has long been known as a possible tracer for volcanic activity (e.g., Noguchi and Kamiya, 1963; Menyailov, 1975; Pennisi and Le Cloarec, 1998). This is due to the different solubility of volatiles in magma (e.g., Carroll and Holloway, 1994) and its dependence on pressure. As a consequence, different gaseous species are exsolved in equilibrium at different magmastatic pressures, i.e., at different depths in the magma column. The most commonly used example of halogen/sulphur ratios has been the measurement of the HCl/SO₂ molar ratio (e.g., Noguchi and Kamiya, 1963). Another

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halogen species is BrO, which has now been detected at several volcanoes (e.g., Bobrowski et al., 2003; Bobrowski and Platt, 2007; Boichu et al., 2011; Kelly et al., 2012; Hörmann, 2013) and whose abundance was suggested as an additional indicator for changes in volcanic activity (Bobrowski and Giuffrida, 2012). One major advantage of measuring the BrO/SO₂ molar ratio is that both species can be detected in a single spectroscopic remote sensing measurement using Differential Optical Absorption Spectroscopy (DOAS) in the UV (Platt and Stutz, 2008), which is a rather simple-to-implement and sensitive technique.

Scanning DOAS has become the most widespread method for measuring the emission rate of volcanic SO₂ (e.g., Galle et al., 2003). In particular, within the framework of the EU project NOVAC (Network for Observation of Volcanic and Atmospheric Change, Galle et al., 2010) to date about 70 scanning DOAS systems have been installed at 26 volcanoes worldwide, with the goal of performing automated spectroscopic gas emission rate measurements. These instruments measure the volcanic SO₂ emission rates by acquiring scattered UV radiation spectra over a scan through a surface intercepting the volcanic plume and combining the DOAS-derived gas column densities with geometrical factors and the component of transport speed normal to the scanned surface. Typically, about 40 individual gas emission rate measurements are obtained daily at each volcano by NOVAC instruments, which have allowed operational volcanic gas monitoring to reach temporal resolutions comparable to other methods of geophysical surveillance.

While the spectra are routinely evaluated for SO₂ by the local observatories, this is not the case for BrO. The BrO absorption cross-section (in this work the one of Fleischmann et al., 2004 is used) is roughly a factor of 150 larger than that of SO₂ (in this work the one of Vandaele et al., 2009 is used) in the wavelength ranges typically used for DOAS evaluations (Vogel, 2013), but the abundance of BrO is significantly lower. BrO/SO₂ ratios between 8×10^{-5} and 1×10^{-3} have been found in volcanic plumes (Bobrowski and Platt, 2007), thus leading to one to two orders of magnitude weaker BrO absorption structures compared to SO₂. The smaller optical density makes

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it technically more challenging to detect and accurately measure BrO. In particular, small instrumental imperfections like changes in the instrument's slit function and the wavelength-channel-alignments due to e.g., changes of the instrument's temperature (e.g., Chapter 3 in Kern, 2009), which have only a negligible effect on the SO₂ evaluation, pose a challenge for the BrO evaluation. Additionally, the noise due to photon statistics has to be lower in order to obtain a good signal to noise ratio for the BrO evaluation. One way to achieve this is by co-adding several spectra obtained by the same instrument under similar measurement conditions (e.g., within the same horizon to horizon scan or from consecutive scans with close time proximity).

This work presents an algorithm to evaluate the spectra recorded by the NOVAC instruments in order to obtain BrO column densities and BrO/SO₂ ratios. We give detailed information about the parameters of the DOAS evaluation used for the analysis of the NOVAC spectra. The feasibility of the BrO evaluation will be demonstrated as well as the magnitude of DOAS fit errors. As an example, a first long-term time-series from the Colombian volcano Nevado del Ruiz is presented.

Nevado del Ruiz is a 5400 m high stratovolcano located in the Andes in Colombia, approximately 130 km west of Bogotá. Nevado del Ruiz became infamous in 1985, when on the 13 November, approximately 23 000 people were killed by Lahars in the aftermath of an eruption. A map showing the location of Nevado del Ruiz and the original two NOVAC instruments whose data is used in this work and their scanning directions is given in Fig. 1.

2 Method

The NOVAC Version 1 instruments installed at all volcanoes in NOVAC use a “flat” or “conical” scanning geometry, i.e., all viewing directions of a scan lie in a plane or on the surface of a semi-cone open towards the volcano (Galle et al., 2010). The set of consecutive scattered sunlight spectra collected from horizon to horizon (in this work only viewing directions between -75° to $+75^\circ$ elevation angle were evaluated) is referred to

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as a plume scan in the following. The instruments utilize Ocean Optics S2000 spectrometers that are not thermally stabilized, which results in a robust, energy efficient design suitable for operation in remote locations that are sometimes difficult to access.

All spectra of each plume scan are pre-evaluated for SO₂ using a zenith spectrum acquired at the beginning of each plume scan as a reference spectrum. At this time underexposed and overexposed spectra (intensity below 15 % or above 85 % of the maximum exposure in the spectral region used for the DOAS evaluation) were removed from further evaluation. In the next step, the ten adjacent spectra with the highest mean SO₂ column density value are selected and defined as the volcanic plume region. Then a set of ten adjacent spectra with the lowest mean SO₂ value is defined as the reference region (see Fig. 2). Next, the spectra from the plume region are co-added to obtain a collective plume spectrum with higher signal to noise ratio, as well as the spectra from the reference region to obtain a collective reference spectrum.

The collective plume and reference spectra are then evaluated using the DOAS method (see below). To obtain an even better signal to noise ratio we also co-added the collective reference and plume spectra of four consecutive scans and evaluated the resulting spectra, which improved our BrO detection limit by a factor of two.

3 Spectroscopic retrieval

All spectra are evaluated with a fitting routine that combines a non-linear Levenberg–Marquard fit and a standard least-squares fit (Platt and Stutz, 2008) using the DOASIS software-package (Kraus, 2006).

