



Using WRF-Chem Volcano to model the in-plume halogen chemistry of Etna's 2018 eruption

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



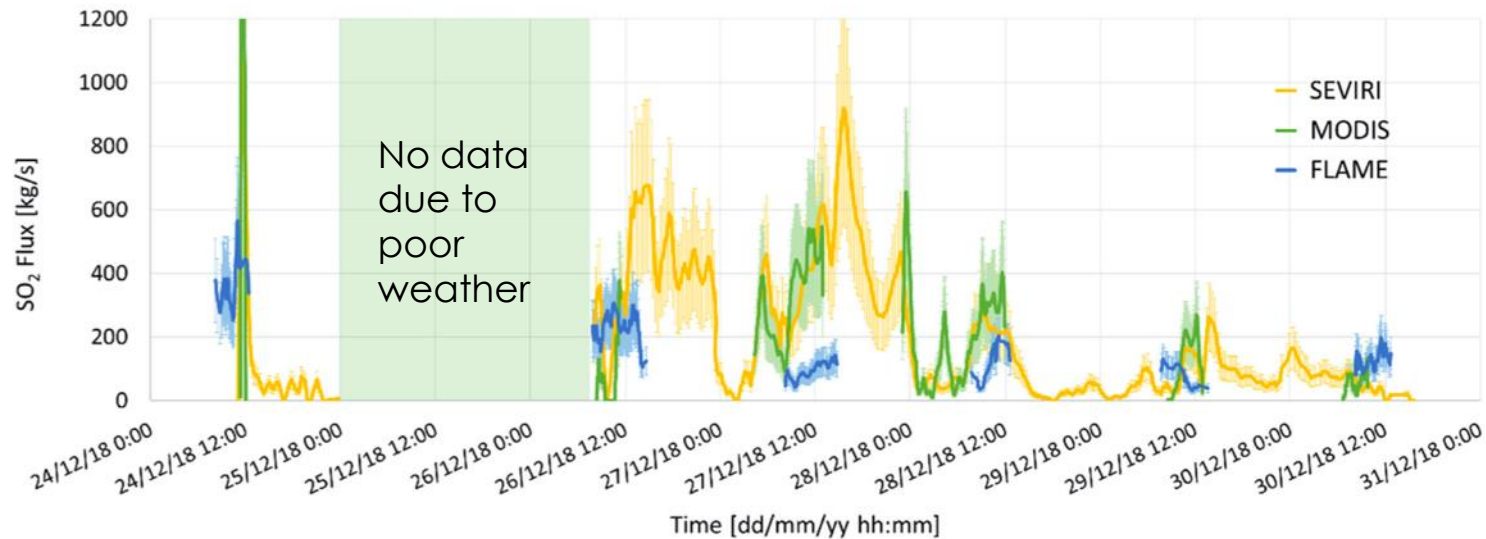
Etna's 2018 Christmas eruption

- VEI 2 flank eruption, beginning in the morning of 2018-12-24



Etna's 2018 Christmas eruption

- Large event at ~1115 the 24th, moderate activity for the next week



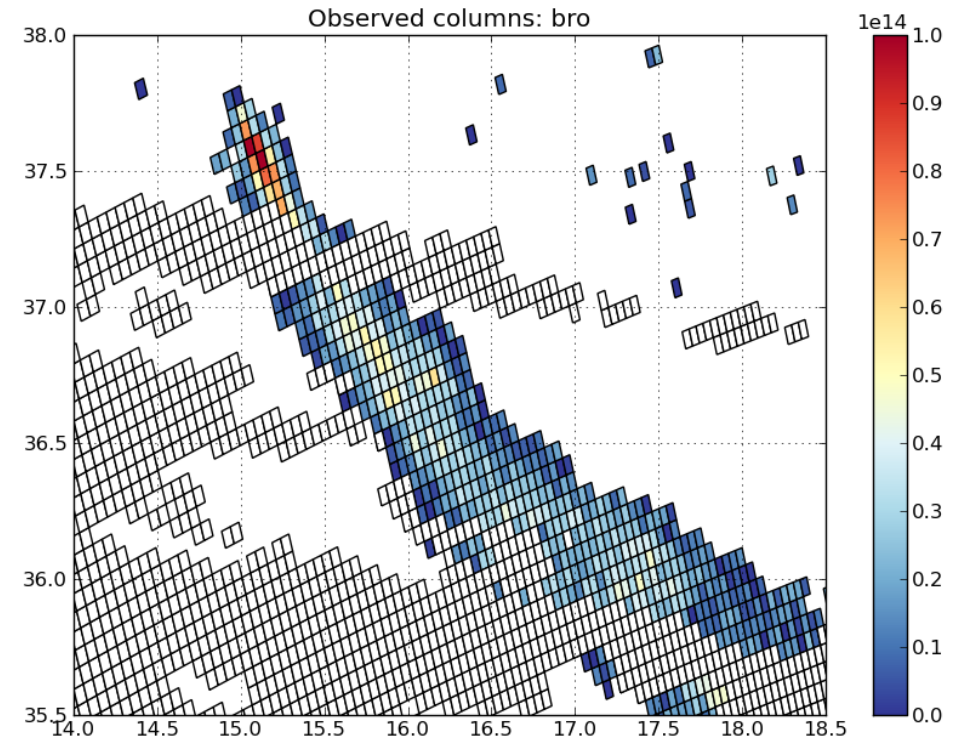
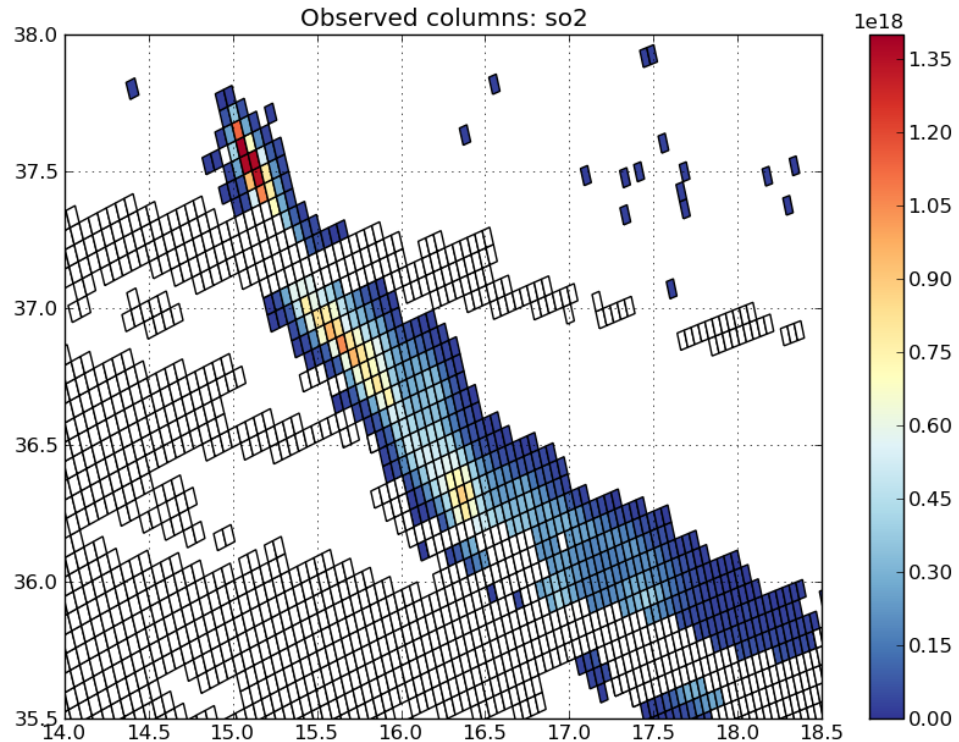
Date December 2018	VPTH [km]
24	8.0
26	4.0
27	4.5
28	5.5
29	4.5
30	4.5

