

Alexandra Gutmann¹, Nicole Bobrowski^{2,3}, Marcello Liotta⁴, Julian Rüdiger⁵ and Thorsten Hoffmann¹

¹ Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, Germany, ² Institute for Environmental Physics, University of Heidelberg, Germany, ³ Max Planck Institute for Chemistry, Mainz, Germany, ⁴ Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italy, ⁵ Atmospheric Chemistry, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany
✉ agutmann@uni-mainz.de

A Halogens in volcanic plumes

Quantities of emission, transformation and phase partitioning of the different bromine and other **halogen species** are still in details **not known**.^[1]

BrO/SO₂ ratio was suggested as an indicator for changes in **volcanic activity** and can be measured by remote sensing techniques.^{[1][2]}

Fig. 1: **Model descriptions** suggest transformation of gaseous bromine species related to plume age^[2]

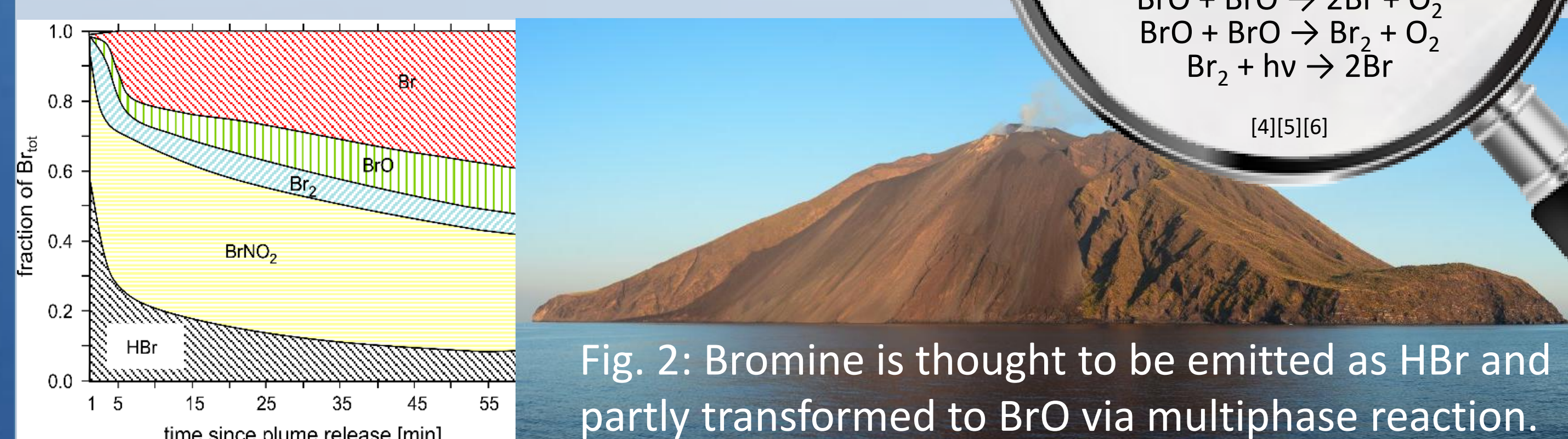


Fig. 2: Bromine is thought to be emitted as HBr and partly transformed to BrO via multiphase reaction.

B Selective quantification of halogen species - Gas diffusion denuder

Gas molecules diffuse to coated denuder walls while particles pass denuder when pumping air through^{[7][8]}

