



# Using the 3D MOCAGE CTM to simulate the chemistry of halogens in the volcanic plume of Etna's eruption in December 2018 at the regional scale

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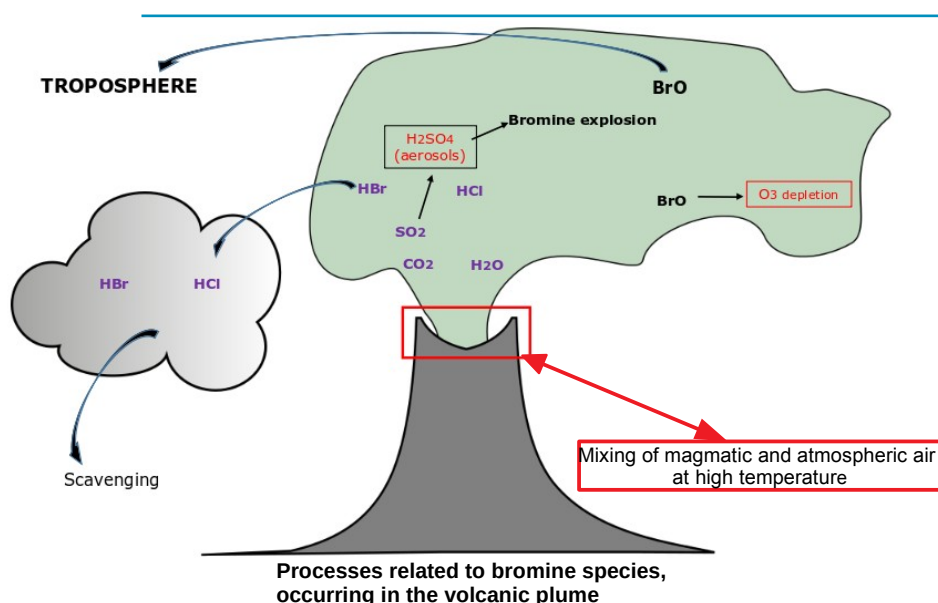
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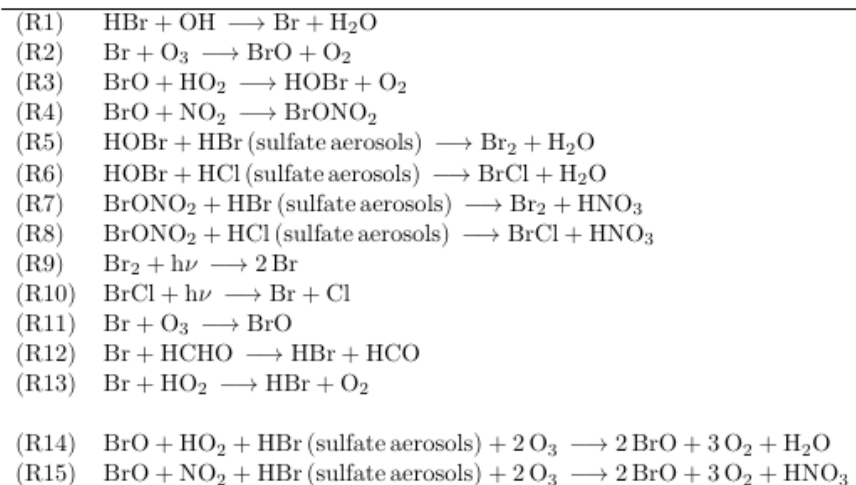
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# Halogen chemistry in volcanic plumes



- Volcanoes emit large amounts of gases in particular SO<sub>2</sub> and halogens (HCl and HBr)
- Rapid mixing of magmatic and atmospheric gases at temperatures ~1000°C :  
⇒ Formation of primary sulfate aerosol and new bromine species from HBr
- Plume measurements and modeling work show :  
⇒ HBr rapidly converts into BrO in plumes resulting in depletion of ozone (O<sub>3</sub>)



**Bromine-explosion cycle**

**This is the process of bromine-explosion :**  
**⇒ Significant and rapid production of BrO leading to a destruction of O<sub>3</sub>**

# State of the art on the modeling of halogens chemistry in volcanic plumes

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- Halogen chemistry in the volcanic plume was mainly modelled/studied at the local scale close to the volcanoes and over short time scales (one- two hours)
  - Only one modelling study at the regional scale : Jourdain et al. (ACP 2016) on the Ambrym volcano emissions (Vanuatu) :
    - Ambrym volcano (southwest Pacific) located in the tropics where the troposphere is characterized by low ozone levels
    - Main results of this modeling study  $\Rightarrow$  the effects of the halogen emissions on the tropospheric chemistry is found even far from the source
- $\rightarrow$  need for more regional studies on other volcanoes in different environments**

# General objectives and strategy

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## Objectives :

- To test the capability of the regional Chemistry-transport model MOCAGE to simulate the « bromine-explosion » and associated ozone depletion with a  $\sim 20\text{km} \times \sim 20\text{km}$  horizontal resolution on a case study : Mt Etna emissions around Christmas 2018
- To analyse the impact of halogen species on air composition from this event at the regional scale

## Strategy:

- Part a : Evaluate the results of MOCAGE against the WRF-Chem simulations at finer resolution using idealised emissions
- Part b : Simulation of the Christmas 2018 event in the most realistic way ; i.e. with varying emission fluxes and altitude, and evaluation against TROPOMI satellite observations