For all evaluations, the reference spectrum is first wavelength calibrated using a high-resolution solar spectrum (Chance and Kurucz, 2010) that was convoluted with the line shape of the 334.15 nm line of a low-pressure mercury lamp to match the lower spectral resolution of the spectrometers used in the NOVAC instruments (of about 0.8 nm FWHM). This line of the Hg spectrum was also used for the convolution of the high resolution absorption cross-sections; it was selected due to its proximity to the spectral

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region of interest for our evaluations. The calibration from the reference spectrum is also used for the plume spectra. The fit coefficient of the reference spectrum in the DOAS fit is fixed to -1 . Two Ring spectra are included in the DOAS fit to correct for the Ring-effect (Grainger and Ring, 1962). The first Ring spectrum is a standard Ring spectrum calculated using the DOASIS software-package; the second is created from the first Ring spectrum by multiplying it with a wavelength dependent term (in this work λ^{-4}) to account for multiple Rayleigh scattering in the atmosphere (Wagner et al., 2009).

A 3rd order polynomial is included in the fit to account for broadband absorption structures and Rayleigh as well as Mie-scattering structures in the spectra. An additional wavelength independent offset in the intensity space is allowed to correct for stray-light inside the spectrometer.

The SO₂ evaluation is performed in the wavelength range between 314.8 nm and 326.8 nm including one SO₂ absorption cross-section at 298 K (Vandaele et al., 2009) and one O₃ absorption cross-section at 221 K (Burrows et al., 1999).

The BrO evaluation is performed between 330.6 nm and 352.75 nm using the following absorption cross-sections: BrO at 298 K (Fleischmann et al., 2004), the same SO₂ and O₃ as above, O₄ (Hermans, 2003), NO₂ at 298 K (Vandaele et al., 1998) and CH₂O at 298 K (Meller and Moortgat, 2000). An example of a BrO fit is shown in Fig. 3. The evaluation ranges and trace-gases included in the SO₂ as well as in the BrO fit were chosen accordingly to (Vogel, 2013), who performed a series of studies on the optimal evaluation wavelength-range for BrO and SO₂ in a combination of real measurement data and theoretical studies.

All trace gas reference cross-sections are convoluted to match the instrument resolution using the 334.15 nm line of a mercury lamp, a sample of the instrument function, recorded with the respective spectrometer. To account for the I_0 -effect (Platt and Stutz, 2008) an iterative approach is used. First, a fit is performed to retrieve uncorrected column densities of the trace gases; these column densities are then used to create I_0 corrected absorption cross-sections (Wagner et al., 2002).

In order to correct for small inaccuracies in the wavelength calibration, the reference spectrum and both Ring spectra, as one set, and all trace gas absorption cross-sections, as another set, are allowed to be shifted and squeezed against the measurement spectrum.

4 Results

Scans between November 2009 and the end of June 2013 were evaluated for two instruments at Nevado del Ruiz, Colombia. Figure 4 shows the number distribution of the BrO DOAS retrieval errors for both instruments (with identification numbers D2J2200 for Bruma and D2J2201 for Alfombrales, see Fig. 1). The fit error is shown for the evaluation of spectra from individual scans as well as for spectra resulting from co-adding four consecutive scans. The DOAS fit errors for the two instruments are essentially equal. For a single scan the fit error is centred around 2×10^{13} [molecules cm^{-2}], for the co-added spectra the fit error is centred around 1×10^{13} [molecules cm^{-2}], i.e. averaging four scans reduces to half the fit error, which indicates that the evaluation is still limited by photon shot noise.

Adding up spectra from different scans is always a trade-off between gaining in signal to noise and losing in absolute signal (for some spectra) and time resolution of the retrieved slant column densities (SCD). An additional problem may be caused by a drifting spectral instrument response due to changes of the instrument temperature, which would compromise the accuracy of the results when summing up spectra. The variability of the instrument slit function and the wavelength-channel-alignment with changing instrument temperature for the spectrometers used in this study is shown in Fig. 5. For this example, one zenith looking spectrum was fitted to spectra from half a year of data with a fit range covering the SO_2 and the BrO evaluation range. Figure 5 shows, as one example, the shift and squeeze of the reference spectrum, which both clearly vary with changes of the ambient temperature.

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However, as the signal to noise ratio for four consecutive scans is still close to the ideal photon statistics limited case, the approach to add up spectra from four consecutive scans is thought to not be influenced by these temperature issues and used in the rest of this manuscript.

SO₂ and BrO column densities time-series are shown in Figs. 6 and 7. Both, the SO₂ and the BrO column densities start to increase at the beginning of 2012, as well as the SO₂ emission rates (see Fig. 8). Towards the beginning of 2013, the SO₂ column densities start to decline while the BrO column densities stay elevated thus leading to increasing BrO/SO₂ ratios. Unfortunately, both instruments have some periods without transmitted data. D2J2201 has very few scans between July 2011 and November 2011 and the instrument with the serial number D2J2200 has a gap between June 2012 and September 2012. These gaps are due to technical difficulties that can occur when operating the instruments in remote locations, i.e., the gap of D2J2200 after June 2012 can be explained by ash from the eruption falling onto the surface of the solar panels which leads to a lack of power supply.

