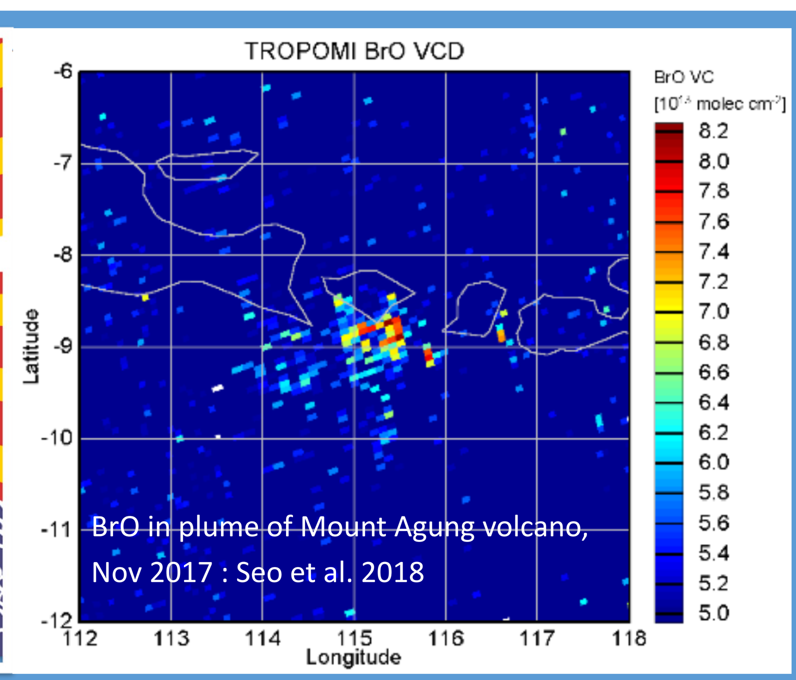
Modelling halogen chemistry of volcanic plumes with WRF-Chem Volcano

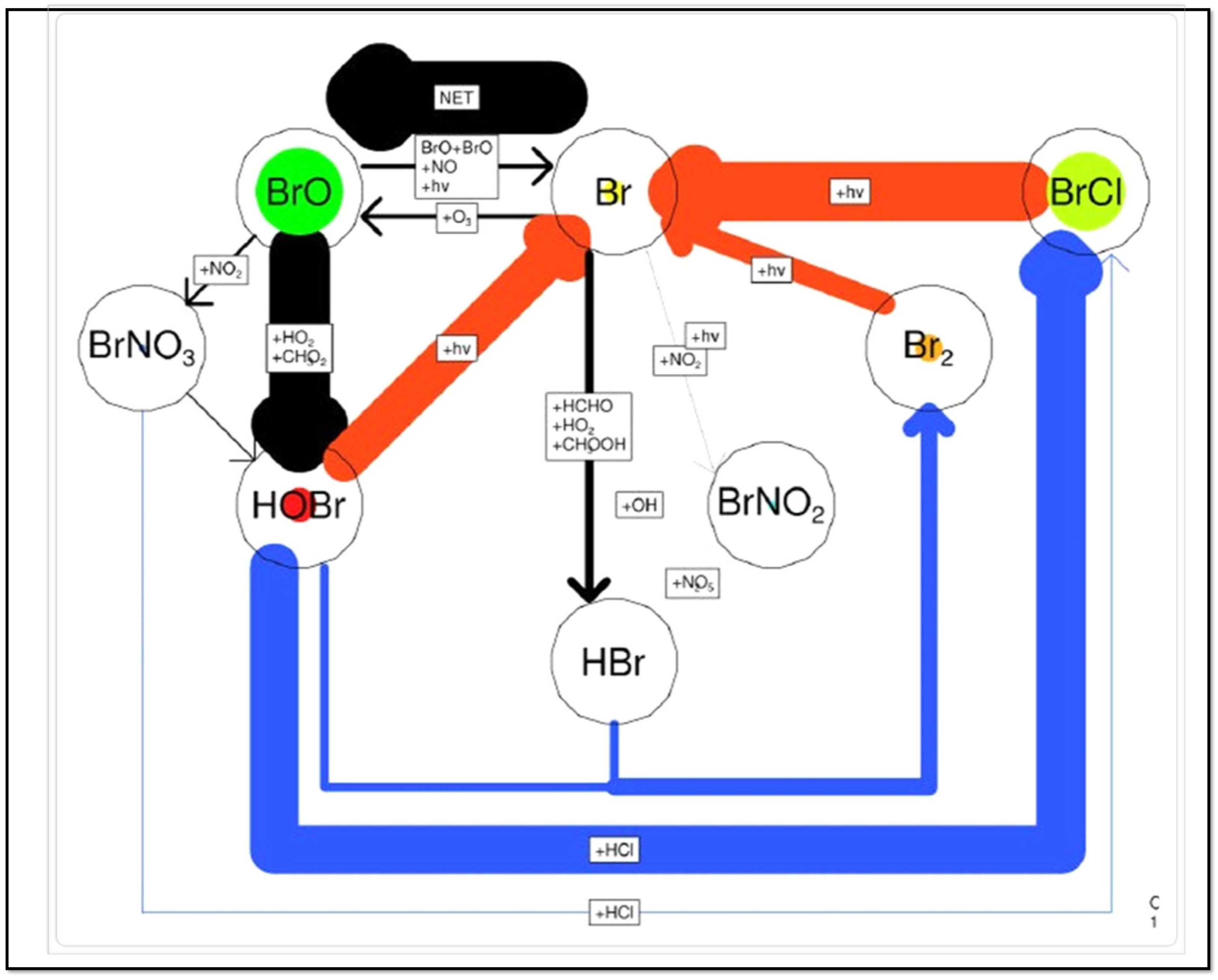
Luke Surl[1,3,4], Tjarda Roberts[1], Slimane Bekki[2]