# Case study : Mt Etna 'Christmas' 2018 eruptions

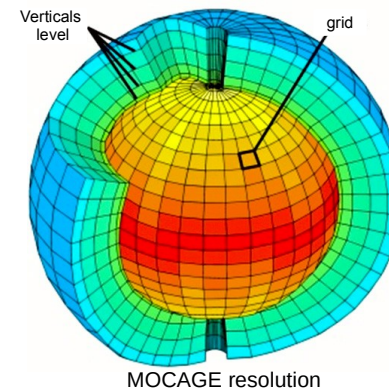
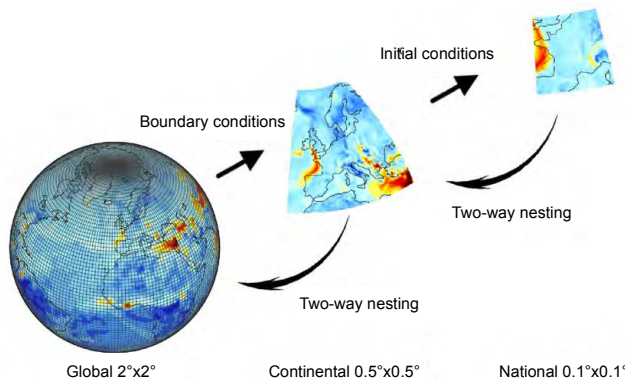
- 2 small eruptions on the 24th of December
- Strong passive degassing over a few days after
- BrO signal captured by TROPOMI satellite measurements even far from the volcano
  - ➔ Signature of bromine explosion



Eruption of Mt Etna (Sicily, Italy) on 24th of December 2018  
Source : Corradini et al, (2020), Remote Sens. 2020, 12(8), 1336; <https://doi.org/10.3390/rs12081336>

# Description of MOCAGE CTM model and general configuration

- MOCAGE : Chemistry-Transport Model developed at CNRM (Météo-France/CNRS)
- Describes the evolution of the composition of the troposphere and stratosphere for gas and aerosol species
- Possibility to make nested domains :



- Resolution: 2° (Global), **0.2° (Mediterranean region)**
- Vertical grid uses a hybrid coordinates : **47 verticals level with a top at 5 hPa**
- Using MOCAGE CTM model in 'chemistry mode' (no explicit representation of aerosols)
- Still, it considers the sulfate aerosol surface for heterogeneous reactions by:
  - Calculating the oxidation of  $\text{SO}_2$  in aqueous phase  $\Rightarrow \text{SO}_4^{2-}$
  - Then,  $\text{SO}_4^{2-}$  is assumed to be entirely converted in the form of sulfate aerosols.
  - Sulfate aerosols are assumed to have a uniform distribution of radius  $1\mu\text{m}$  (consistent with aerosol measurements in volcanic plumes)

# Emissions for the model simulations :

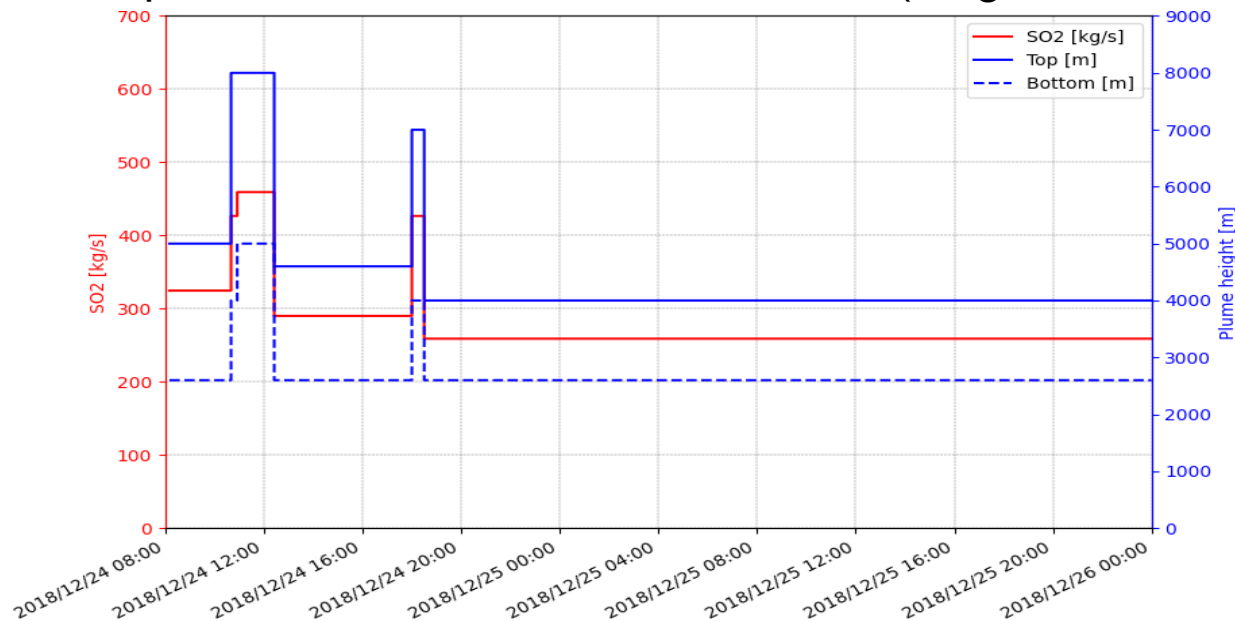
- Numerical experiments for Part a and Part b :
  - ➔ Duration of simulations : 2018/12/24/ 00:00 UTC to 2018/12/26 00:00 UTC
  - ➔ Simulation without volcanic emission to serve as a reference: **NOVOLC**
  - ➔ Simulation with volcanic emission : **VOLC**
- Ratios with respect to SO<sub>2</sub> volcanic emissions used in the VOLC simulations :