As there is only a relative small amount of data points (~ 1–30) per day after the co-addition of scans, the usual approach of calculating the linear regression for a large amount of data points (Bobrowski et al., 2003) to find the BrO/SO₂ ratio cannot be used here. We therefore calculated daily averages of the BrO/SO₂ ratios from the spectra created from co-adding four consecutive scans for the sake of lower noise. Averaging over all ratios can lead to erroneous results, since the average would include many scans without significant volcanic gas and therefore negligible SO₂ and BrO column densities. Rationing two values (i.e., SO₂ and BrO SCDs) that are close to zero gives unpredictable and unrealistic results. Therefore, SCD's measured outside the volcanic plume have to be excluded. One possibility is setting a BrO threshold equivalent to a certain factor of the retrieval error as a BrO detection limit. An example of a time-series created for all scans containing BrO above the detection limit (in this case 4 times the retrieval error was chosen) is shown in Fig. 9. The BrO/SO₂ ratio is almost constant between January 2011 and January 2012 with a value of roughly $6\text{--}8 \times 10^{-5}$.

first ash emissions (see Fig. 8 for daily averages of the SO₂ emission rates). Although a detailed analysis of this process is beyond the scope of this paper, the correspondence with the overall eruptive activity shows the potential of measuring both gases simultaneously as a precursory signal of volcanic eruptions.

The lack of BrO/SO₂ ratios from the spectrometer D2J2201 before January 2012 is due to the lack of spectra with high volcanic gas content, therefore no BrO or SO₂ could be detected above the detection limit. Despite the fact that both instruments have some gaps due to technical difficulties (see above), the BrO/SO₂ ratios in general agree nicely between both instruments.

5 Conclusions and outlook

We have for the first time demonstrated that BrO column densities can be automatically evaluated from spectra routinely recorded by the NOVAC type 1 instruments of the NOVAC network. This proof of concept shows the possibility to achieve five year or even longer time-series of BrO/SO₂ ratios at many (if not all) volcanoes observed by the NOVAC network. The instruments the data of which were analysed in this study are exactly of the same design as any other NOVAC type 1 instrument. In fact two years of data (January 2011 – December 2012) at Galeras, Colombia were also evaluated. While in general showing too low SO₂ levels for a successful BrO detection, the BrO DOAS retrieval error was comparable to the error from the instruments at Nevado del Ruiz. Since Nevado del Ruiz was chosen for this study due to the interesting activity and the good continuous dataset, not for superior instrument performance, we have no indications that the other instruments from NOVAC should perform differently. Furthermore, there are other networks (i.e., the Flame network at Stromboli, Italy, Burton et al., 2009) that use comparable spectrometers, which could give further insight into volcanic BrO/SO₂ ratios.

The large NOVAC dataset already gives the possibility to determine other influences than changes of the volcanic activity on the BrO/SO₂ molar ratio. BrO is not primarily

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emitted by volcanoes, but formed from HBr when the volcanic gases are released into the atmosphere (e.g., Bobrowski et al., 2003; Oppenheimer et al., 2006, von Glasow, 2010). While this potentially makes it more difficult to use the BrO/SO₂ ratio as an indicator of volcanic activity, Bobrowski and Giuffrida, (2012) have found that the BrO/SO₂ molar ratio increases only in the first minutes after release into the atmosphere. The authors found that in a distance of approximately 5 km after release into the atmosphere the BrO/SO₂ molar ratio is constant (of course depending on the wind-speed). The vast amount of available data in the NOVAC database allows to further investigate influences like the residence time of the volcanic gas in the ambient atmosphere by estimating the time of transport from the volcanic vent to the point of measurement, or meteorological influences on the BrO/SO₂ molar ratio, as well as its dependence on height and latitude.

The BrO evaluation scheme presented in this manuscript was implemented for automatic operation to re-process the archived data. In the future, it is planned to be implemented into the routine evaluation for the NOVAC observatories. Besides the automated evaluation there are chances to further improve the quality of the BrO/SO₂ ratios.

One possible pitfall in the DOAS evaluation of volcanic gas measurements is the requirement for a reference spectrum free of volcanic gas. For instance, this problem is discussed in Salerno et al. (2009), where the authors state that wide volcanic gas plumes, covering the complete range of viewing directions, are frequently observed. This problem is probably most frequently observed during periods of low wind-speeds when meaningful gas emission rate measurements are difficult anyways. Therefore it is not the main concern for SO₂ emission rate measurements. However, using gas free reference spectra can improve the BrO retrieval. An approach similar to that described by Salerno et al. (2009) for the evaluation of SO₂ without a reference spectrum could be implemented. The background spectrum for the evaluation is modelled on the basis of an extra-terrestrial solar reference spectrum (Chance and Kurucz, 2010). Unfortu-

nately, while working well for volcanic SO₂, the approach of using modelled spectra does not yield sufficient accuracy for the BrO evaluation at this time.

However, this method could be used to identify “plume free” spectra, by their SO₂ signatures, which subsequently can be used as reference spectra to evaluate the data for both, BrO and SO₂. If all spectra from a particular scan of the sky contain significant SO₂ column densities, one could, i.e., use a reference spectrum from a different scan or day, with similar atmospheric conditions and a similar instrument temperature.

Another possible approach to further improve the accuracy of our algorithm is taking temperature effects of the instruments into account. Figure 5 shows the range of temperatures the instruments at Nevado del Ruiz are exposed to and that the temperature has an effect on the instrument calibration as well as the instrumental line shape. This can lead to two different problems: The first problem appears when co-adding spectra. The spectral intensities are summed up for each channel, if the pixel-wavelength alignment changes between different spectra which are co-added, the resulting spectrum can be erroneous. However, the temperature changes slowly and most spectra that are co-added were recorded within a time of 15 min up to one hour, therefore, the effect should be negligible.

The second effect of the instrument’s temperature regards the convolution of the reference absorption cross-sections. Currently all spectra are convolved with the 334.15 nm line of a mercury lamp that was recorded at room temperature. Instrumental characterization of S2000 spectrometers performed within the NOVAC project (i.e., Kern, 2009) reported changes of up to 10 % for the SO₂ column densities caused by temperature-induced changes of the instrument line shape for temperatures between 5–40 °C (comparable to the temperatures occurring in the field). For the BrO evaluation there are no comparable studies that treat the influence of changes in the instrumental line shape. Since for most NOVAC spectrometers there are no records of the particular instrument’s line shape at different temperatures available, one possible solution would be to determine the line shape from a comparison between the high-resolution solar reference spectrum and measurement spectra at different temperatures.

