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Six years of BrO/SO2 molar ratios in the volcanic gas plume of Masaya

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The Network for Observation of Volcanic and Atmospheric Change (NOVAC) monitors the SO_2 and BrO emissions of more than 40 volcanoes using scanning UV spectrometers. The volcanic gas emissions are retrieved from the recorded spectra by applying Differential Optical Absorption Spectroscopy (DOAS). We present semi-continuous (only during daytime) time series of the slant column densities (SCDs) of SO_2 and BrO as well as of the calculated BrO/SO_2 molar ratios in the volcanic gas plume of Masaya (Nicaragua, 12°N, 86°W, 635m a.s.l.) from March 2014 until May 2019. The volcanic gas emissions have been significant throughout the overall period, with most of the time SO_2 SCDs of at least $3x10^{18}$ molec/cm^2 and daily maximum BrO SCDs of at least $2x10^{14}$ molec/cm^2. The BrO/SO_2 molar ratios varied between 1-10x10^{-5}. Two major patterns have been observed in the BrO/SO_2 time series: (1) An annual periodicity with an amplitude of about $2x10^{-5}$ and (2) a step increase in the periodicity corrected data in late 2015 from an annual mean of $2.7x10^{-5}$ until mid 2016 to $4.1x10^{-5}$ from late 2015 on (the actual increase is not observed due to a data gap). The step increase coincides with the formation of a shallow lava lake and is thus most likely caused by a change in the magmatic system. A comparison of the BrO/SO_2 data with meteorological data from the ECMWF forecast model indicates an anti-correlation between BrO/SO_2 molar ratios and the specific humidity (correlation coefficient of -38%) and a similar annual cyclicity as the ozone background concentration (though accompanied by a low correlation coefficient of +17%). The annual periodicity in the BrO/SO_2 time series may thus be caused by atmospheric effects. Furthermore, no systematic dependency between the BrO/SO_2 molar ratios and the atmospheric plume age has been observed for an age range of 1-12min after the release from the volcanic edifice indicating an early stop of the autocatalytic, partial transformation of bromide solved in aerosol particles to atmospheric BrO (the so called "bromine explosion"). As a possible direct causality, high humidity levels may have diluted the bromide concentration in the aerosols and thus the bromine explosion would have been humidity limited in these cases. Alternatively, the humidity variations may be just a proxy for coinciding variations in other meteorological parameters such as the position of the ITCZ which affects e.g. the ozone background and the irradiation conditions.

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