Flux ratio	Value	Note
Molar ratios HCl/SO <sub>2</sub>	0.44	Average ratios at Bnand NEC craters from Wittmer et al. (2014)
Br <sub>tot</sub> /SO <sub>2</sub> HBr/Br <sub>tot</sub> Br/Br <sub>tot</sub>	6.6E-04 0.75 0.25	To take into account the effects of high temperature processes at vent
Mass ratio Aerosol/SO <sub>2</sub>	0.03	Roberts et al. (2018) – assumed all sulfate



## Specific model setup for part a and part b:

- **Part a :** Idealized volcanic source of SO<sub>2</sub> and halogens with constant emissions from 24<sup>th</sup> of Dec.at 00UTC to 26<sup>th</sup> of Dec.at 00UTC
  - 320 kg SO<sub>2</sub>/s flux rate beginning at 11h15 on December 24
  - 4km injection height into single model layer (~300m thick )
  - Other species emitted at fixed ratio to SO<sub>2</sub> (as given in the previous slide)
- **Part b :** Simulation with varying emission fluxes and altitude as used in Lamotte et al. EGU presentation based on Corradini et al. (2020)
  - Other species emitted at fixed ratio to SO<sub>2</sub> (as given in the previous slide)



- Etna Christmas 2018 emissions with two small eruptions on the 24th of December and strong passive degassing over a few days after



# Part a : Results of the WRF-Chem-MOCAGE comparison

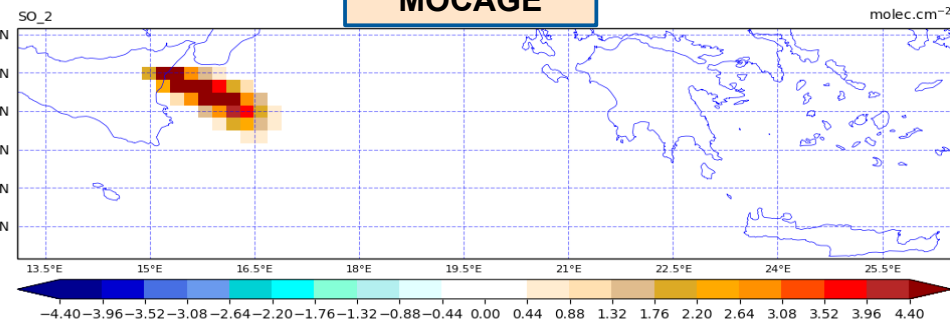
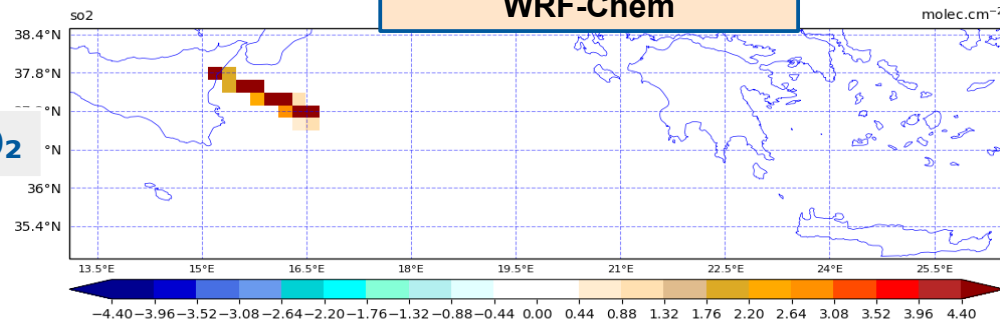
## Tropospheric columns of SO<sub>2</sub>, BrO and O<sub>3</sub> [molec/cm<sup>2</sup>]