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- Burrows, J. P., Richter, A., Dehn, A., Deters, B., Himmelmann, S., Voigt, S., and Orphal, J.: Atmospheric remote-sensing reference data from GOME-2. Temperature-dependent absorption cross sections of O₃ in the 231–794 nm range. *J. Quant. Spectrosc. Ra.*, 61, 509–517, doi:10.1016/S0022-4073(98)00037-5, 1999.
- 5 Burton, M. R., Caltabiano, T., Murè, F., Salerno, G., and Randazzo, D.: SO₂ flux from Stromboli during the 2007 eruption: results from the FLAME network and traverse measurements, *J. Volcanol. Geoth. Res.*, 182, 214–220, doi:10.1016/j.jvolgeores.2008.11.025, 2009.
- Carroll, M. R. and Holloway, J. R.: Volatiles in Magmas, Mineralogical Society of America, Washington DC, 517 pp, 1994.
- 10 Chance, K. and Kurucz, R. L.: An improved high-resolution solar reference spectrum for earth's atmosphere measurements in the ultraviolet, visible, and near infrared, *J. Quant. Spectrosc. Ra.*, 111, 1289–1295, doi:10.1016/j.jqsrt.2010.01.036, 2010.
- Fleischmann, O. C., Hartmann, M., Burrows, J. P., and Orphal, J.: New ultraviolet absorption cross-sections of BrO at atmospheric temperatures measured by time-windowing Fourier transform spectroscopy, *J. Photoch. Photobio. A*, 168, 117–132, doi:10.1016/j.jphotochem.2004.03.026, 2004.
- 15 Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A. J. S., Edmonds, M., and Horrocks, L.: A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: a new tool for volcano surveillance, *J. Volcanol. Geoth. Res.*, 119, 241–254, 2003.
- 20 Galle, B., Johannson, M., Rivera, C., Zhang, Y., Kihlmann, M., Kern, C., Lehmann, T., Platt, U., Arellano, S., and Hidalgo, S.: Network for Observation of Volcanic and Atmospheric Change (NOVAC) – a global network for volcanic gas monitoring: Network layout and instrument description, *B.Volcanol.*, 115, D05304, doi:10.1029/2009JD011823, 2010.
- Garzon, G., Silva, B., Narvaez, A., Chacon, Z., and Galle, B.: Assessment of SO₂ emissions from three Colombian active volcanoes (2007–2012), *GEOCHANGE: Problems of Global Changes of the Geological Environment*, vol. 2, edited by: Khalilov, E., Science Without Borders, London, 6–14, 2013.
- 25 Grainger, J. F. and Ring, J.: Anomalous Fraunhofer line profiles, *Nature*, 193, 762, doi:10.1038/193762a0, 1962.
- 30 Hermans, C., Vandaele, A. C., Fally, S., Carleer, M., Colin, R., Coquart, B., Jenouvrier, A., Merienne, M.-F.: Absorption cross-section of the collision-induced bands of oxygen from the UV to the NIR, in: *Weakly Interacting Molecular Pairs: Unconventional Absorbers of Radiation*

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in the Atmosphere, edited by: Camy-Peyret, C. and Vigasin, A., Springer, Netherlands, 193–202, 2003.

Hörmann, C.: Space-based Monitoring of Volcanic Emissions Using the GOME-2 Instrument, Ph. D. thesis, Institute of Environmental Physics, University of Heidelberg, 2013.

5 Kelly, P. J., Kern, C., Roberts, T. J., Lopez, T., Werner, C., and Aiuppa, A.: Rapid chemical evolution of tropospheric volcanic emissions from Redoubt Volcano, Alaska, based on observations of ozone and halogen-containing gases, *J. Volcanol. Geoth. Res.*, 259, 317–333, doi:10.1016/j.jvolgeores.2012.04.023, 2012.

10 Kern, C.: Spectroscopic measurements of volcanic gas emissions in the ultra-violet wavelength region, Ph.D. Thesis, Institute of Environmental Physics, University of Heidelberg, 2009.

Kraus, S.: DOASIS, A Framework Design for DOAS, Ph.D. Thesis, University of Mannheim, 2006.

15 Meller, R. and Moortgat, G. K.: Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 K in the wavelength range 225–375 nm, *J. Geophys. Res-Atmos.*, 105, 7089–7101, doi:10.1029/1999JD901074, 2000.

Menyailov, I. A.: Prediction of eruptions using changes in composition of volcanic gases, *B. Volcanol.*, 39, 112–125, doi:10.1007/BF02596951, 1975.

Noguchi, K. and Kamiya, H.: Prediction of volcanic eruption by measuring the chemical composition and amounts of gases, *B. Volcanol.*, 26, 367–378, doi:10.1007/BF02597298, 1963.

20 Oppenheimer, C., Tsanev, V. I., Braban, C. F., Cox, R. A., Adams, J. W., Aiuppa, A. Bobrowski, N., Delmelle, P., Barclay, J., and McGonigle, A. J. S.: BrO formation in volcanic plumes, *Geochim. Cosmochim. Ac.*, 70, 2935–2941, doi:10.1016/j.gca.2006.04.001, 2006.

25 Pennisi, M. and Le Cloarec, M.-F.: Variations of Cl, F, and S in Mount Etna's plume, Italy, between 1992 and 1995, *J. Geophys. Res-Sol Ea.*, 103, 5061–5066, doi:10.1029/97JB03011, 1998,.

Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy – Principles and Applications, Physics of Earth and Space Environments, 1st edn., Springer, Berlin, Heidelberg, New York, 597 pp., 2008.

30 Salerno, G. G., Burton, M. R., Oppenheimer, C., Caltabiano, T., Tsanev, V. I., and Bruno, N.: Novel retrieval of volcanic SO₂ abundance from ultraviolet spectra, *J. Volcanol. Geoth. Res.*, 181, 141–153, doi:10.1016/j.jvolgeores.2009.01.009, 2009.