Volcanic Plume Top Height

TROPOMI detection of plume

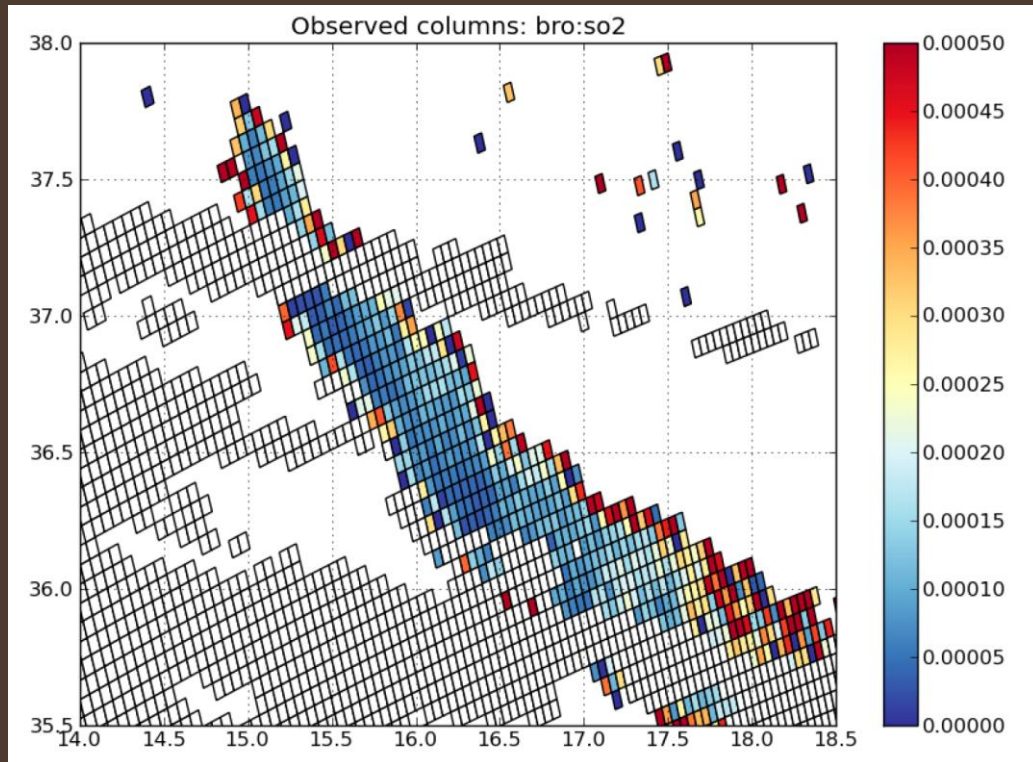
- TROPOMI overpass at ~12h each day.
 - Best observation on the 25th !
- Detect SO₂, BrO and their ratio.
 - BrO/SO₂ ratios common measurement of Br-chemistry in plumes

TROPOMI detection of plume : SO₂, BrO



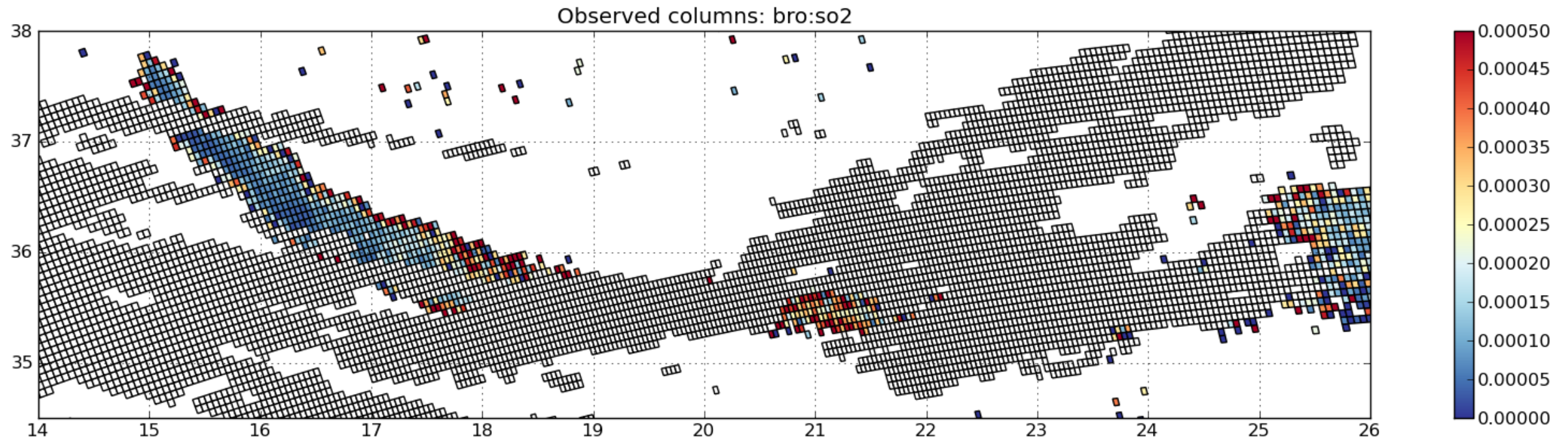
Cloud filter, cloud fraction > 0.5 and top height > 4km. Only pixels with SO2 VCD > 2e16 molec.cm⁻² plotted

TROPOMI detection of plume : BrO/SO₂



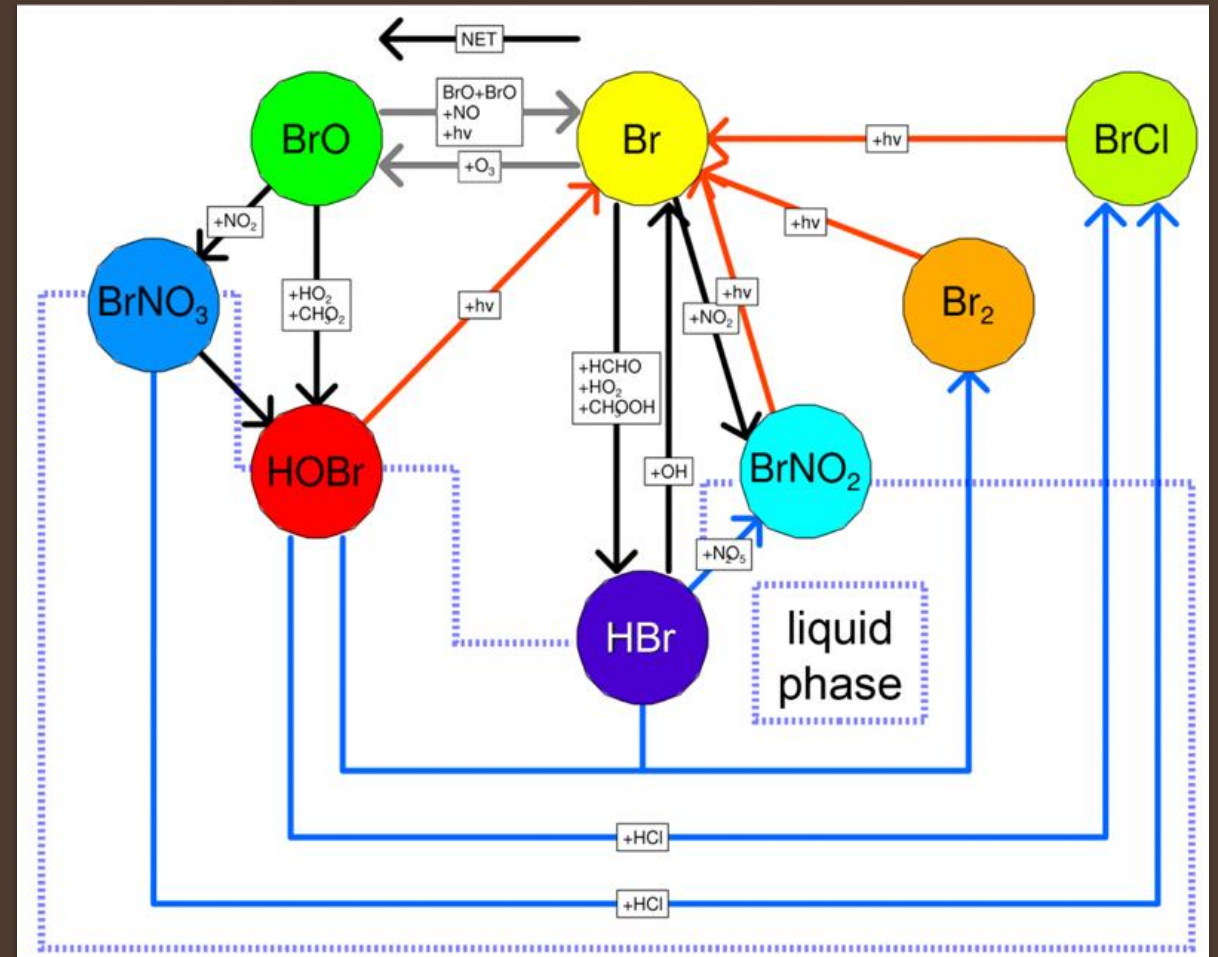
- BrO production
- Across-plume variation.
 - High at edges ($\sim 4 \times 10^{-4}$)
 - "Core" of plume lower values ($\sim 1 \times 10^{-4}$)

TROPOMI detection of plume : BrO/SO₂



Bromine chemistry

- Bromine chemistry – converts HBr to other forms and continually cycles bromine
- Several requirements:
 - Sunlight for photolysis
 - Acidic aerosol for liquid phase steps
 - Oxidants (esp. O_3) for gas-phase reactions
 - Consumes these oxidants
- Heterogenous reaction: HOBr uptake (rate limiting), followed by reaction with Br^- or Cl^- (from aqueous phase HBr or HCl)
 - Br_2 vs. $BrCl$ product ratio dependant on ratio of HBr and HCl. Br_2 production 'preferred' unless bromide mostly depleted.



