Annual BrO/SO$_2$ variations in the volcanic gas plume of Nevado del Ruiz

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Nevado del Ruiz volcano (4°53’N, 75°19’W, Colombia) has become infamous for its eruption in 1985 which caused 25000 causalities. Since 2010, Nevado del Ruiz exhibits a new and still ongoing period of activity accompanied by strong gas emissions. On June 30 2012, major phreatomagmatic explosions occurred. Since 2009, Nevado del Ruiz is part of the Network for Observation of Volcanic and Atmospheric Change (NOVAC). The NOVAC data provides the possibility for deriving semi-continuous (at daytime only) time-series of the slant column densities (SCD) of SO$_2$ and BrO in the volcanic gas plume. We present and discuss the BrO/SO$_2$ molar ratios in the volcanic gas plume of Nevado del Ruiz from December 2009 until late 2017. Variation of the BrO/SO$_2$ ratio can be caused by atmospheric chemistry and/or by volcanic activity changes.

The SO$_2$-SCDs have been below $1 \cdot 10^{18}$ molec cm$^{-2}$ after the NOVAC instruments had been installed until September 2010, have been up to $3 \cdot 10^{18}$ molec cm$^{-2}$ between September 2010 and early 2012, have increased in the first half of 2012 to extreme values of up to $24 \cdot 10^{18}$ molec cm$^{-2}$ prior to the explosions on June 30 2012, and vary at still extreme levels of $8 - 16 \cdot 10^{18}$ molec cm$^{-2}$ since July 2012. The BrO-SCDs have been up to $2 \cdot 10^{14}$ molec cm$^{-2}$ after the NOVAC instruments had been installed until early 2012, have increased to $3 \cdot 10^{14}$ molec cm$^{-2}$ prior to the explosions on June 30 2012, and vary between $3 - 7 \cdot 10^{14}$ molec cm$^{-2}$ since July 2012.

Despite the large changes in SO$_2$-SCDs and BrO-SCDs, the time series of the BrO/SO$_2$ molar ratios shows only few discontinuities but a linear trend and a periodic pattern. The mean BrO/SO$_2$ molar ratio increased with a linear trend of $0.4 \cdot 10^{-5}$ per year from $2 \cdot 10^{-5}$ in late 2010 to $5 \cdot 10^{-5}$ in late 2017. The trend has been superimposed by a periodic pattern which has been identified as an interference of an annual cyclicity and a semi-annual cyclicity. This pattern has a minimum every year in July and a maximum every year in October, each with amplitudes of $1.5 \cdot 10^{-5}$. For comparison, the residual (after subtracting trend and periodic pattern) time series has a standard deviation of $1.8 \cdot 10^{-5}$. Furthermore, the residual time series has a drop of $2 \cdot 10^{-5}$ between January and May 2012. This drop has been discussed by Lübcke et al. (2014) as a possible precursor of the magmatic crisis in June 2012. Another drop by $3 \cdot 10^{-5}$ has been observed between May and October 2014. This drop has been followed by enhanced seismic activity and thermal anomalies in November 2014. A drop in mid 2013 and a peak in mid 2017, both with an amplitude of $2 \cdot 10^{-5}$, have not yet been assigned to a possible volcanic origin.