Vandaele, A. C., Hermans, C., Simon, P. C., Carleer, M., Colin, R., Fally, S., Merienne, M., Jenouvrier, A., and Coquart, B.: Measurements of the NO₂ absorption cross-section from

42 000 cm⁻¹ to 10 000 cm⁻¹ (238–1000 nm) at 220 K and 294 K, J. Quant. Spectrosc. Ra., 59, 171–184, 1998.

Vandaele, A. C., Hermans, C., and Fally, S.: Fourier transform measurements of SO₂ absorption cross sections: I I.: Temperature dependence in the 29 000–44 000 cm⁻¹ (227–345 nm) region, J. Quant. Spectrosc. Ra., 110, 2115–2126, doi:10.1016/j.jqsrt.2009.05.006, 2009.

Vogel, L., Sihler, H., Lampel, J., Wagner, T., and Platt, U.: Retrieval interval mapping: a tool to visualize the impact of the spectral retrieval range on differential optical absorption spectroscopy evaluations, Atmos. Meas. Tech., 6, 275–299, doi:10.5194/amt-6-275-2013, 2013.

von Glasow, R.: Atmospheric chemistry in volcanic plumes, P. Natl. Acad. Sci. USA, 107, 6594–6599, 2010.

Wagner, T., Beirle, S., and Deutschmann, T.: Three-dimensional simulation of the Ring effect in observations of scattered sun light using Monte Carlo radiative transfer models, Atmos. Meas. Tech., 2, 113–124, doi:10.5194/amt-2-113-2009, 2009.

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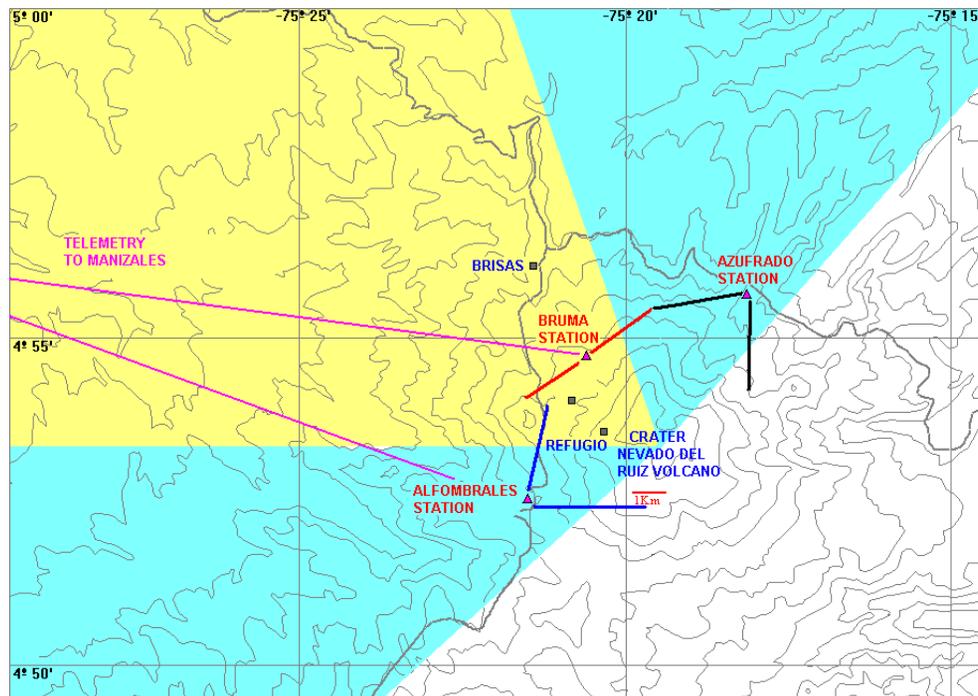


Fig. 1. Topographic map (contour levels every 200 m, the upper contour level is at 5200 m, Bruma station is at 4800 m a.s.l.) showing the location of Nevado del Ruiz volcano (Colombia) and the three NOVAC stations used for gas monitoring. The blue, red and black lines depict the viewing directions of the scanning DOAS systems. The two original instruments at Alfombrales Station and Bruma Station were installed in November 2009 and transmit data in real time to the volcanological observatory located at Manizales city. The third instrument at Azufrado Station was installed in May 2012; its data is not included in this paper. The yellow background colour shows the wind direction for approximately 70 % of the time, the light blue shaded area shows the wind-direction for the remaining 30 %.

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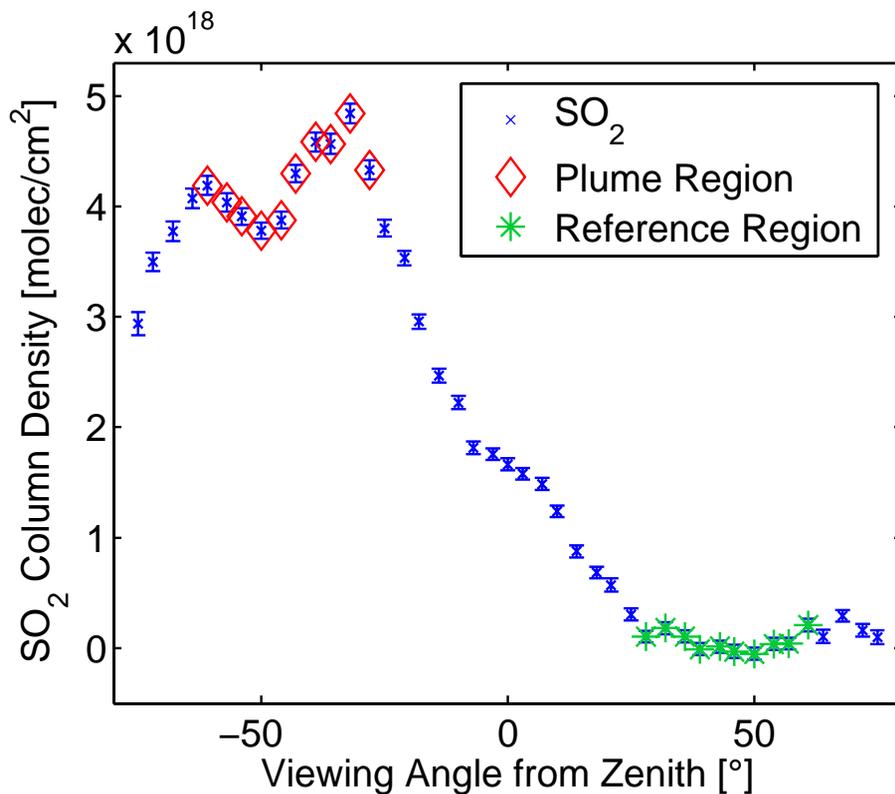