Can we model this?

- WRF-Chem Volcano (WCV) is our custom version of [WRF-Chem](#) [v4.1.5] that includes:
 - Bromine, chlorine and mercury chemistry in reaction mechanism
 - Volcanic emissions (pre-processed with modified version of [PREPCHEM-SRC](#))
 - On-line calculation of aerosol surface areas and heterogenous reaction rates.
 - Includes calculation of wet area, incorporating aerosol water.
 - Includes gas-phase diffusion limitation of heterogenous reactions
- Run in multiple-nested mode, up to 1 km * 1 km resolution

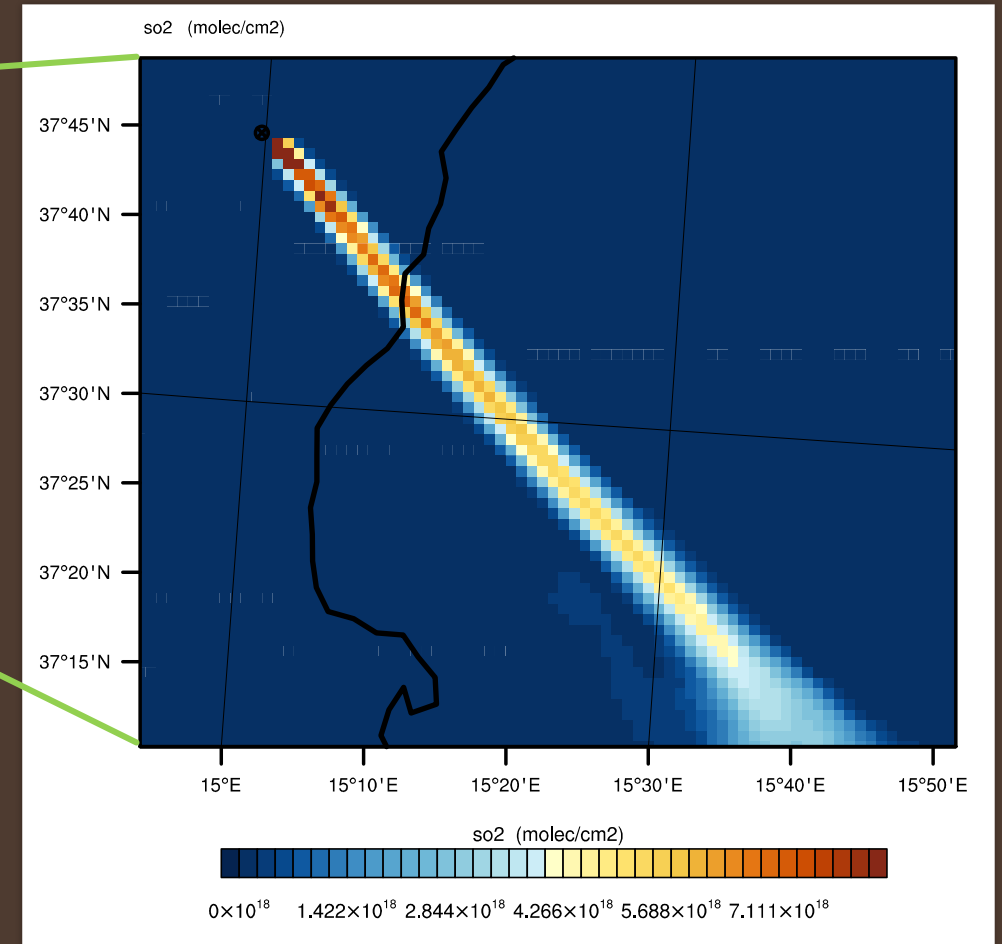
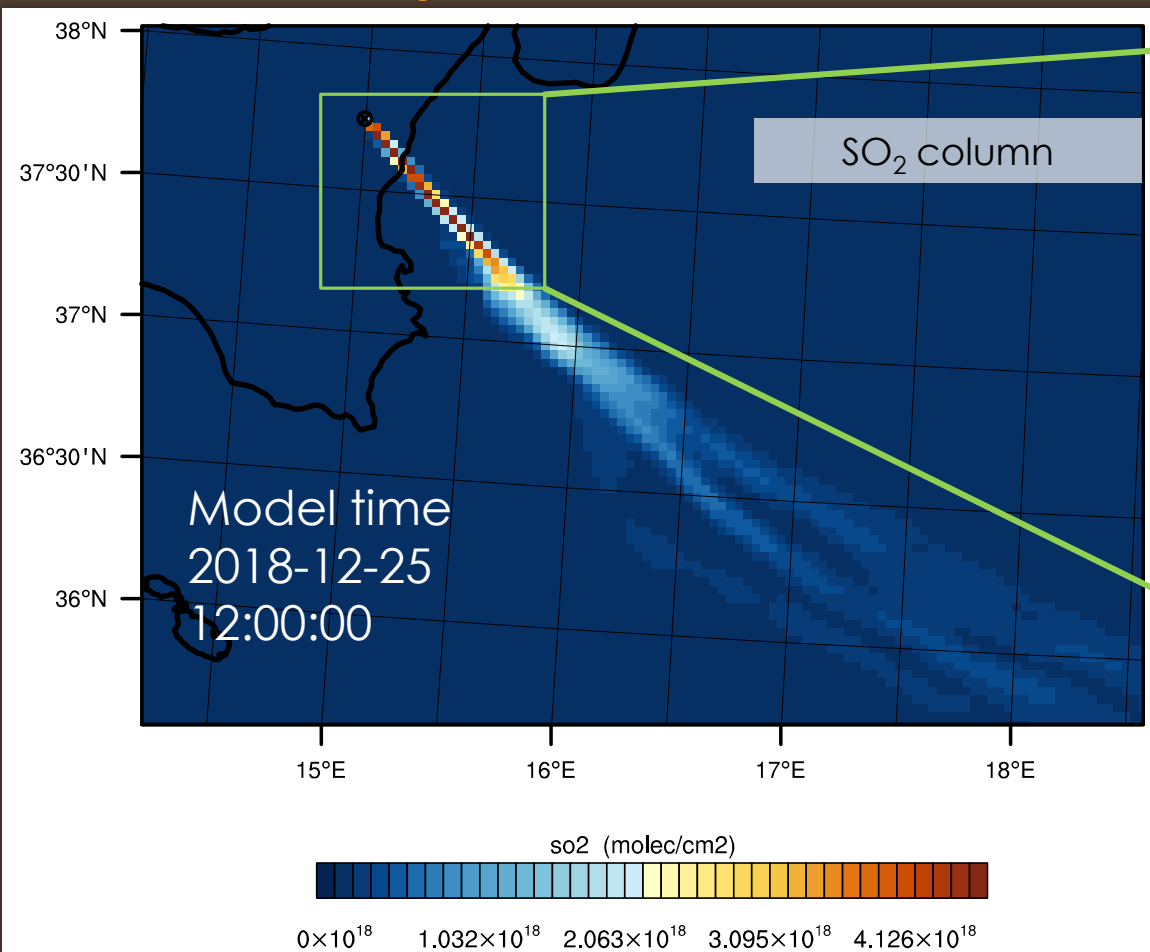
Model setup

- 320 kg SO₂/s flux rate
 - based on inversions from preliminary runs
 - Within range for fluxes estimated for 26th and 27th in Corradini et al.,
- 4 km injection height, into single model layer (317m thick)
- Other species emitted at fixed ratio to SO₂.