(1) LPC2E/CNRS, 3A avenue de la recherche scientifique, F4500 Orléans, France, (2) LATMOS/CNRS, 11 Blvd d'Alembert, 78280 Guyancourt, France, (3) LATMOS/CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, France **(luke.surl@latmos.ipsl.fr)** (4) Formerly at: School of Environmental Sciences, University of East Anglia, Norwich, UK



When volcanoes erupt or passively degas, they release a large volume of material into the atmosphere. SO_2, H_2O, CO_2, aerosol (ash and others), and **halogen species** — including **HBr**

Bromine species, in the presence of ozone, acidic aerosol, and sunlight, undergo an autocatalytic, heterogenous and ozone-destructive reaction cycle—the **bromine explosion.**



Evidence of this reaction cycle can be seen in measurements of substantial BrO and increasing ozone depletion within the plume (von Glasow, 2010; Surl et al 2015).

BrO can be observed spectroscopically, from ground-based DOAS and from satellite instruments. TROPOMI is beginning to deliver unprecedented high-resolution observations of volcanic BrO (Seo et al 2018).

Method

This study develops WRF-Chem Volcano (WCV) - a modified version of the WRF-Chem 3D atmospheric chemistry and transport model, to investigate the chemical processes occurring within the plume. The model includes aerosol, bromine, chlorine and mercury chemistry, including photolysis and heterogeneous reactions.

Nesting is used to get a high resolution (1km x 1km) . Tracers are used to precisely determine the age of the plume.