Fig. 2. Example of the SO₂ column densities from one complete scan (−75° – zenith – +75° elevation angle, measured clockwise when looking towards the volcano). The red diamonds show the column densities defining the volcanic plume region, while the green asterisks show the column densities defining the reference region.

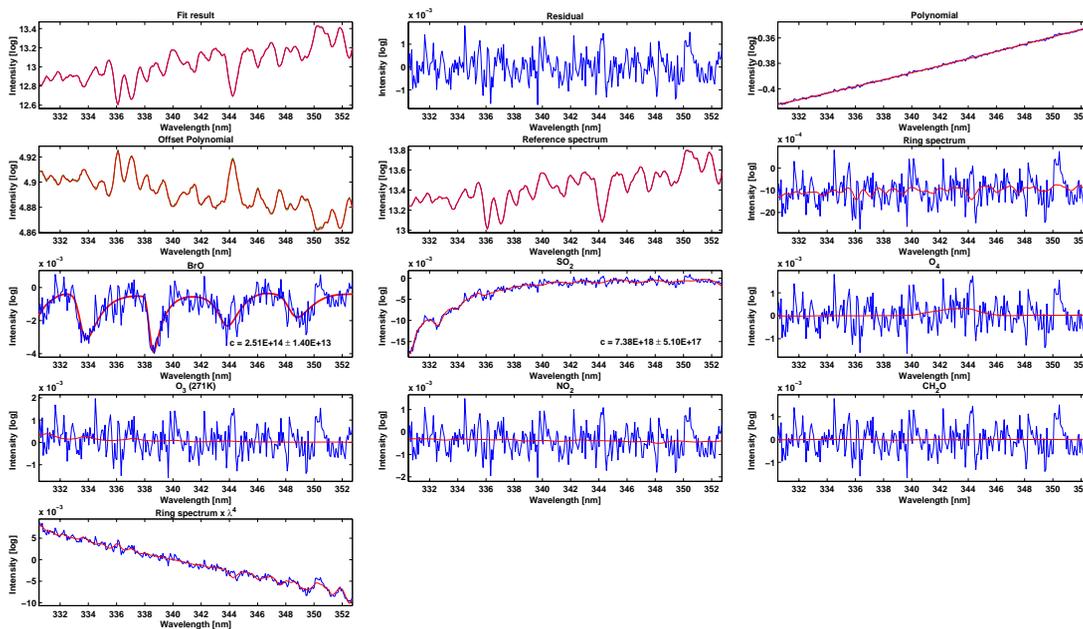


Fig. 3. Example of a DOAS BrO evaluation performed in the wavelength range of 330.6 nm – 352.75 nm. The red lines show the fit, the blue lines the measurement data. A reference spectrum and two Ring spectra were included in the DOAS fit. The BrO column density is 2.51×10^{14} [molecules cm⁻²]. Besides BrO, other trace gases (SO₂, O₄, O₃, NO₂, and CH₂O) were included in the DOAS evaluation. The spectra recorded for this example were recorded on 31.10.2012 between 16:32 and 17:05 GMT.

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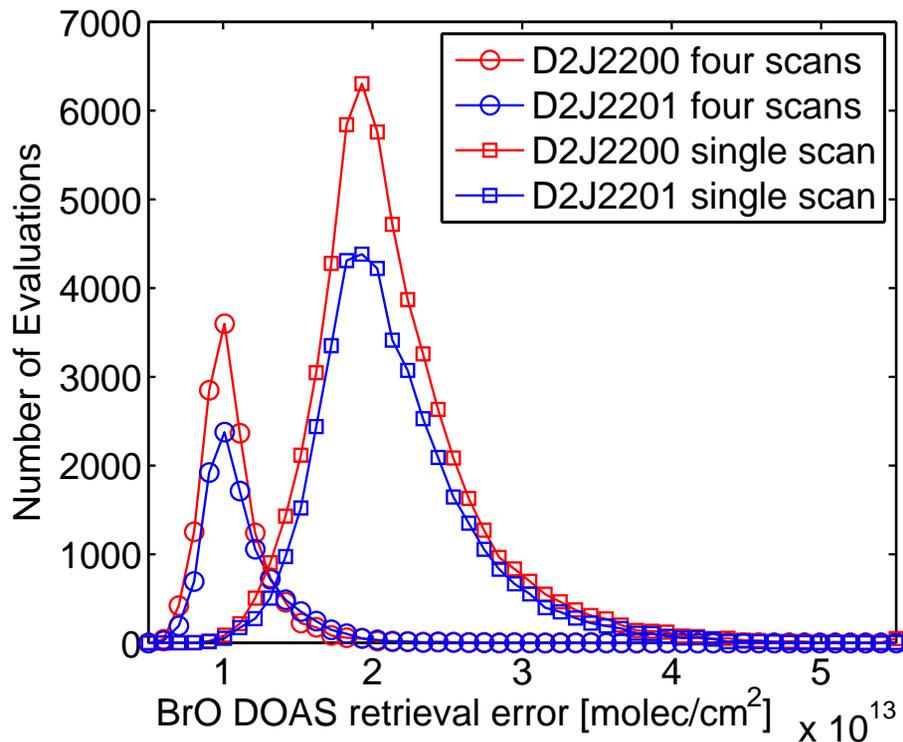


Fig. 4. The BrO DOAS fit errors for both instruments which data is presented in this study. The plot shows the results for spectra from single scans and for spectra co-added from 4 consecutive scans. The latter have a 50 % lower BrO DOAS fit error than single scans.

