

Retrieval advances of BrO/SO₂ molar ratios from NOVAC

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4 Network for Observation of Volcanic and Atmospheric Change

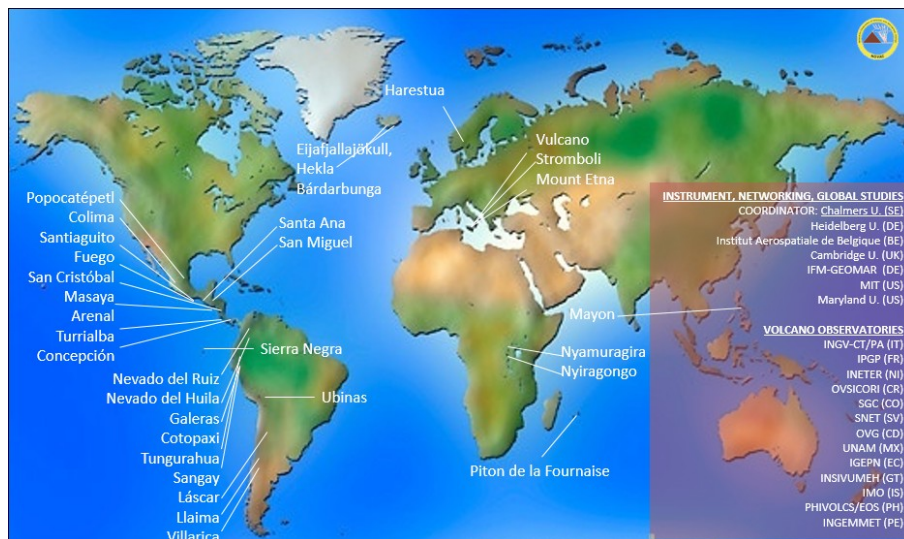


Figure 4.1: Global map of the volcanoes monitored by NOVAC. Used with friendly permission of Santiago Arellano.

The Network for Observation of Volcanic and Atmospheric Change (NOVAC) is a network of instruments monitoring volcanoes over the whole world. NOVAC was installed to gain another tool for risk assessment, for gas emissions and geophysical researches.

NOVAC was originally funded by the European Union on the first October in 2005. The aim of NOVAC is to establish a global network of stations for the quantitative measurement of volcanic gas emissions. At the beginning, NOVAC encompassed observatories of 15 volcanoes in Africa America and Europe, including some of the most active and strongest degassing volcanoes in the world. Although the EU-funding has stopped, the network has been constantly growing since it was founded. In 2017 more than 80 instruments are installed at over 30 volcanoes in more than 13 countries. Figure 4.1 shows a map, with all volcanoes of the Network for Observation of Volcanic and Atmospheric Change.

The great advantage of the data monitored in NOVAC is the fact that NOVAC provides continues gas emission data over many years. This ensures statistically meaningful results for the data evaluation.