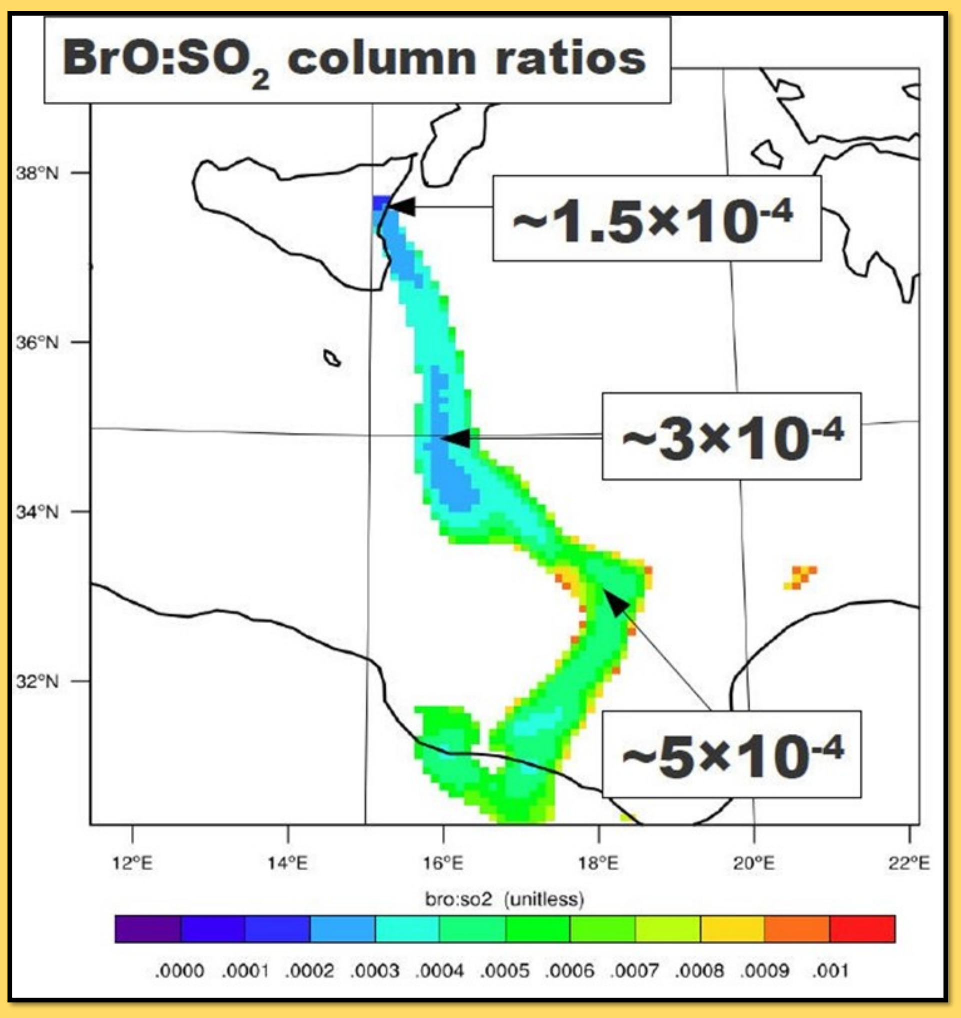
The base case study is a passive degassing of Mount Etna.