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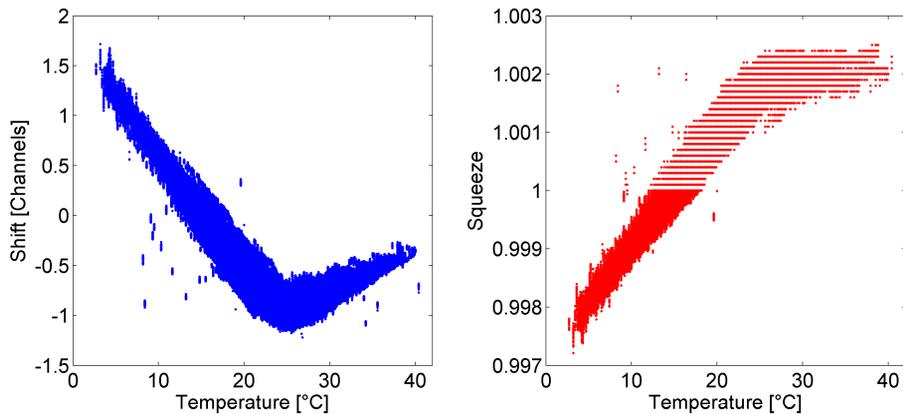


Fig. 5. Shift and squeeze for a DOAS fit only containing one reference spectrum with an instrument temperature of 15 °C. For this plot half a year of data was evaluated. It can be clearly seen, that the instrument pixel-to-wavelength alignment is influenced by changes in the ambient temperature.

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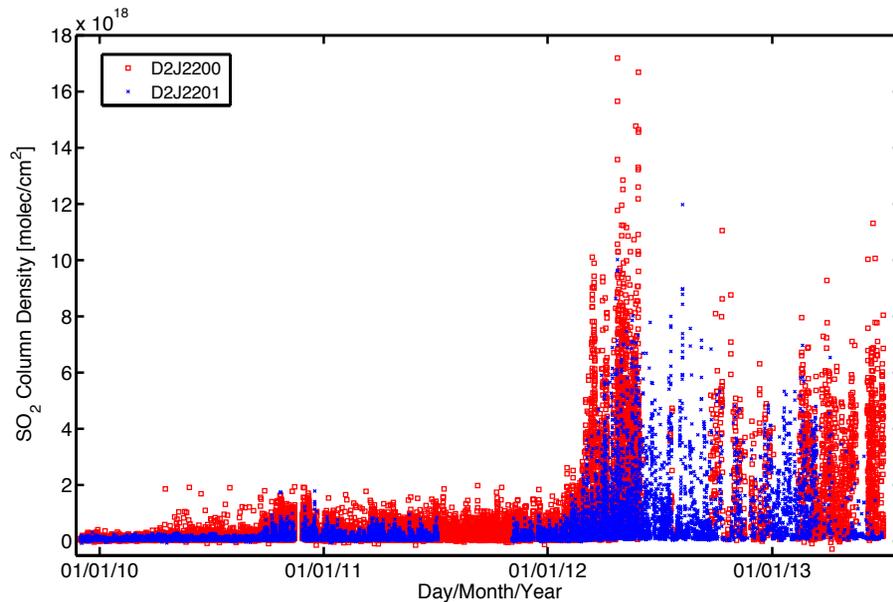


Fig. 6. SO₂ column density time-series from the two instruments at Nevado del Ruiz. The instrument D2J2200 is located in a way that measures elevated SO₂ column density values in most of the cases (see Fig. 1). The spectra evaluated were created from co-adding reference and plume spectra from four consecutive scans.

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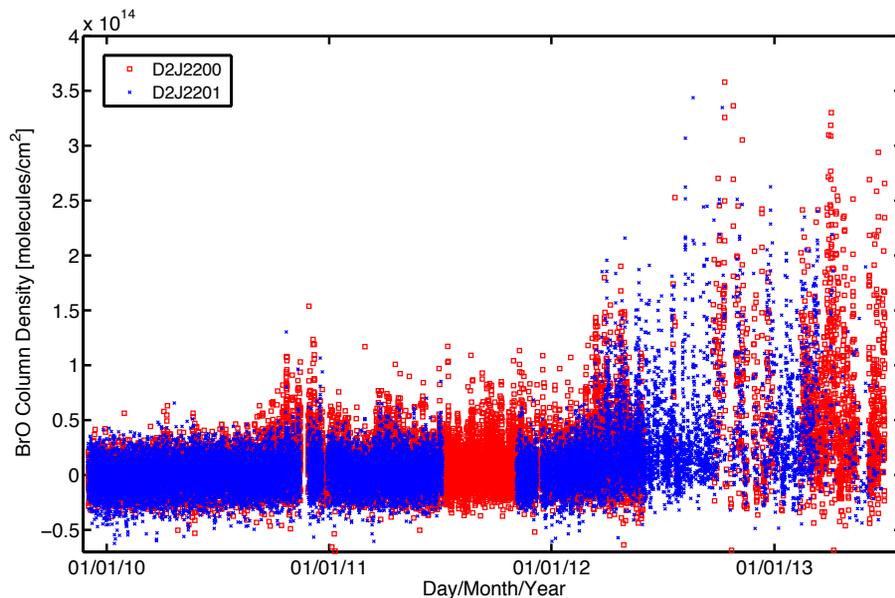


Fig. 7. BrO column densities time-series from the two instruments at Nevado del Ruiz. The spectra evaluated were created from co-adding reference and plume spectra from four consecutive scans.

