Retrieval advances of BrO/SO2 molar ratios from NOVAC

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Part I
Introduction

Part II
Theoretical Background

1 Volcanism and volcanic chemistry

1.1 Volcanism

1.2 Volcanic degassing

1.3 Volcanic gases and their impact on the climate

1.4 Volcanic plume chemistry

1.5 Sulphur species

1.6 Bromine oxide

1.7 Using volcanic gases to study volcanic activity

2 Remote sensing of volcanic gases

2.1 Absorption spectroscopy

2.2 Beer-Lambert Law

2.3 Scattering processes in the atmosphere

2.4 Differential Optical Absorption Spectroscopy(DOAS)

Part III
Evaluation of the Data of Tungurahua and Nevado Del Ruiz

3 Network for Observation of Volcanic and Atmospheric Change

- funded by European Union, with the aim to establish a global network of stations for the quantitative measurement of volcanic gas emissions
- It started on 1 October, 2005

- initially the network encompassed observatories of 15 volcanoes from five continents, including some of the most active and strongest degassing volcanoes in the world. After the first year 4 more volcanoes was added with additional support from EC
- Although the EU-funding has stopped the NOVAC Network is still active and growing and in January 2012 it consists of 24 volcanoes from 13 countries
- type of instrument: Scanning Dual-beam mini-DOAS
- The Scanning Dual-beam Mini-DOAS instrument represents a major breakthrough in volcanic gas monitoring; it is capable of real-time automatic, unattended measurement of the total emission fluxes of SO_2 and BrO from a volcano.
- Primarily the instruments are used to provide new parameters in the toolbox of the observatories for risk assessment, gas emission estimates and geophysical research on the local scale
- The basic mini-DOAS system consists of a pointing telescope fiber-coupled to a spectrograph. Ultraviolet light from the sun, scattered from aerosols and molecules in the atmosphere, is collected by means of a telescope with a quartz lens defining a field-of-view of 12 mrad.
- The Novac-instruments need to be very robust to stand the conditions around volcanoes. Therefore the design of the instruments is rather simple, this means the instruments do not have internal stabilisation features like temperature stabilization to keep the measurement independent of external parameters (for example Temperature). This comes along with a reduced precision of the data, but the huge amount of data produced by NOVAC compensates this disadvantage.

3.1 Measurement Routine

- The instrument is set up 5-10 km downwind of the volcano, and typically two to four instruments are deployed at each volcano in order to cover different wind directions and to facilitate measurements of plume height and plume direction
- The measurement plane is orthogonal to the plume
- Instruments record spectra in different viewing angle from -90° to 90° (0° is at the zenith).
- First Measurement is a spectra at 0°: The pre reference
- Instrument turns automatically to the side, recording spectra at the Elevation Angle from -90° to 90° with steps of 3°
- One measurement takes about 15 minutes.

4 Evaluation Routine

4.1 NOVAC-Evaluation

Technical implementation of the DOAS approach: Finding reference and plume spectra

- Measurement at the volcano
- DOAS Evaluation
  - choosing a spectra at 0° as pre-reference
  - Evaluate spectra at every viewing angle with the pre-reference
  - to increase the quality and to get a more robust result the sum over several plume and reference spectra is taken.
    * use a gauss fit to detect the plume region
      → if the gauss curve is too wide use only the 10 spectra with the highest SO2 amount
    * use the spectra with the lowest So2 value as reference
- use the reference spectra that are found as described above to fit it on the So2 absorption lines of Gases to get the absolute column densities of SO2 and BrO
- Amount of BrO just slightly above the detection limit → use SO2 to get the position of the plume and the reference
- to increase the fit quality add more than the spectra of one timespan
- Get the BrO/SO2 Ratio

4.2 Contamination Problem

- It might occur that in rare scenarios, the volcanic plume covers the whole scan region.
- In consequence, the reference is contaminated
- Thus the gas amount is underestimated by DOAS.
- This is the case for ca 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.
- One possibility is a volcanic-gas-free reference spectrum recorded in the temporal proximity by the same instrument
- Another alternative spectra is a theoretical solar atlas spectrum (see below) this comes with the drawback of reduced precision