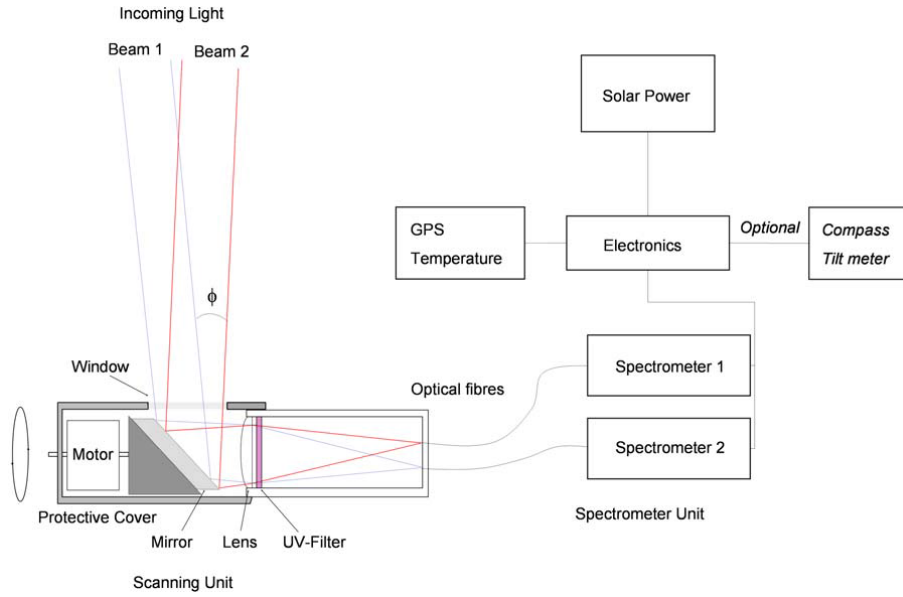


Figure 4.2: schematic sketch of a NOVAC instrument. From [Galle et al. \[2010\]](#)

The instruments used in NOVAC are scanning UV-spectrometer named Mini Doas instruments.

The Mini DOAS instrument represents a major breakthrough in volcanic gas monitoring as it is capable of real-time semi-continuous unattended measurement of the total emission fluxes of SO_2 and BrO from a volcano. Semi-continuous in this case means that the measurement is only possible during daytime and if the sunlight is sufficient.

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. **NOV**

The spectrometers measure in the UV region in a wavelength range of 280 to 420 nm. In this range the differential structures of SO_2 and BrO are dominant.

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.

This comes with a reduced precision of the data, but the huge amount of data produced by NOVAC compensates for this limitation.

4.1 Measurement Routine

The instruments are set up five to ten km downwind of the volcano. To cover most of the occurring wind directions two to five instruments are installed at each vol-

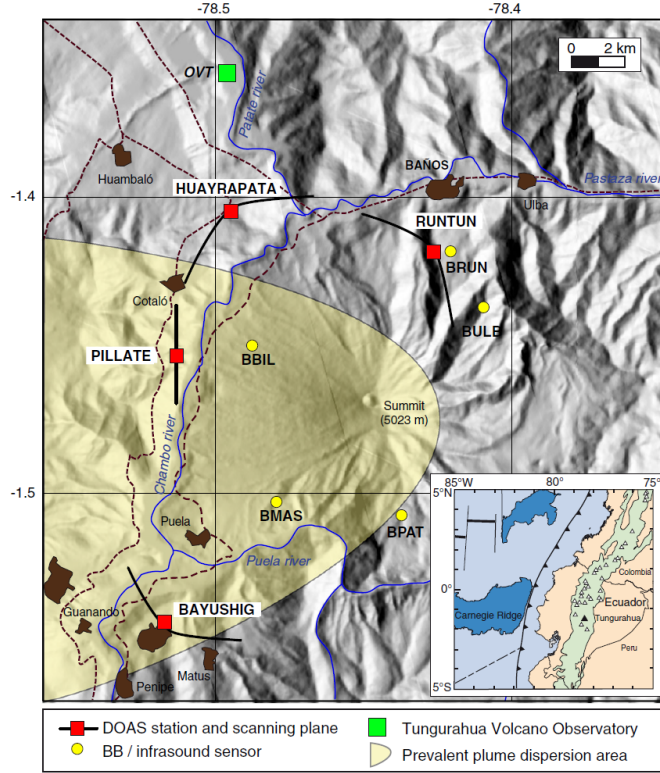


Figure 4.3: Topographic Map of the Tungurahua Volcano. The predominant plume direction is shaded in yellow. Four NOVAC stations are shown as red squares, the corresponding scanning geometry is sketched with black lines. From [Hidalgo et al. \[2015\]](#).

cano. Ideally, the measurement plane is orthogonal to the plume, to get the best measurement results. In reality, the measurement plane might be rotated.

For the calculations of gas data from the DOAS retrieval a scan of the Plume and a scan without any volcanic trace gases (reference spectrum) is needed. The is done without any knowledge of the plume location by scanning the whole sky. The measurement routine starts with a spectrum in zenith direction: the pre-reference. The exposure time of the pre-reference will be used for the whole scan. Afterwards, the dark current spectrum is recorded for the correction of the dark current and offset

Then the instrument turns automatically to the side, recording spectra at the elevation angle from -90° to 90° with steps of 3.6° .