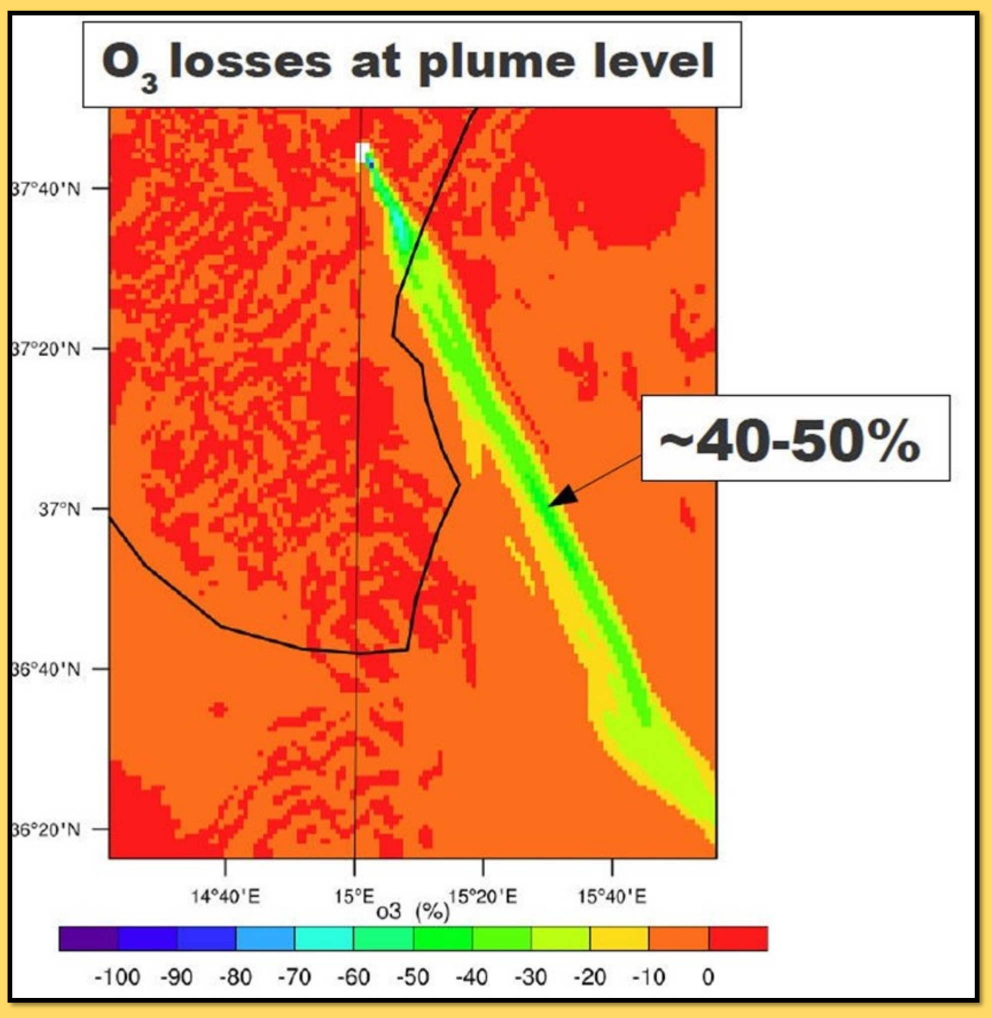
Species	Emission /s
SO_2	60 kg
HCl	14 kg
HBr	35 g
Br	11 g
Aerosol	2.4 kg