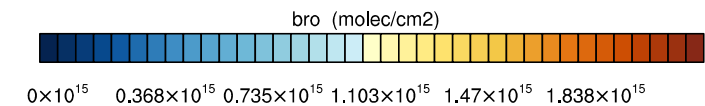
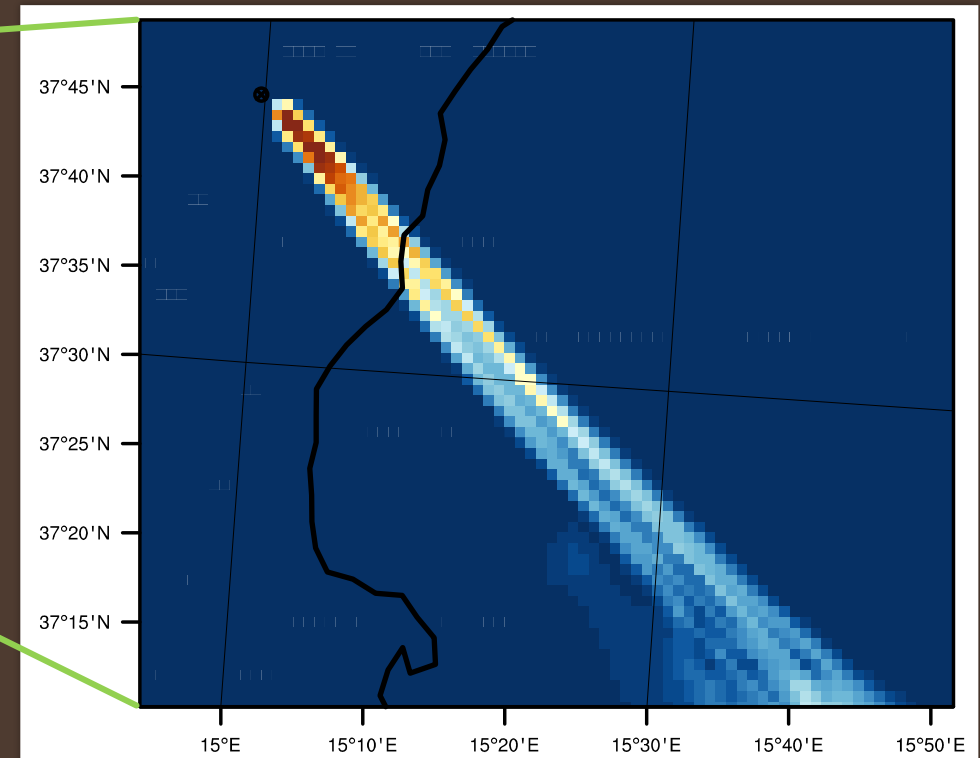
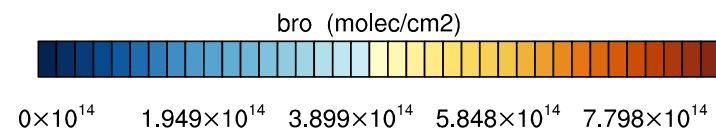
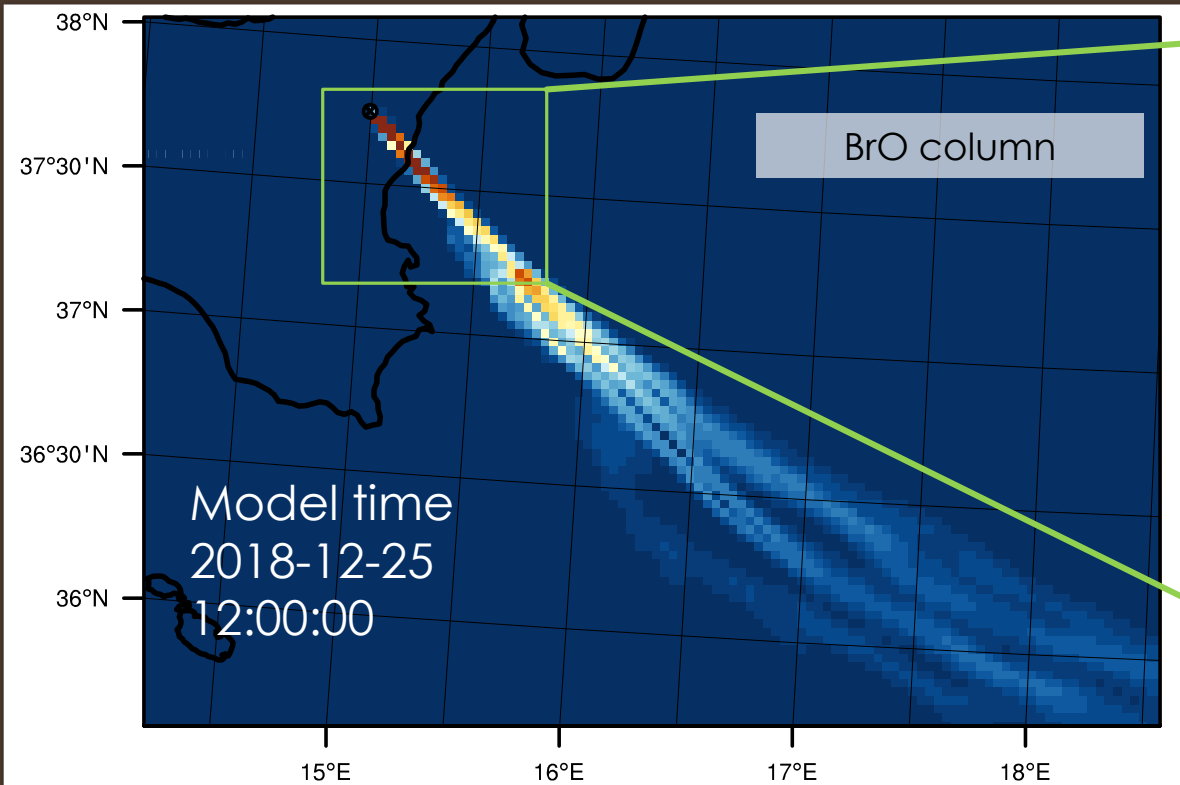
Flux ratio	Value	Notes
<i>molar ratios</i>		
HCl/SO ₂	0.44	Average of ratios at the BN and NEC craters from Wittmer et al. (2014)
Br _{tot} /SO ₂	6.6×10^{-4}	
HBr/Br _{tot}	0.75	as per HSC output used in Roberts et al. (2014)
Br/Br _{tot}	0.25	
OH/SO ₂	0.001	Average for Etnean eruptive periods from Aiuppa et al. (2008)
H ₂ O/SO ₂	15	
Hg/SO ₂	7.8×10^{-6}	Bagnato et al. (2014) (general volcanic value)
<i>mass ratio</i>		
Aerosol/SO ₂	0.03	Roberts et al. (2018) - assumed all sulphate.

Corradini et al. (2020) doi:[10.3390/rs12081336](https://doi.org/10.3390/rs12081336) ; Wittmer et al (2014) doi:[10.1002/2013GC005133](https://doi.org/10.1002/2013GC005133); Roberts et al. (2018) doi:[10.1016/j.gca.2017.09.040](https://doi.org/10.1016/j.gca.2017.09.040); Aiuppa et al. (2008) doi:[10.1029/2008GL035871](https://doi.org/10.1029/2008GL035871); Bagnato et al. (2014) doi:[10.1144/SP410.2](https://doi.org/10.1144/SP410.2); Roberts et al. (2014) doi:[10.5194/acpd-14-5445-2014](https://doi.org/10.5194/acpd-14-5445-2014)