24/12/2018 at 14h UTC

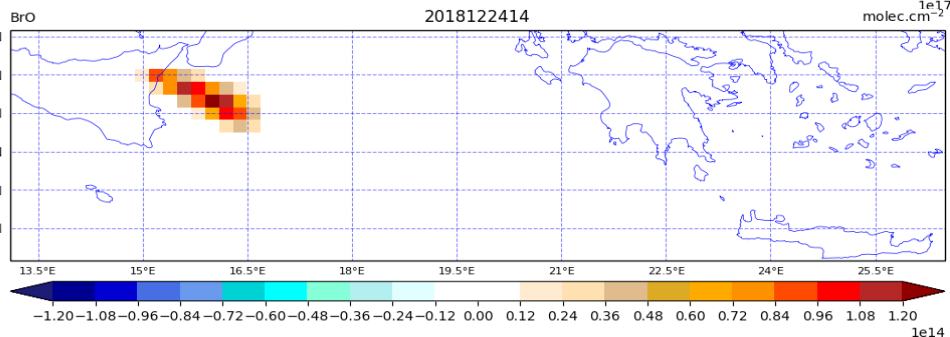
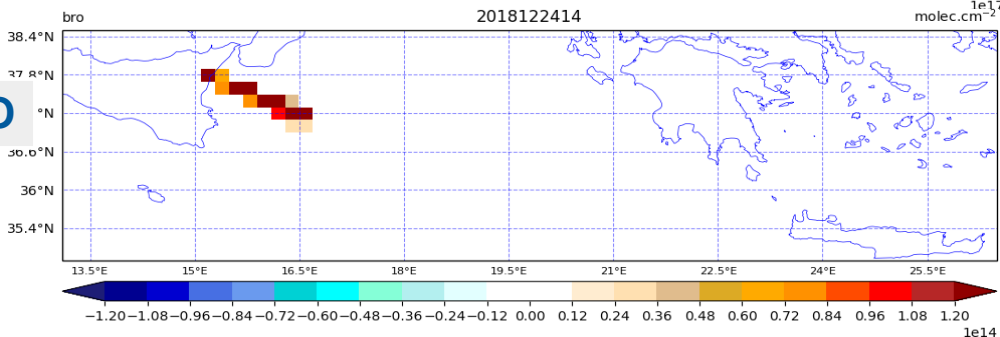
WRF-Chem

MOCAGE

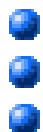
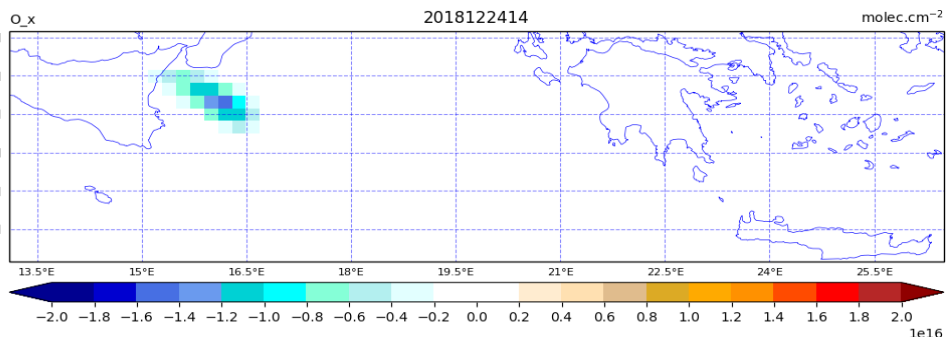
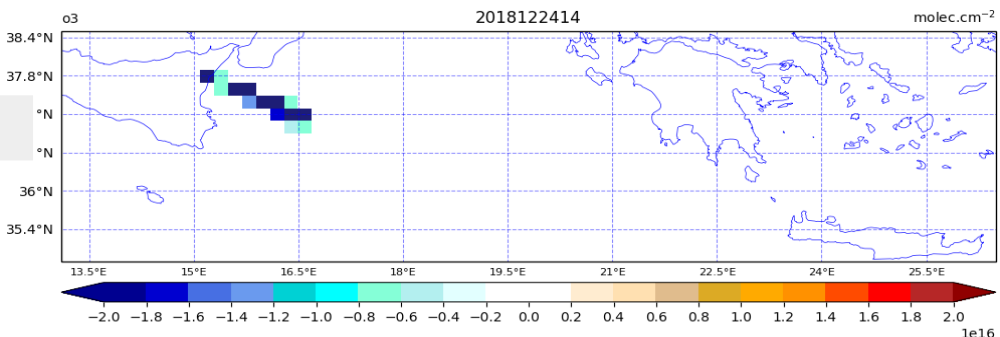
SO<sub>2</sub>



BrO



O<sub>3</sub>



WRF-Chem simulation is at 10km resolution  
The domain shown is that of the WRF-Chem simulation  
WRF-Chem is interpolated at MOCAGE resolution (0.2°x0.2°)



# Part a : Results of the WRF-Chem-MOCAGE comparison

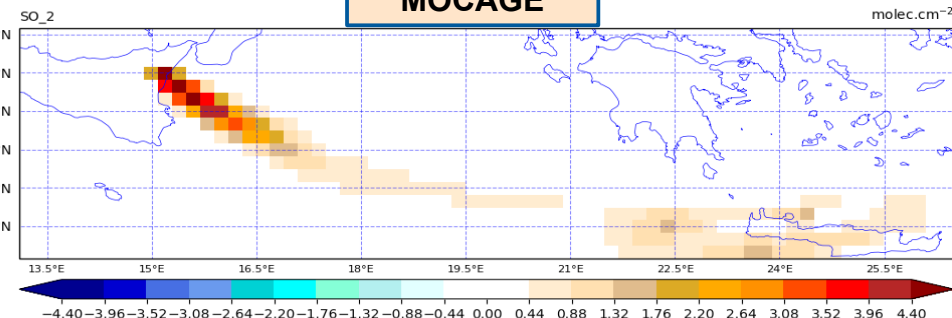
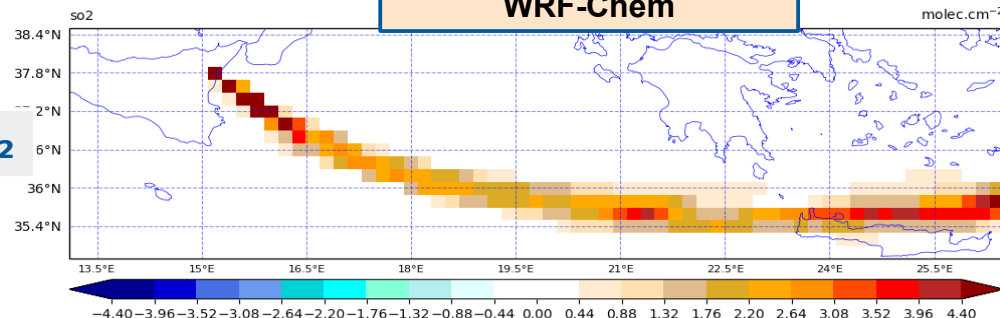
## Tropospheric columns of SO<sub>2</sub>, BrO and O<sub>3</sub> [molec/cm<sup>2</sup>]