4.3 Evaluation using a Solar Atlas Spectrum

Using a high-resolution solar atlas as a reference spectrum

- An alternative to choose the region with the lowest column density as reference region is to use a theoretical solar atlas spectrum as reference
- a theoretical solar atlas spectrum is far more precise than the spectra of the NOVAC instruments
- The advantage of using a solar atlas spectrum as reference is, that we know that there are no volcanic trace gases, we do not need to assume, that the minimum SO2 amount is zero.
- the disadvantage is, that using a solar atlas spectrum comes along with a drawback of precision since the instrument functions need to be modeled
- 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

5 Limitations for the evaluation of BrO

- Since the SO2 amount in a volcano plume is rather high, the measurement 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
- 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

5.1 BrO Error dependence on external parameters

- The measurement depends on the surrounding conditions like temperature or cloudiness
- 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 the plume is measured, the lower is the BrO error
- The surrounding conditions we take into account are temperature, colorindex, exposure time, elevation-angle and daytime.

5.1.1 Time

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

5.1.2 Temperature

- 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.

$$\rightarrow BrO_{Error} = f(ext.P) + 3.53 \cdot 10^{12} \cdot \frac{\Delta T}{1^\circ} + \mathcal{O}\left(\right) \qquad Tungurahua$$
$$\rightarrow BrO_{Error} = f(ext.P) + 7.56 \cdot 10^{12} \cdot \frac{\Delta T}{1^\circ} + \mathcal{O}\left(\right) \quad NevadoDelRuiz$$

5.1.3 Daytime

- We found a dependency of the BrO error on the daytime. We assume, that this dependency comes from other external parameters which change during the day.
- The BrO Error increases with the daytime differences like:

$$\rightarrow BrO_{Error} = f(ext.P) + 1.33 \cdot 10^{12} \cdot \frac{\Delta DT}{1h} + \mathcal{O}\left(\right) \qquad Tungurahua$$
$$\rightarrow BrO_{Error} = f(ext.P) + 1.58 \cdot 10^{13} \cdot \frac{\Delta DT}{1h} + \mathcal{O}\left(\right) \quad NevadoDelRuiz$$

5.1.4 Colorindex

- The BrO Error increases with the Colorindex differences as

$$\rightarrow BrO_{Error} = f(ext.P) + 1.01 \cdot 10^{13} \cdot \frac{\Delta Cidx}{0.1} + \mathcal{O}\left(\right) \qquad Tungurahua$$
$$\rightarrow BrO_{Error} = f(ext.P) + 4 \cdot 10^{13} \cdot \frac{\Delta Cidx}{0.1} + \mathcal{O}\left(\right) \qquad NevadoDelRuiz$$

5.1.5 Elevation Angle

- 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.

5.1.6 Exposure Time

- The BrO Error increases with the exposure time differences as

$$\begin{aligned}
&\rightarrow BrO_{Error} = f(ext.P) + 1.92 \cdot 10^{12} \cdot \frac{\Delta ET}{10^{-2}s} + \mathcal{O}\left(\right) \qquad Tungurahua \\
&\rightarrow BrO_{Error} = f(ext.P) + 1.0 \cdot 10^{13} \cdot \frac{\Delta T}{10^{-2}s} + \mathcal{O}\left(\right) \qquad NevadoDelRuiz
\end{aligned}$$

6 Method

6.1 Fit data

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

6.2 Other approaches

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

6.2.1 Nearest neighbours

- Description of the Nearest Neighbours Method

6.2.2 Iterative

- Description of the iterative Method

7 Comparison with NOVAC Evaluation

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

8 Issues of our method

Interpretation of the BrO/SO2 ratio time-series

8.1 Tungurahua

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8.2 Nevado Del Ruiz

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9 Problems

9.1 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.

10 Conclusion

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