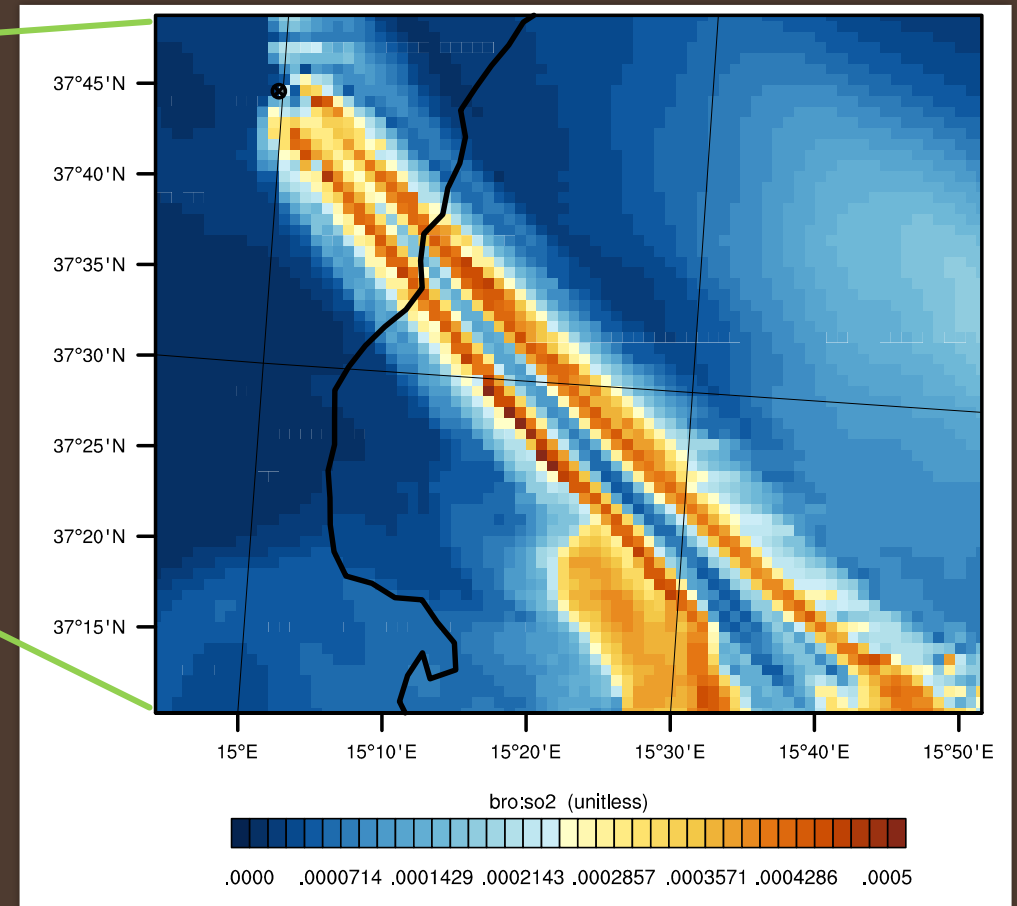
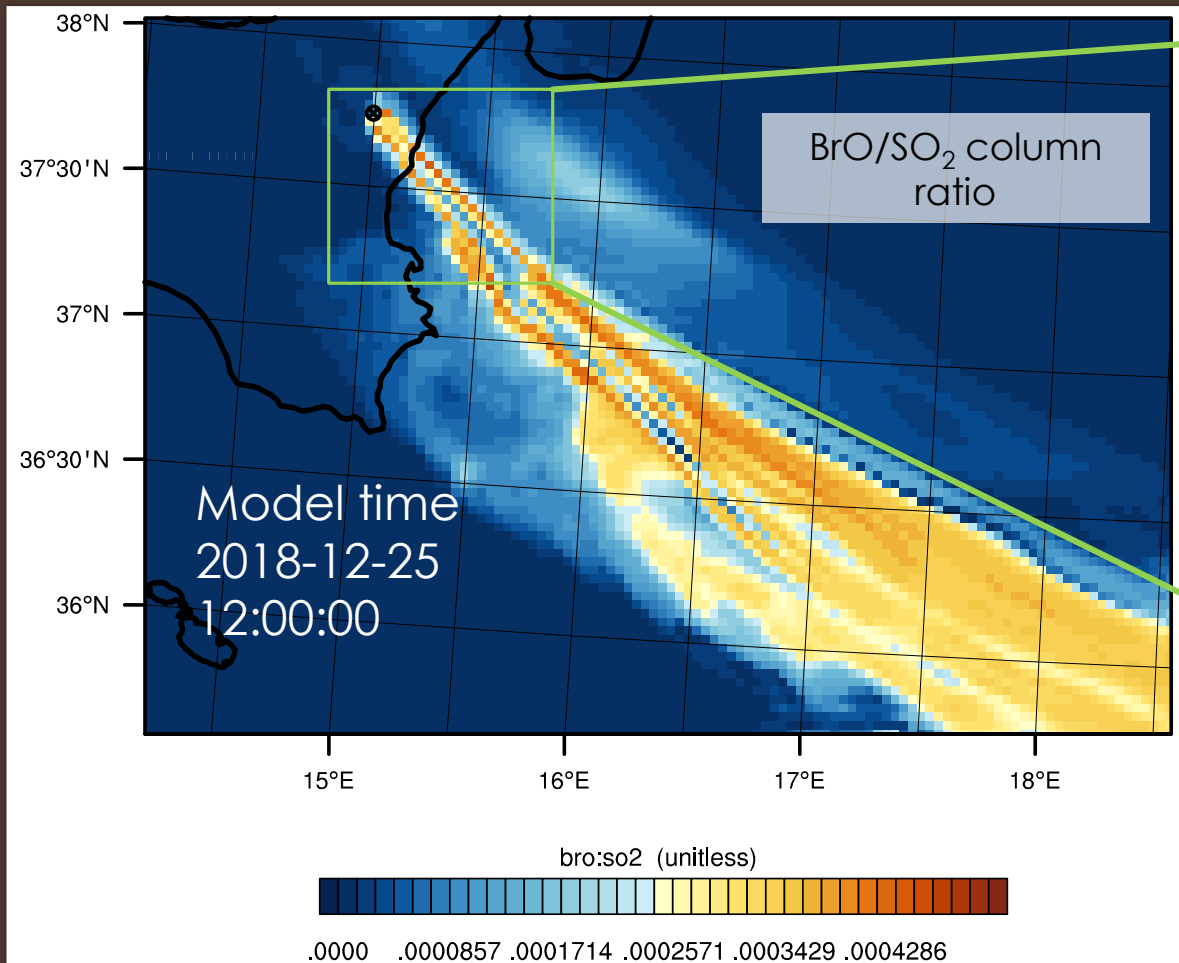
Modelled columns: SO₂