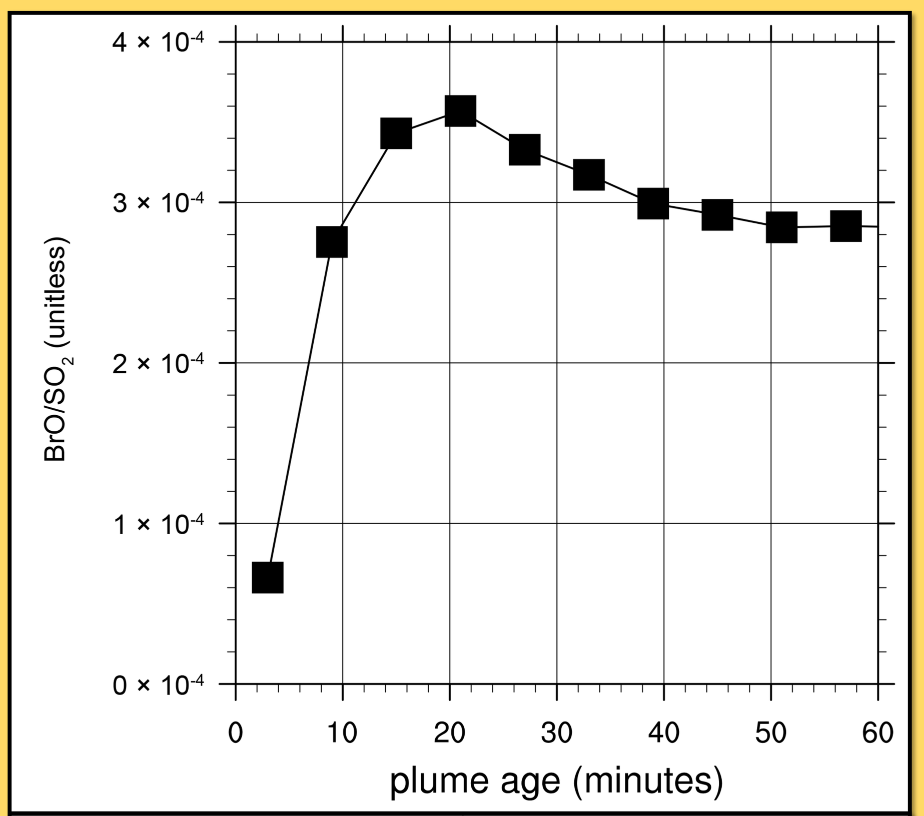
Results

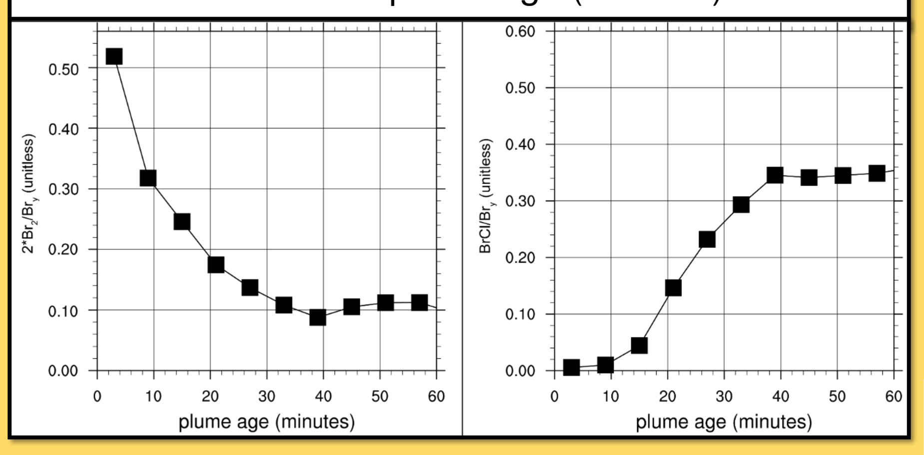
Validation: The model output reproduces observed phenomena:

BrO/SO_2 column ratios of the order 10^{-4}. — Moderate O_3 depletion









Early plume — three phases

0-15 min: HBr is converted into 'reactive bromine', BrO rises.

15-35 min: Switch from Br_2 to BrCl as dominant photolysable reservoir.

35– min: BrCl system.

The resulting BrO/SO_2 ratio vs time trend observations by ground-based DOAS (Bobrowski & Giuffrida ,2012)

The results displayed were generated during Luke Surl's NERC-funded PhD (2011-2015) at the School of Environmental Sciences, University of East Anglia under the supervision of Roland von Glasow with support from Deanna Donohoue.

This fellowship is continuing this work with an upgraded version of WRF-Chem.