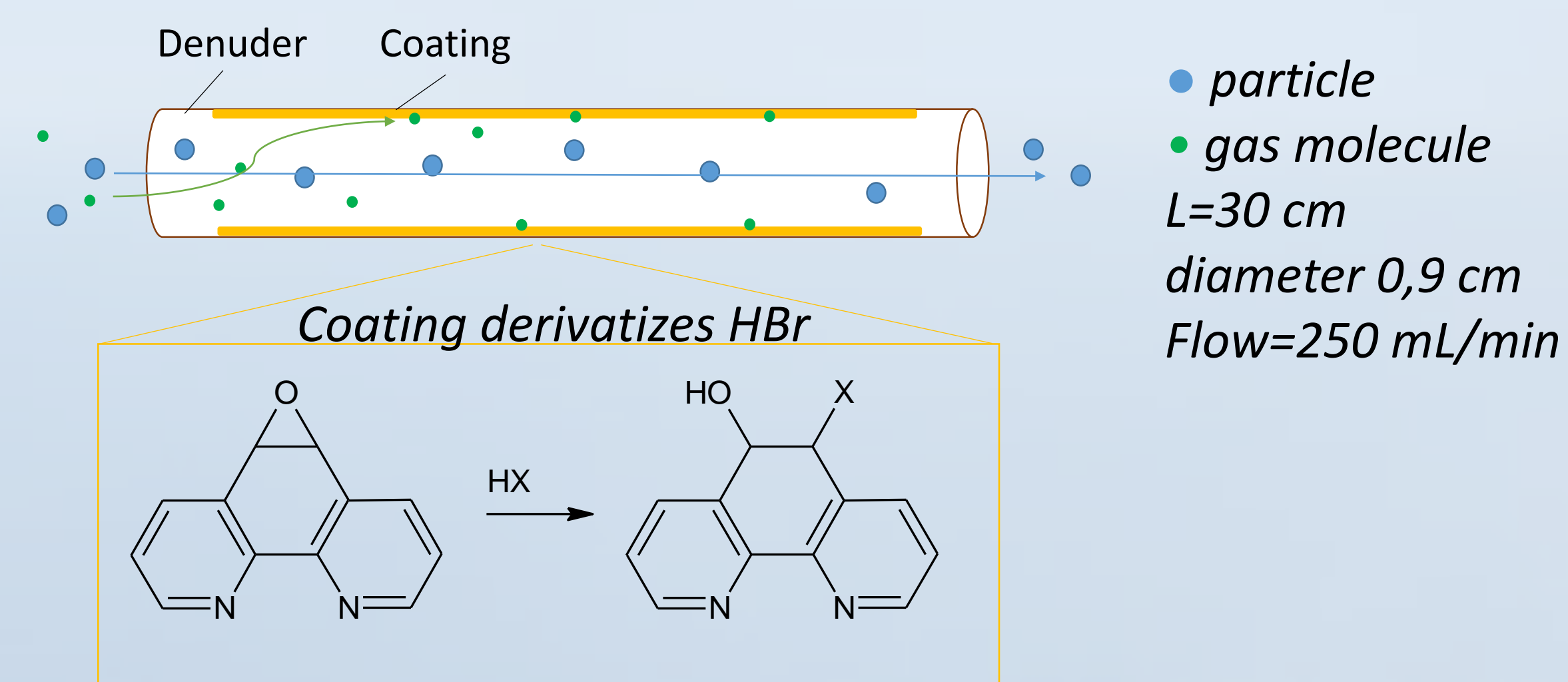


Fig. 3: Diffusion process in gas diffusion denuder, with 5,6-epoxy-5,6-dihydro-1,10-phenanthroline (EP) as coating

Analytical procedure

1. sampling
2. elute coating with solvent
3. evaporate for concentration
4. Analysis with high pressure liquid chromatography coupled to ESI mass spectrometry and UV
5. Standard addition calibration
6. Standard addition calibration

Bromine speciation with several coatings

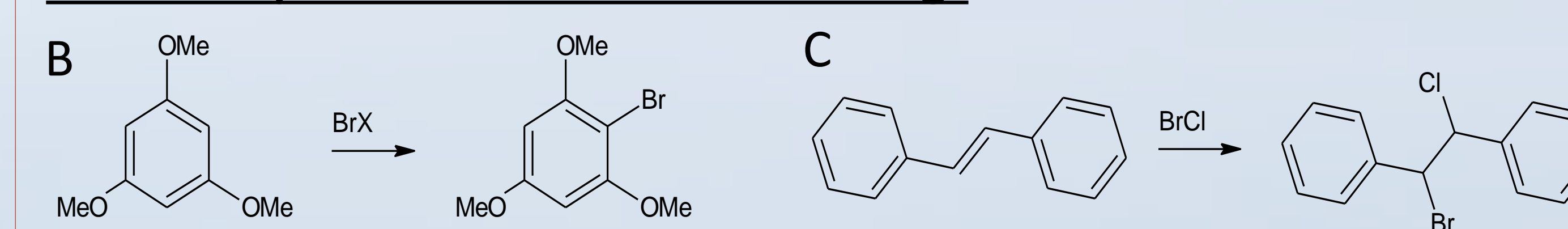
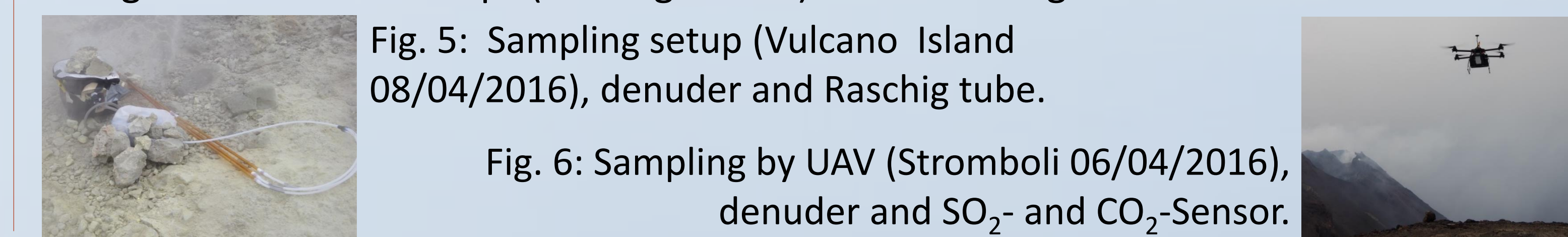