Modelled columns: BrO

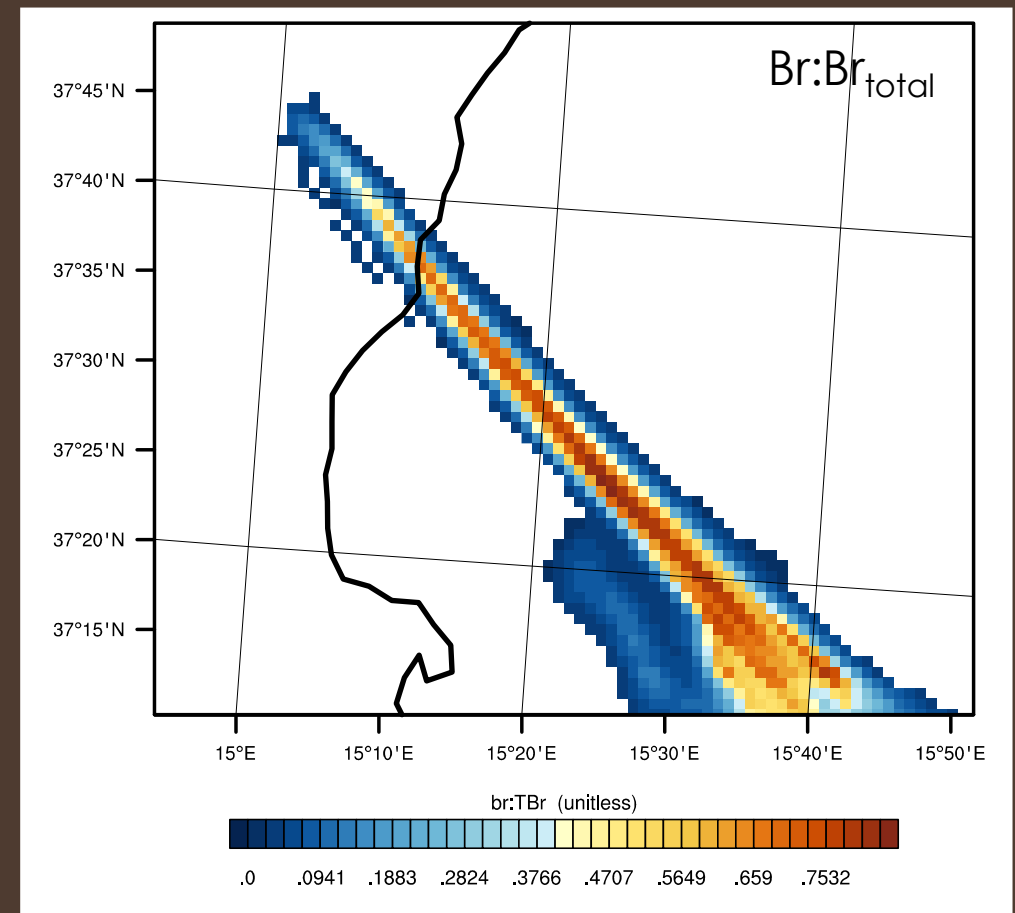


Modelled columns: BrO:SO₂ ratio



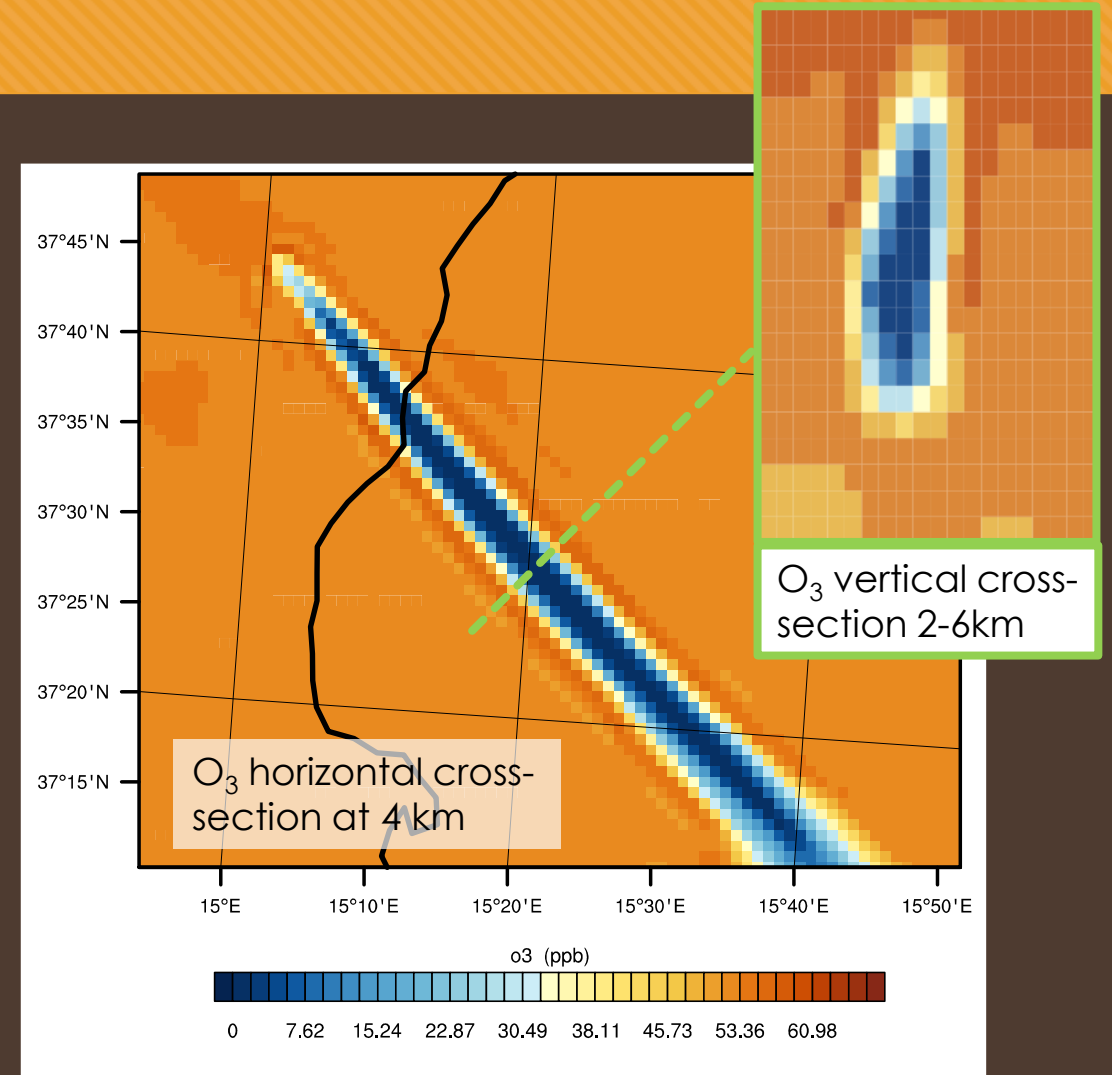
Br speciation variability

- In the core of the plume $\text{BrO}:\text{SO}_2$ ratios are much less than at the edges.
- In this core Br atom is modelled to be a significant species, >50% of the bromine.



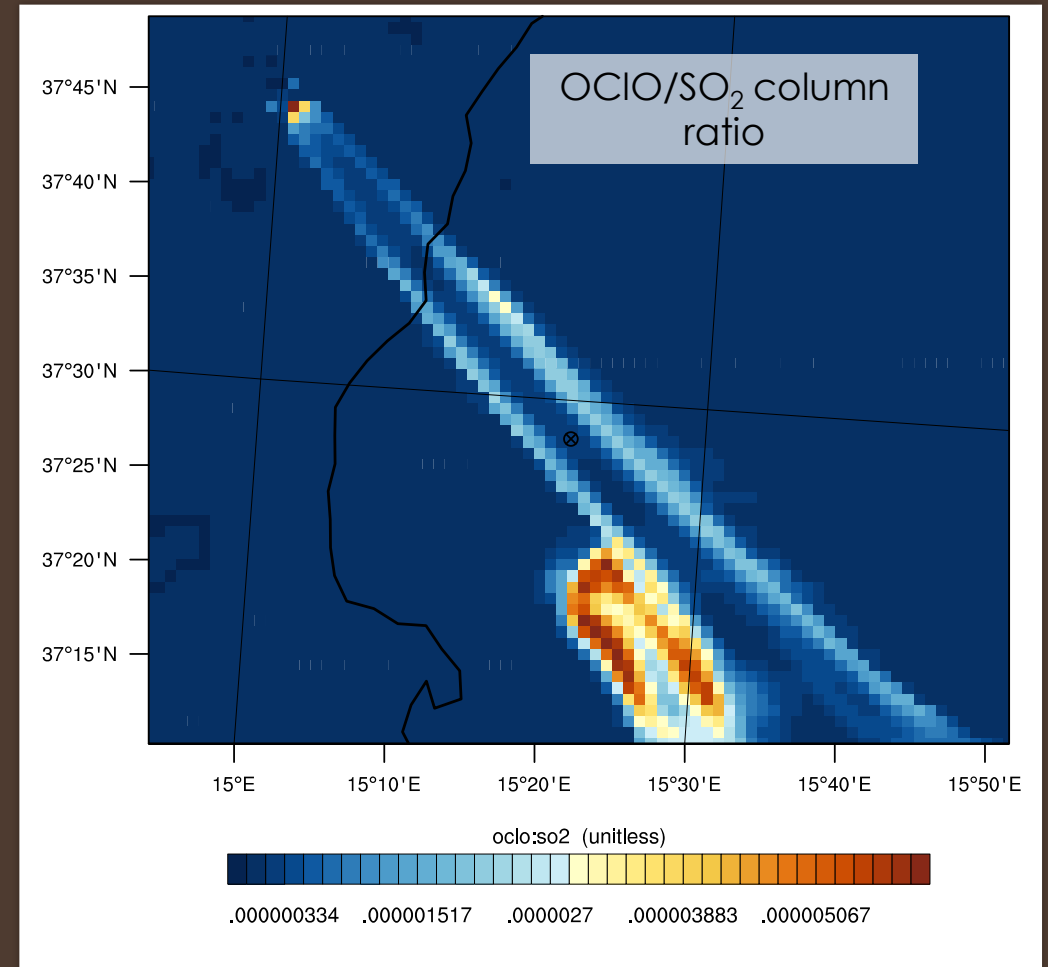
Cause of “coring” effect : O₃ depletion

- Bromine chemistry depletes O₃
- In the core of the plume, O₃ is destroyed faster than it mixes in from background.
 - More total bromine in denser plume
 - O₃ destroyed in surrounding region before reaching core
- O₃ depletion shifts BrO:Br steady-state towards Br.



Coring in OCIO

- WCV also shows production of OCIO
 - OCIO/SO₂ column ratio $1-3 \times 10^{-6}$
- BrCl is produced via chloride reaction in aerosol
- Photolysis of this produces reactive Cl
- OCIO Even more of an “edge species” than BrO
 - Need both Br-cycling, and bromide absence so chloride reaction occurs