The instruments records 53 spectra per Scan, the pre-reference, the dark current spectrum and 51 spectra at different elevation angles. One hole measurement takes 6 to 15 minutes.

B Bibliography

- NOVAC novac-site. <http://www.novac-project.eu/>. Accessed: 2018-01-29.
- Python scikit-learn.org. http://scikit-learn.org/stable/modules/generated/sklearn.linear_model.LinearRegression.html. Accessed: 2018-01-19.
- Nicole Bobrowski, R Von Glasow, A Aiuppa, S Inguaggiato, I Louban, OW Ibrahim, and U Platt. Reactive halogen chemistry in volcanic plumes. *Journal of Geophysical Research: Atmospheres*, 112(D6), 2007.
- JP Burrows, A Richter, A Dehn, B Deters, S Himmelman, S Voigt, and J Orphal. Atmospheric remote-sensing reference data from gome 2. temperature-dependent absorption cross sections of o₃ in the 231 794 nm range. *Journal of quantitative spectroscopy and radiative transfer*, 61(4):509 517, 1999.
- Markus Bussemer. Der ring-effekt: Ursachen und einfluß auf die spektroskopische messung stratosphärischer spurenstoffe. *Diplomathesis, University of Heidelberg*, 1993.
- K Chance and RL Kurucz. An improved high-resolution solar reference spectrum for earth’s atmosphere measurements in the ultraviolet, visible, and near infrared. *Journal of quantitative spectroscopy and radiative transfer*, 111(9):1289 1295, 2010.
- Oliver C Fleischmann, Matthias Hartmann, John P Burrows, and Johannes Orphal. New ultraviolet absorption cross-sections of bro at atmospheric temperatures measured by time-windowing fourier transform spectroscopy. *Journal of Photochemistry and Photobiology A: Chemistry*, 168(1-2):117 132, 2004.
- Bo Galle, Mattias Johansson, Claudia Rivera, Yan Zhang, Manne Kihlman, Christoph Kern, Thomas Lehmann, Ulrich Platt, Santiago Arellano, and Silvana Hidalgo. Network for observation of volcanic and atmospheric change (novac) a global network for volcanic gas monitoring: Network layout and instrument description. *Journal of Geophysical Research: Atmospheres*, 115(D5), 2010.
- Hans-F Graf, Johann Feichter, and Bärbel Langmann. Volcanic sulfur emissions: Estimates of source strength and its contribution to the global sulfate distribution. *Journal of Geophysical Research: Atmospheres*, 102(D9):10727 10738, 1997.
- Minard L Hall, Claude Robin, Bernardo Beate, Patricia Mothes, and Michel Monzier. Tungurahua volcano, ecuador: structure, eruptive history and hazards. *Journal of Volcanology and Geothermal Research*, 91(1):1 21, 1999.