25/12/2018 at 11h UTC

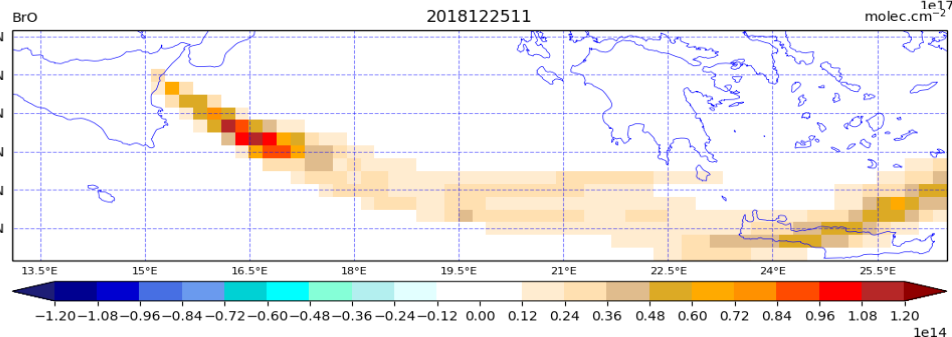
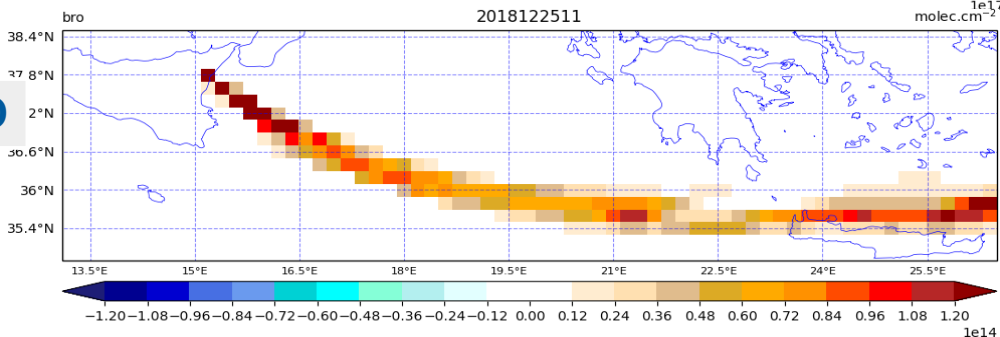
WRF-Chem

MOCAGE

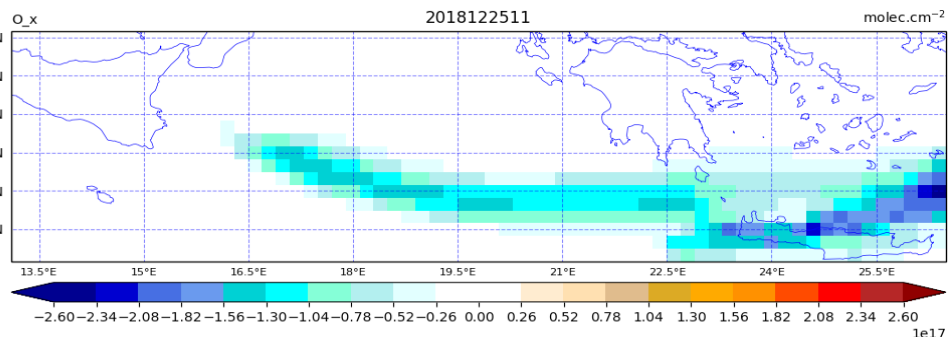
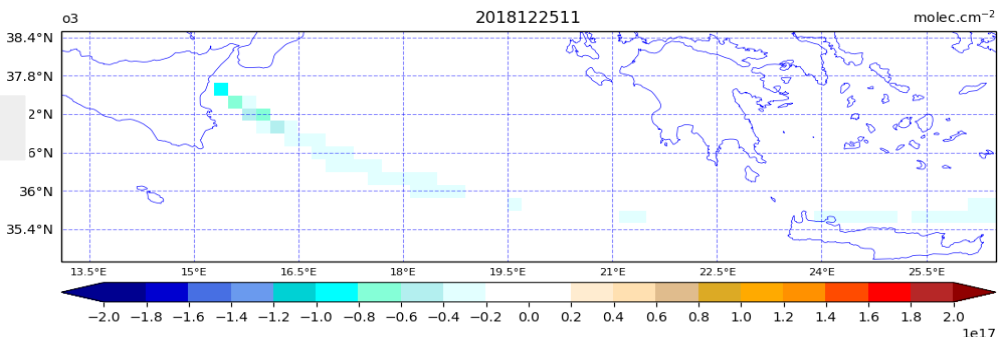
SO<sub>2</sub>