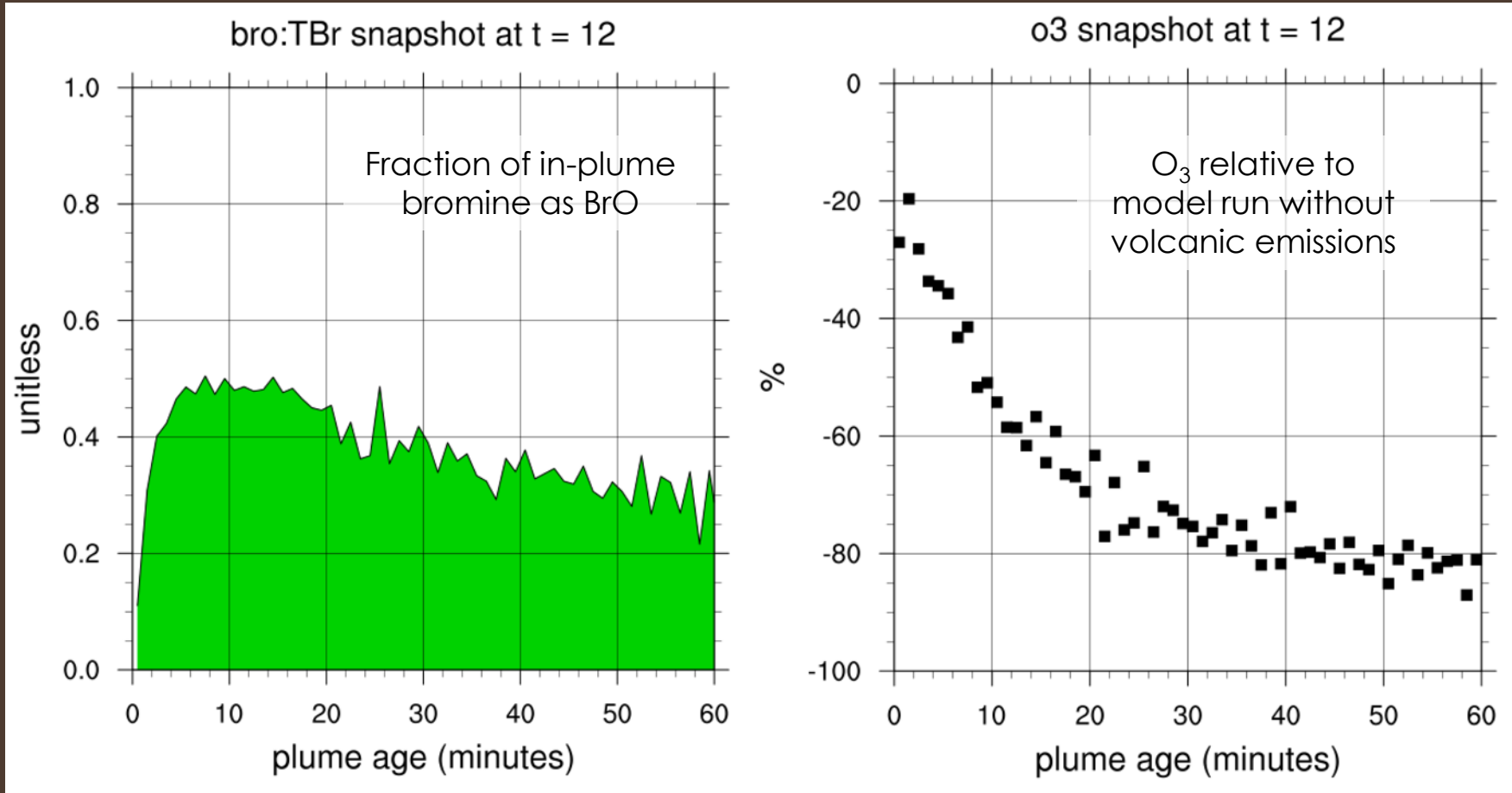


Bulk BrO:total bromine ratio

- What % of total bromine is observed in a ground based or satellite observation?
- Use BrO/total bromine ratio.
 - Directly proportional to BrO/SO₂ ratio
- Here looking at **bulk** numbers, averaged over all parts of plume at a particular **age**.
 - Most observational techniques likely to be effectively bulk observations due to lack of spatial resolution

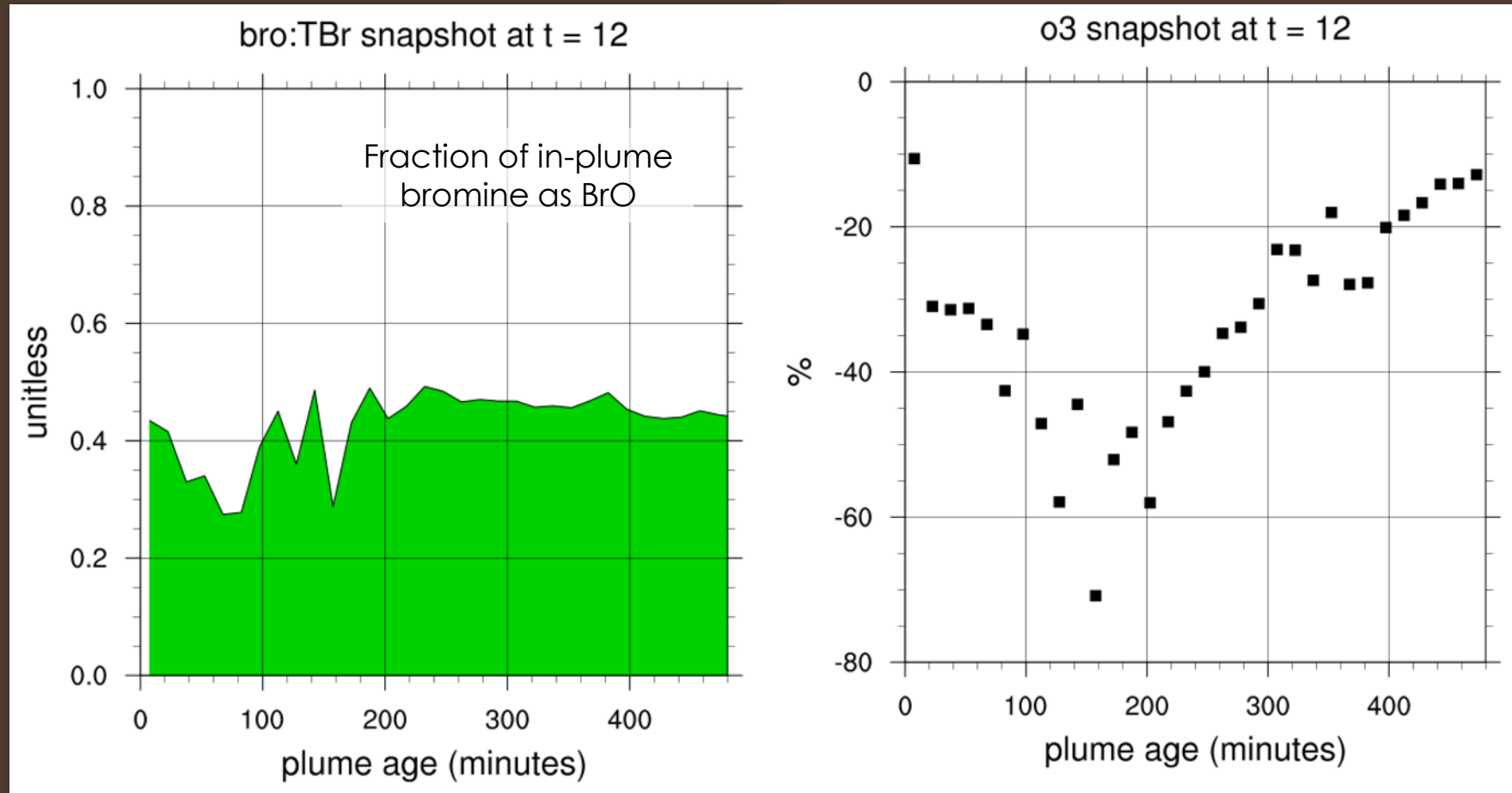
Bulk BrO:total bromine ratio – first hour

- In first few minutes ratio rapidly increases.
- Then decline as O_3 depletion impacts