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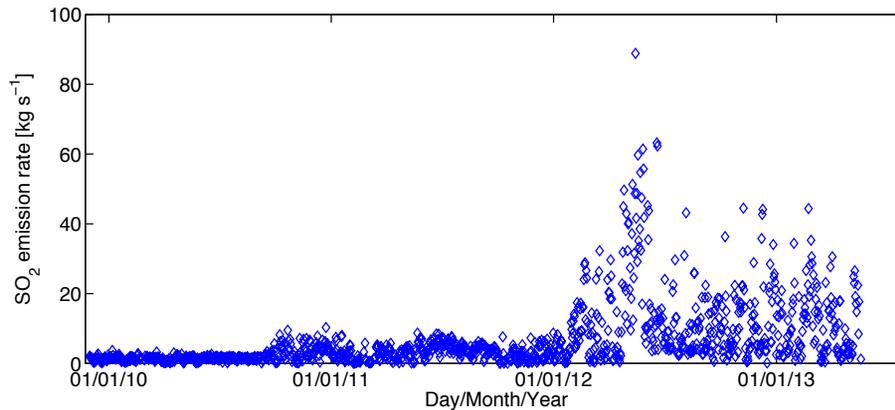


Fig. 8. Daily averages of the SO₂ emission rates. The wind-speed was taken from the ECWMF database, more details in Galle et al. (2010) and Arrellano et al. (2013).

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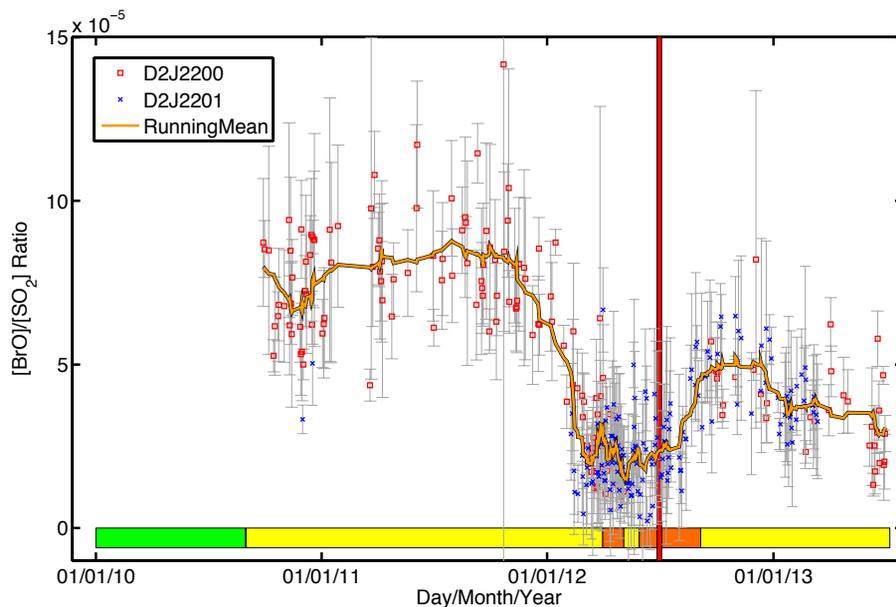


Fig. 9. Daily averages of the BrO/SO₂ molar ratios from Nevado del Ruiz from November 2009–June 2013. The criterion for a valid measurement is a BrO column density above four times the BrO DOAS retrieval error. The ratio drops down to values below 5×10^{-5} , and increases again after the eruption on 30 June 2012 (red vertical bar). Also shown at the bottom of the image is the volcanic activity risk level defined by the Colombian Geological Survey (coloured horizontal bars). The black-orange line shows a running mean around 7 data points (from both instruments).

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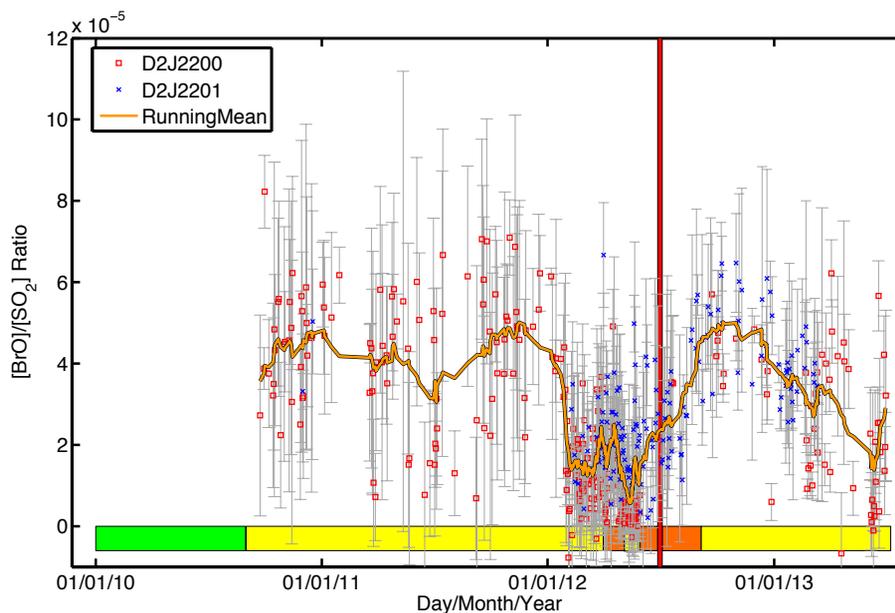


Fig. 10. Daily averages of the BrO/SO₂ molar ratios from Nevado del Ruiz from November 2009–June 2013. For this figure an SO₂ threshold of 7×10^{17} [molecules cm⁻²] was chosen as the criterion for valid data points. The black-orange line shows a running mean around 7 data points (from both instruments).

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