BrO



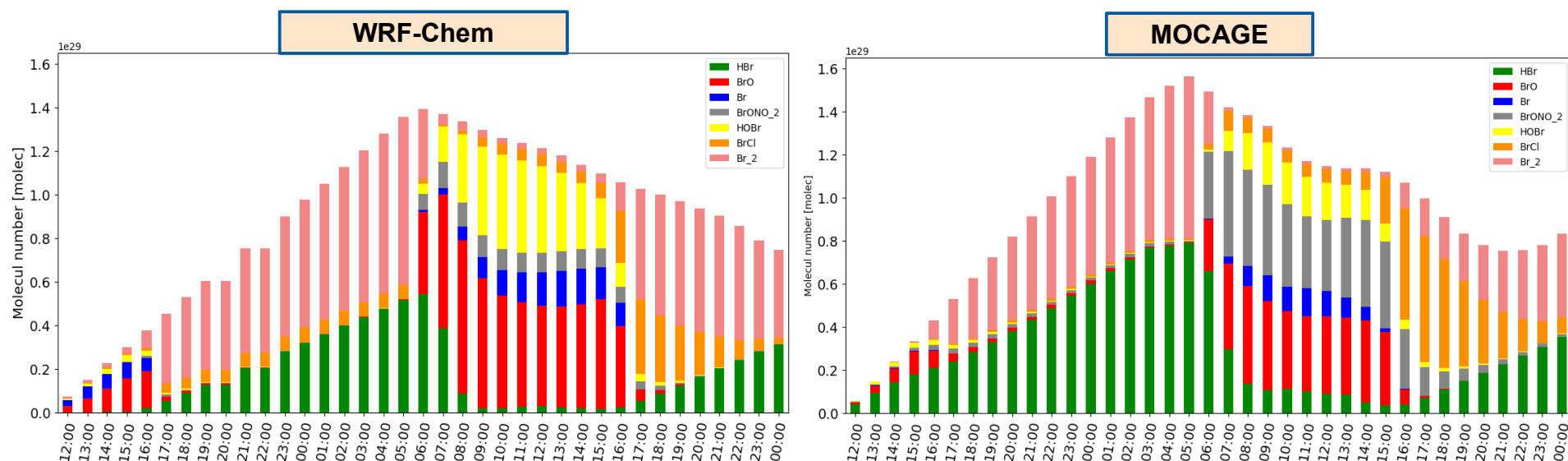
O<sub>3</sub>



- SO<sub>2</sub> plumes in the two models are in the same order of magnitude but more spread in MOCAGE
- Bromine explosion cycle appears in the two models.
- BrO is more quickly formed in WRF-Chem (closer to the volcano)
- Ozone depletion along the plume found in the two models but later and much stronger in MOCAGE

# Partition of bromine compounds from WRF-Chem and MOCAGE

- Comparison of the total molecule number of the bromine compounds between WRF-Chem simulation with 10km horizontal resolution and MOCAGE (~20km resolution)



- During the daytime on the 24<sup>th</sup>
  - BrO starts to form and rapidly increases in WRF-Chem
  - Bromine-explosion cycle is less efficient in MOCAGE
- During nighttime (24<sup>th</sup> to 25<sup>th</sup>)
  - BrCl and Br<sub>2</sub> become reservoirs of bromine species while HBr is still emitted
- The day after (25<sup>th</sup>), good consistency between MOCAGE and WRF-Chem if taking into account the fact that MOCAGE has higher NO<sub>2</sub> in background air leading to more BrONO<sub>2</sub> and less HOBr
- During nighttime (25<sup>th</sup>-26<sup>th</sup>), the ratio between Br<sub>2</sub> and BrCl is a bit different in the two models