The Cycle

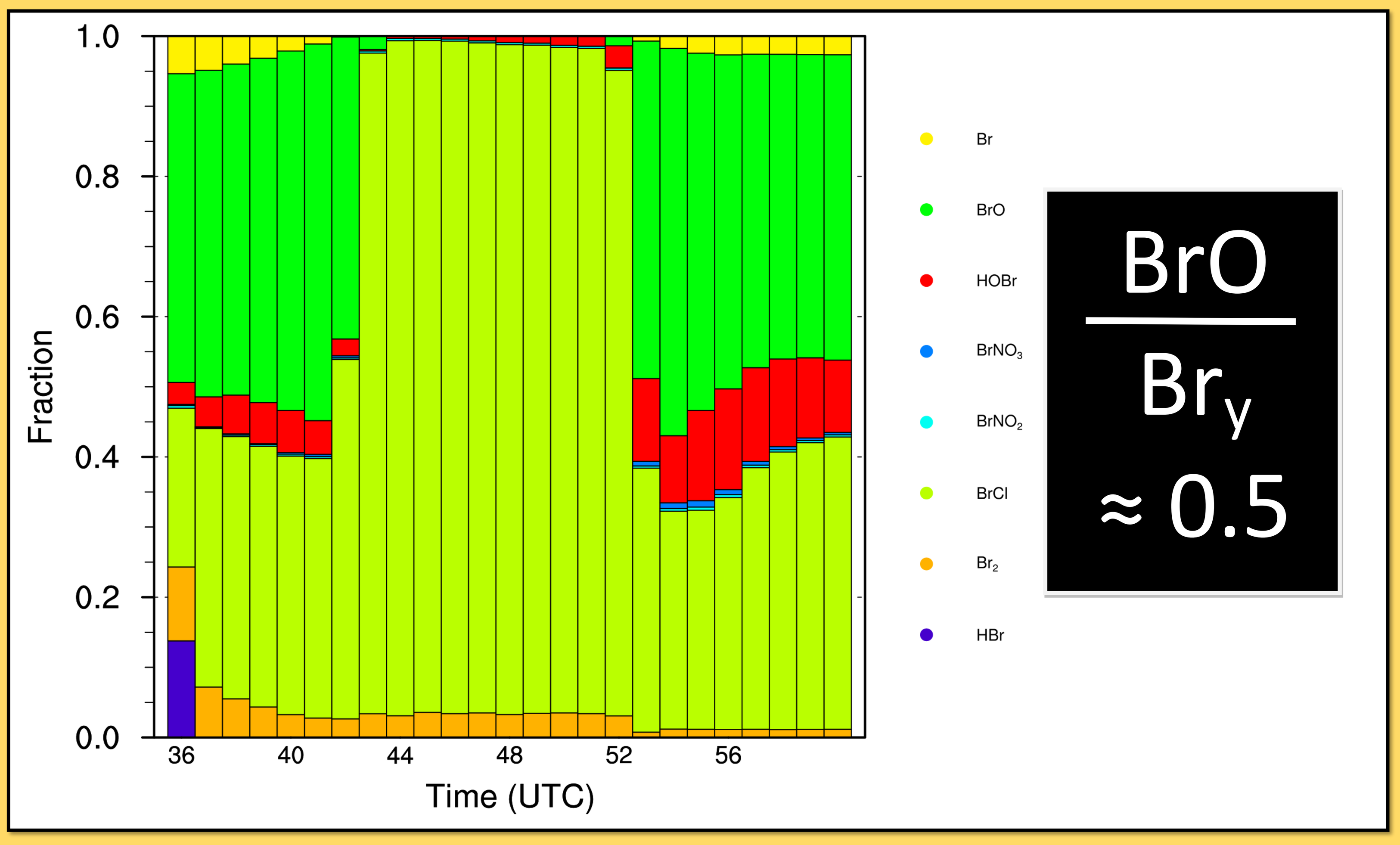
- The bromine cycling quickly subsumes all HBr.
- The HOBr + HCl reaction takes over as the main heterogenous reaction recycling HOBr.
- Photolysis is the rate-limiting step in determining cycling speed (and O_3 loss rate)
- BrCl becomes the main photolysable species.

Br fractionation

Once HBr has been exhausted, Br fractionation is relatively stable during daytime. About **50% exists as BrO**, most of the rest as BrCl.

Suggests for plumes like this, doubling spectroscopic measurements of BrO to give total bromine

During the night BrCl accumulates.



Other findings:

- Primary and secondary aerosol provide an excess of the required surface area for Br cycling
- For denser plumes, a fully-O_3 depleted core forms with little active chemistry within. The chemical phenomena described here occur at the edges
- For emissions at night, chemistry is inactive until sunrise

Seo, S., Richter, A., Blechschmidt, A.-M., Bougoudis, I., and Burrows, J. P.: First high resolution BrO column retrievals from TROPOMI, Atmos. Meas. Tech. Discuss., in review 2018 ● R. von Glasow, Atmospheric chemistry in volcanic plumes, PNAS, 2010, 107 (15) 6594-6599; ● Surl, L., Donohoue, D., Aiuppa, A., Bobrowski, N., and von Glasow, R.: Quantification of the depletion of ozone in the plume of Mount Etna, Atmos. Chem. Phys., 15, 2613-2628, 2015. ● Bobrowski, N & Giuffrida, G. (2012). Bromine monoxide / sulphur dioxide ratios in relation to volcanological observations at Mt. Etna 2006-2009. Solid Earth. 3. 433-445. 10.5194/se-3-433-2012.

This project has received funding from the *European Union's Horizon 2020 research and innovation programme* under grant agreement No 800062

luke.surl@latmos.ipsl.fr