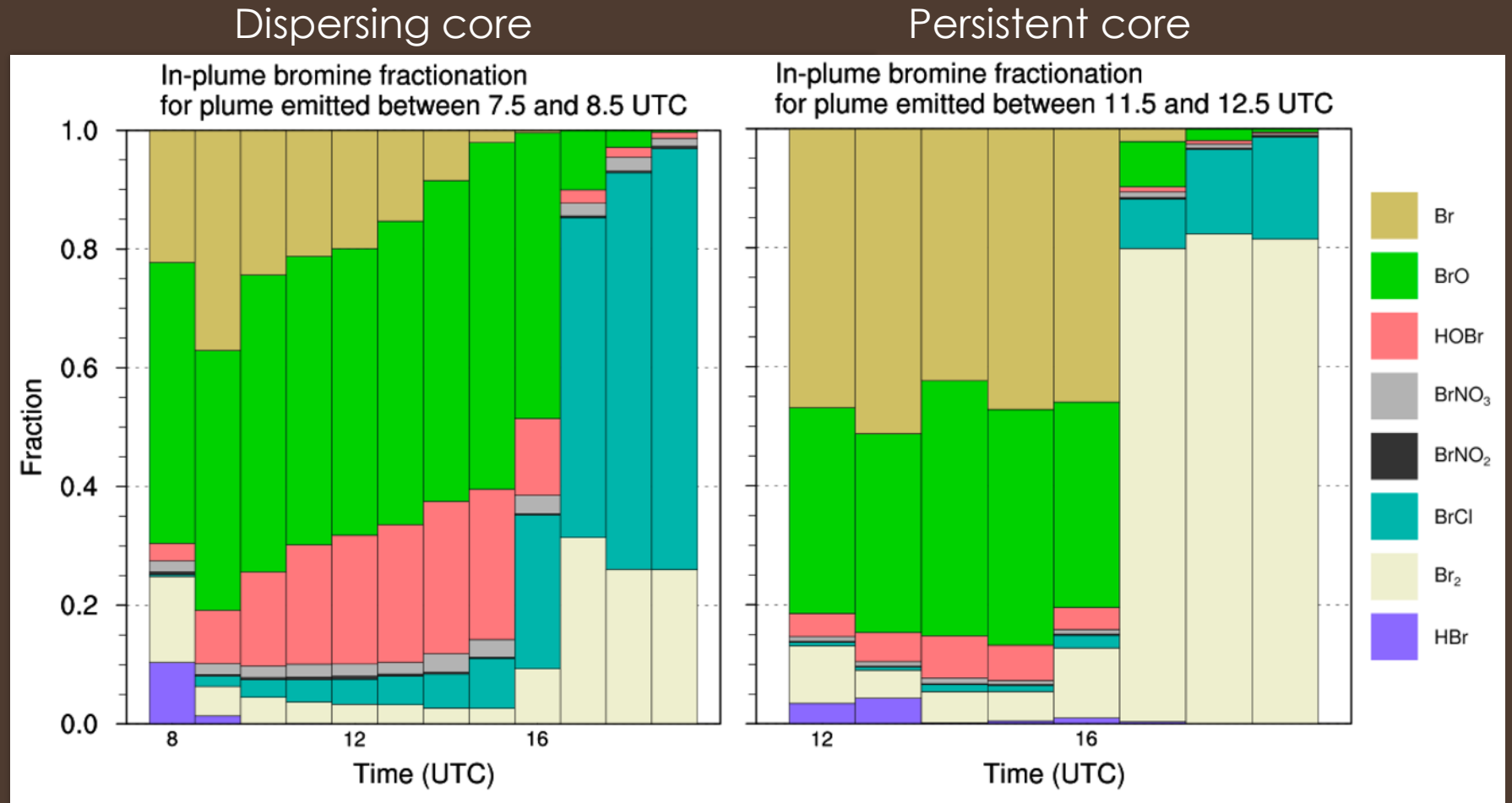
Bulk BrO:total bromine ratio – longer term

- Longer term, O_3 eventually recovers if core “fades”
- BrO reaches approximately stable fraction
 - Stability at ~50% of total Br in this model



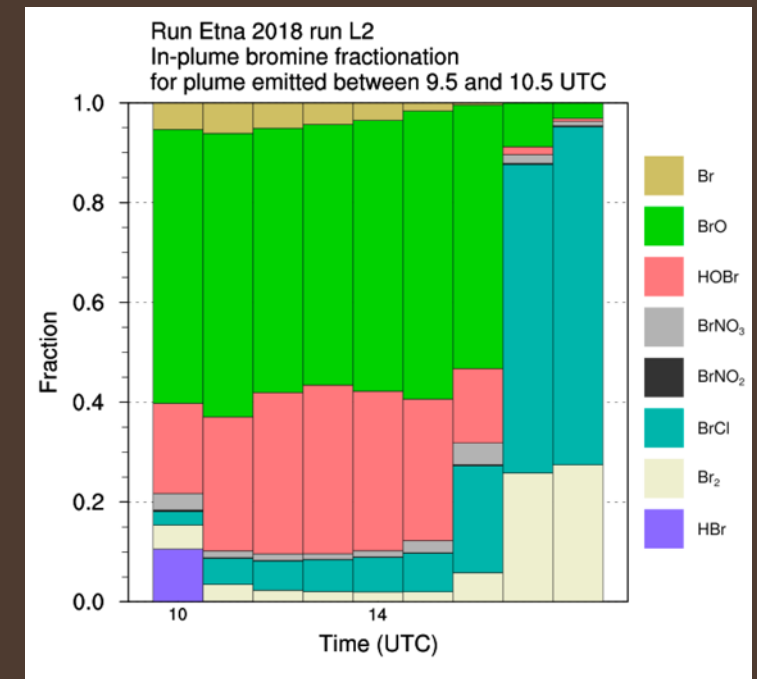
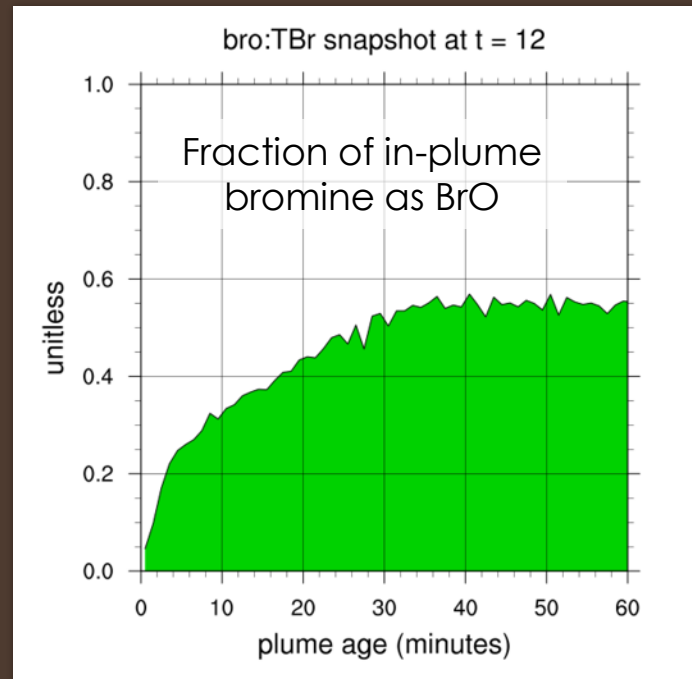
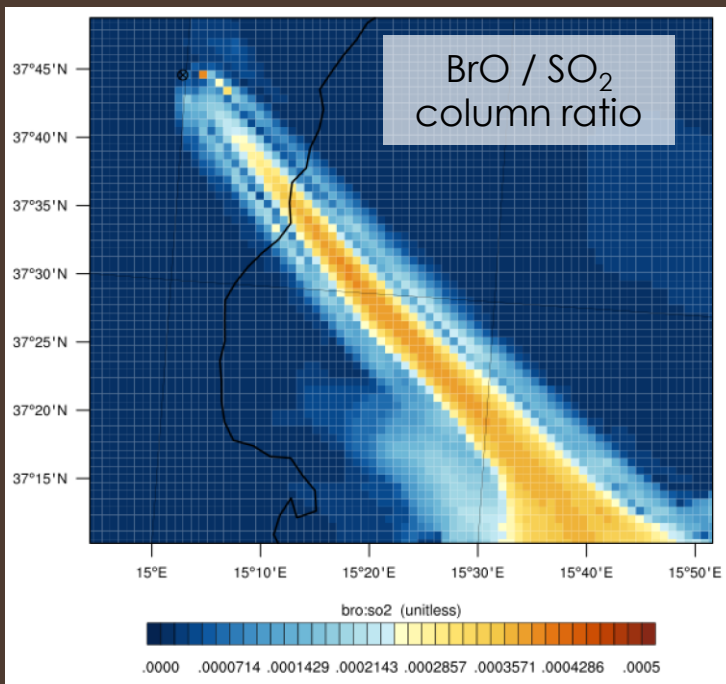
Br fractionation

- Tracking bromine fractionation in one piece of plume over the day...
- Pseudo-lagrangian trace



Weaker plume

- For a plume 1/8 of the strength:
 - No coring - Initial redistribution of bromine slower - then stability



Conclusions

- SO₂ and BrO in the plume of Etna's Christmas 2018 eruption was detected by TROPOMI
- The BrO/SO₂ ratio was of order a few 10⁻⁴, with significant cross-plume variation
- WRF-Chem volcano (WCV) can replicate BrO formation within a volcanic plume, and the "coring" effect
 - OCIO formation also modelled
- This "coring" is caused by bromine chemistry depleting ozone, which interrupts the bromine cycling
- As O₃ chemistry recovers, BrO reaches a steady state as a fraction of total bromine
- Modelling suggests a daytime bulk observation of BrO in aged plume, should observe approximately **half** of total bromine
 - Most reliable once O₃ depletion effect faded
 - O₃ depletion detectable by coring spatial pattern