Fig. 4: coatings for determination of other bromine species
(A) Reactive halogens (BrX, oxidation number +1 or 0) with 1,3,5-Trimethoxybenzene^[8]
(B) Interhalogens (BrCl) with *trans*-Stilben

Field Application

Simultaneous sampling of denuders with different coatings for various reactive halogens and alkaline traps (Raschig tube^[9]) for total halogen amounts.



C matrix influence and calibration

Large matrix (coating + derivatized products) causes precipitation and complicates analysis.

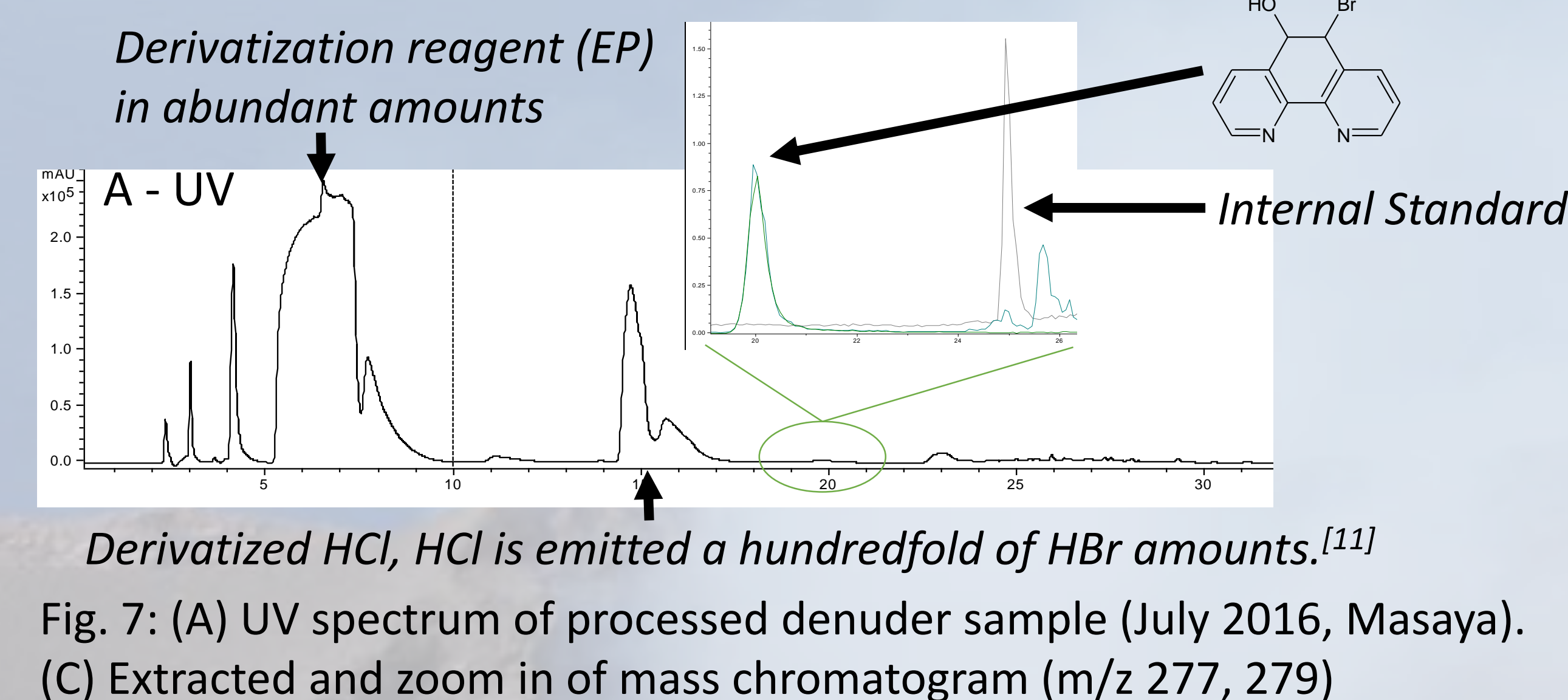


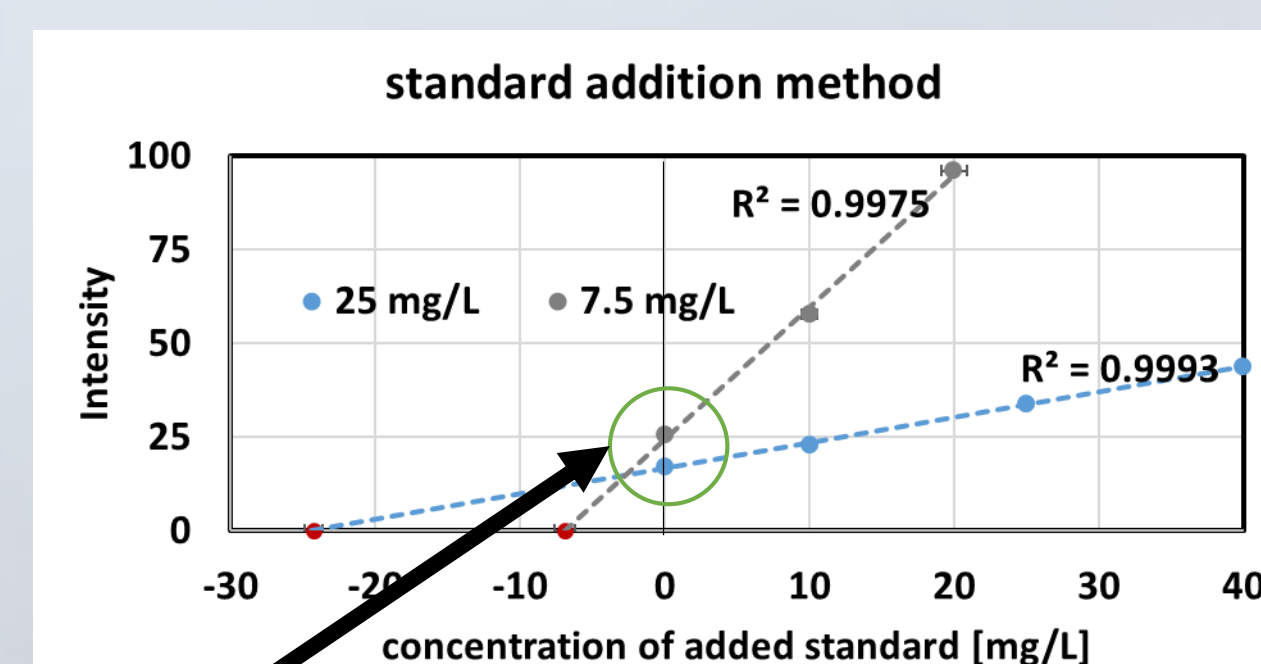
Fig. 7: (A) UV spectrum of processed denuder sample (July 2016, Masaya).
(C) Extracted and zoom in of mass chromatogram (m/z 277, 279)

Calibration

Fig. 8: **standard addition calibration method** demonstrated on lab samples.

Denuders from several batches with known concentrations.

Data points without standard addition represent external calibration results. It seems that **matrix influence** of different denuder batches differ vastly.