- Martina M Halmer, H-U Schmincke, and H-F Graf. The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years. *Journal of Volcanology and Geothermal Research*, 115(3-4): 511–528, 2002.
- C Hermans, AC Vandaele, S Fally, M Carleer, R Colin, B Coquart, A Jenouvrier, and M-F Merienne. 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 in the atmosphere*, pages 193–202. Springer, 2003.
- Silvana Hidalgo, Jean Battaglia, Santiago Arellano, Alexander Steele, Benjamin Bernard, Julie Bourquin, Bo Galle, Santiago Arrais, and Freddy Vásconez. So₂ degassing at tungurahua volcano (ecuador) between 2007 and 2013: Transition from continuous to episodic activity. *Journal of Volcanology and Geothermal Research*, 298:1–14, 2015.
- IPCC. *Summary for Policymakers*, book section SPM, page 1–30. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013. ISBN ISBN 978-1-107-66182-0. doi: 10.1017/CBO9781107415324.004. URL www.climatechange2013.org.
- Christoph Kern. *Spectroscopic measurements of volcanic gas emissions in the ultra-violet wavelength region*. PhD thesis, 2009.
- Stefan Kraus. *DOASIS: A framework design for DOAS*. Shaker, 2006.
- Peter Lübcke. *Optical remote sensing measurements of bromine and sulphur emissions: Investigating their potential as tracers of volcanic activity*. PhD thesis, 2014.
- Peter Lübcke, Nicole Bobrowski, S Arellano, Bo Galle, G Garzón, Leif Vogel, and U Platt. Br/so₂ molar ratios from scanning doas measurements in the novac network. *Solid Earth*, 5(1):409, 2014.
- Richard Meller and Geert K Moortgat. Temperature dependence of the absorption cross sections of formaldehyde between 223 and 323 k in the wavelength range 225–375 nm. *Journal of Geophysical Research: Atmospheres*, 105(D6):7089–7101, 2000.
- D Perner and U Platt. Detection of nitrous acid in the atmosphere by differential optical absorption. *Geophysical Research Letters*, 6(12):917–920, 1979.
- G Pinardi, MV Roozendael, and C Fayt. The influence of spectrometer temperature variability on the data retrieval of so₂. *NOVAC second annual activity report, NOVAC consortium*, 44:48, 2007.

- U Platt and N Bobrowski. Quantification of volcanic reactive halogen emissions. *Volcanism and Global Change*, eds A. Schmidt, K. Fristad, L. Elkins-Tanton, Cambridge University Press, Cambridge, UK, ISBN, 1466525386, 2015.
- Ulrich Platt and Jochen Stutz. Differential absorption spectroscopy. *Differential Optical Absorption Spectroscopy*, pages 135–174, 2008.
- Alan Robock. Volcanic eruptions and climate. *Reviews of Geophysics*, 38(2):191–219, 2000.
- A Schmidt and A Robock. Volcanism, the atmosphere and climate through time. *Volcanism Glob. Environ. Chang.*, pages 195–207, 2015.
- Anja Schmidt, Kirsten Fristad, and Linda T Elkins-Tanton. Volcanism and global environmental change, 2015.
- Hans-Ulrich Schmincke. *Vulkanismus*. Wissenschaftliche Buchgesellschaft, 3 edition, 2000.
- S Solomon, RW Portmann, RR Garcia, W Randel, F Wu, R Nagatani, J Gleason, L Thomason, LR Poole, and MP McCormick. Ozone depletion at mid-latitudes: Coupling of volcanic aerosols and temperature variability to anthropogenic chlorine. *Geophysical research letters*, 25(11):1871–1874, 1998.
- Susan Solomon, Arthur L Schmeltekopf, and Ryan W Sanders. On the interpretation of zenith sky absorption measurements. *Journal of Geophysical Research: Atmospheres*, 92(D7):8311–8319, 1987.
- Thorvaldur Thordarson and Stephen Self. Atmospheric and environmental effects of the 1783–1784 laki eruption: A review and reassessment. *Journal of Geophysical Research: Atmospheres*, 108(D1), 2003.
- S Twomey. Pollution and the planetary albedo. *Atmospheric Environment (1967)*, 8(12):1251–1256, 1974.
- Ann Carine Vandaele, Christian Hermans, Paul C Simon, Michel Carleer, Réginald Colin, Sophie Fally, Marie-France Merienne, Alain Jenouvrier, and Bernard Coquart. 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. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 59(3-5):171–184, 1998.
- Ann Carine Vandaele, Christian Hermans, and Sophie Fally. Fourier transform measurements of so₂ absorption cross sections: II.: Temperature dependence in the 29 000–44 000 cm⁻¹ (227–345 nm) region. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110(18):2115–2126, 2009.

T Wagner, A Apituley, S Beirle, S Dörner, U Friess, J Remmers, and R Shaiganfar. Cloud detection and classification based on max-doas observations. *Atmospheric Measurement Techniques*, 7(5):1289–1320, 2014.

Simon Warnach. Improvements of bro and so₂ retrievals of novac data - tungurahua volcano as a case study. Master's thesis, 2015.