# What you learn from part a ?

**Overall, the behaviour of the 2 models is fairly similar**

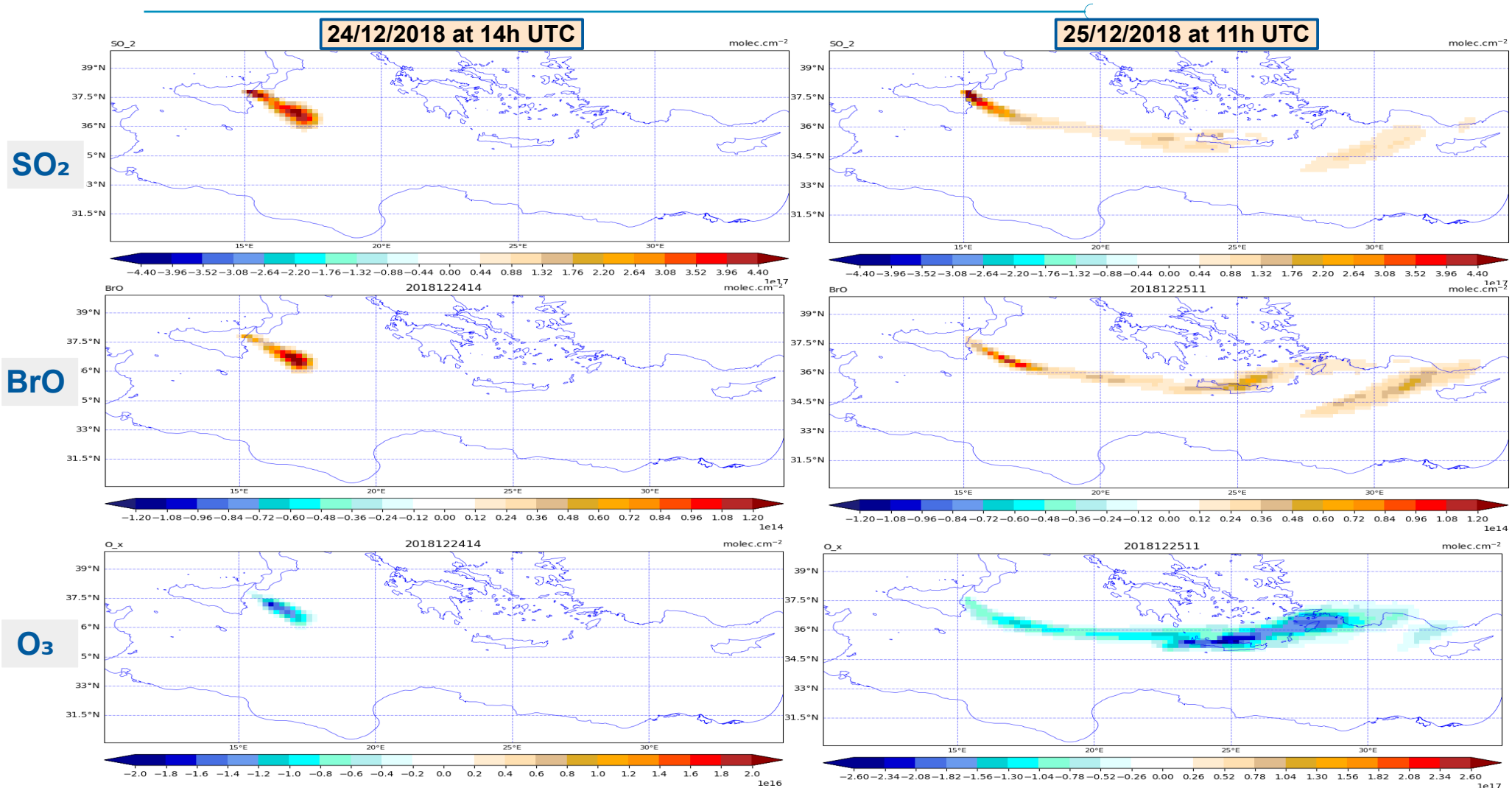
- The comparison of the tropospheric columns from MOCAGE and WRF-Chem have the same order of magnitude and similar location

**But with some differences**

- BrO starts to form and increases rapidly in WRF-Chem while MOCAGE forms BrO later
- Ozone depletion is stronger in MOCAGE than in WRF-Chem
- Part of the differences comes from the (initial) background air composition (NO<sub>x</sub> and ozone) which is different in WRF-Chem and MOCAGE and possibly to the fact that WRF-Chem used OH emissions which are not yet included in MOCAGE simulations
- Differences on bromine and ozone can also be related to differences between WRF-Chem and MOCAGE chemical schemes, in particular some chemical reactions not yet present in MOCAGE (for example, the hydrolysis of BrONO<sub>2</sub>)

# Part b : Results from MOCAGE simulation

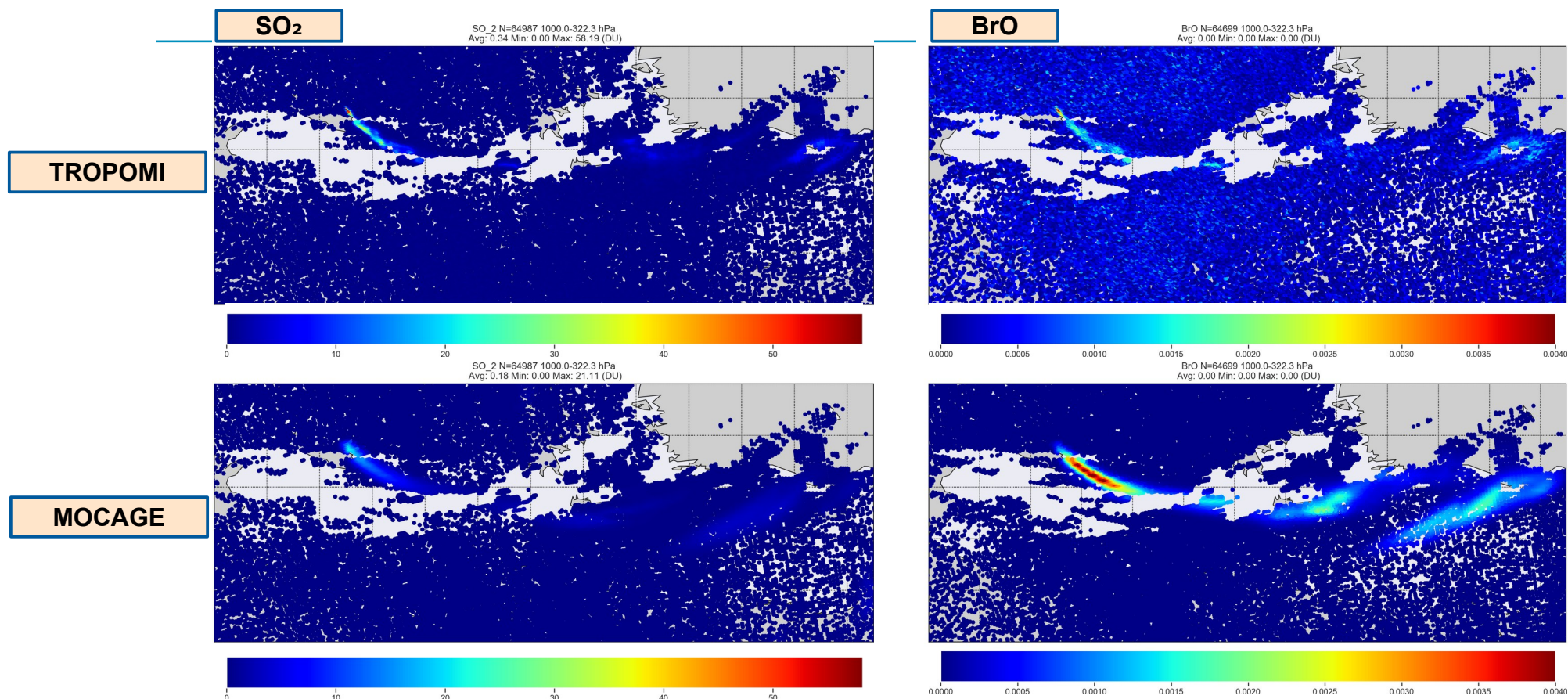
## Tropospheric columns of SO<sub>2</sub>, BrO and O<sub>3</sub> during daytime [molec/cm<sup>2</sup>]



- SO<sub>2</sub> emission and transport of the plume
- Bromine-explosion cycle during daytime
- Depletion of ozone along the plume → bromine explosion
- Results similar to those obtained in Part a, except a slightly different location of the plume



# Part b : Comparison of SO<sub>2</sub> and BrO tropospheric columns between MOCAGE simulation and TROPOMI retrieval on 25/12/2018



- MOCAGE simulations are interpolated at the time and location of the TROPOMI satellite measurements
- The comparison shows
  - Overall good agreement on the plume location between MOCAGE and TROPOMI but with a more spread plume in MOCAGE
  - Similar order of magnitude for SO<sub>2</sub> and BrO between MOCAGE and TROPOMI
  - More rapid formation of BrO "Bromine-explosion cycle" in TROPOMI observations than in MOCAGE, consistent with results of the comparison with WRF-Chem (Part a) . In MOCAGE, BrO formation is slower but high BrO persists further downwind

# What you learn from Part b ?

- The concentrations of the different halogens species are in the same order of magnitude as found in Part a
- The volcanic plumes of SO<sub>2</sub> and BrO is better located using the variation with time of the quantity of species emitted and height of the plume
- TROPOMI vs MOCAGE 3D model :
  - ⇒ because MOCAGE resolution is coarser than TROPOMI pixels and because of model diffusion, the volcanic plume is more spread out in MOCAGE (as expected)
  - ⇒ Tropospheric column of BrO (TROPOMI) is lower than the BrO from MOCAGE 3D model
    - ▶ differences may be related to uncertainties on SO<sub>2</sub>, HBr emissions and on assumptions on changes of emissions at high temperature
    - ▶ uncertainty/missing reactions in MOCAGE halogen chemistry



# Conclusion & perspectives

## ■ Conclusion

- These preliminary results show that MOCAGE CTM (~20km x ~20km of horizontal resolution) is able to represent the bromine explosion
- BrO formation is associated with tropospheric ozone depletion along the volcanic plume but ozone depletion is too strong in MOCAGE
- Fairly good consistency of MOCAGE results with WRF-Chem results
- Fairly good consistency of MOCAGE results with TROPOMI SO<sub>2</sub> and BrO observations
- **However, MOCAGE simulations still need to be improved to better match with WRF-Chem and TROPOMI**

## ■ Perspectives

- Complete the chemical halogen scheme to be more consistent with WRF-Chem model
- Use of the MOCAGE version including the secondary aerosol scheme with explicit formation of sulfate aerosols
- Sensitivity studies to improve even more the location of the plume by testing slight modifications of the emission height (Part b)
- Emissions used as input in MOCAGE can be improved (Part b), in particular :
  - ➔ Sensitivity studies to adjust SO<sub>2</sub> emissions in mass to improve plume SO<sub>2</sub> column with respect to TROPOMI
  - ➔ Sensitivity studies to adjust HBr emissions to improve plume BrO column with respect to TROPOMI
  - ➔ Emissions from high temperature processes at vent:
    - ▶ Use of additional OH emissions as in WRF-Chem
    - ▶ Test the sensitivity to HBr/Br ratio