External calibration cannot work out correct results
Recovery 94.66 ± 5.08 %

D Field applications

Masaya 2016

Sample collection at different distances to emission source

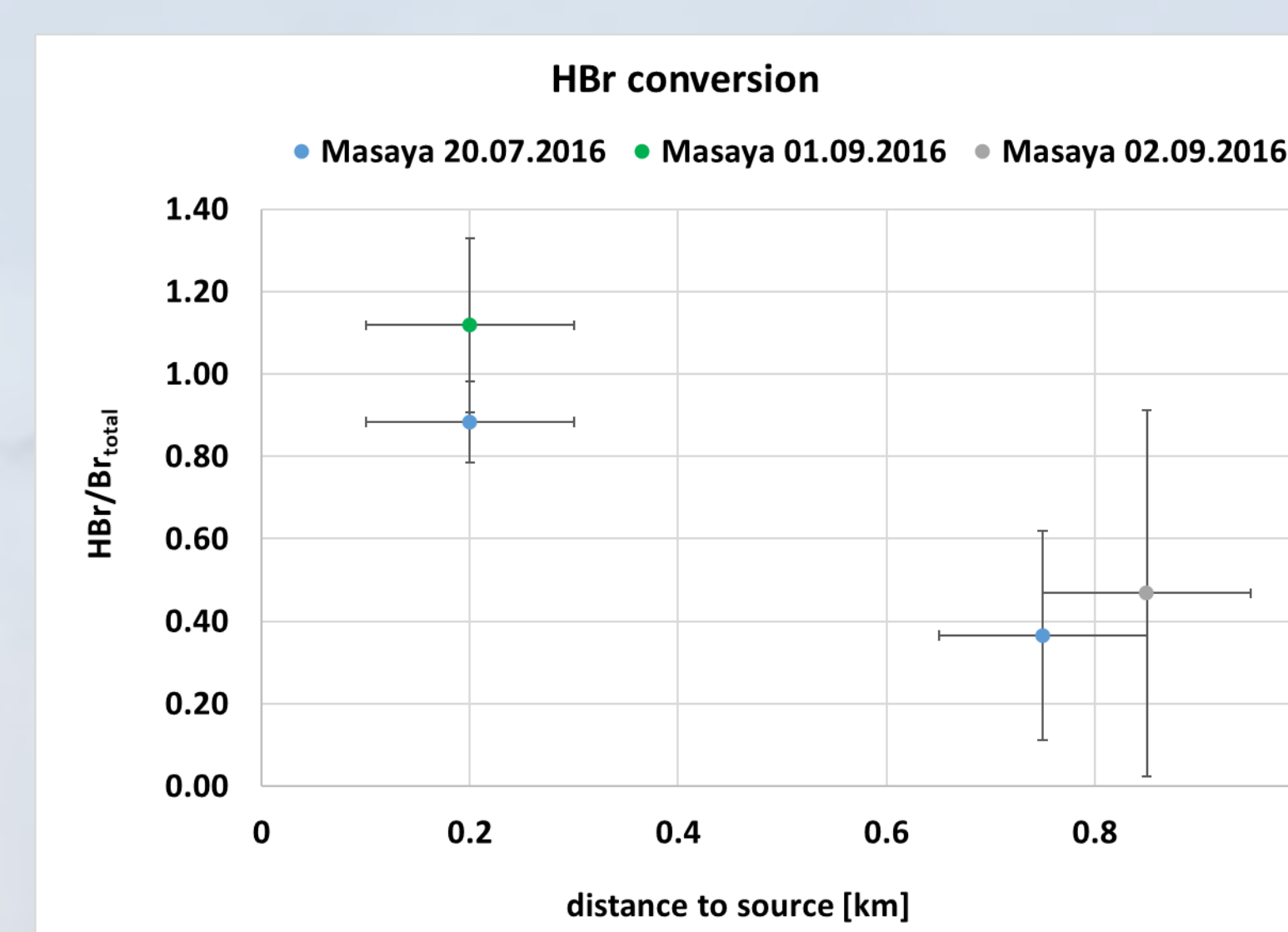


Fig.9: Development of HBr in the plume visible with HBr/Br_{total} ratios depending on distance to the source. HBr determined by denuders, Br_{total} by alkaline traps (analyzed by IC and ICP-MS). Samples collected on the days (20.07.2016 blue, 01.09.2016 green, 02.09.2016 grey). Measurements of the HBr/Br_{total} ratio at Masaya volcano seem to show a decrease over increasing distance.

Sampling Site

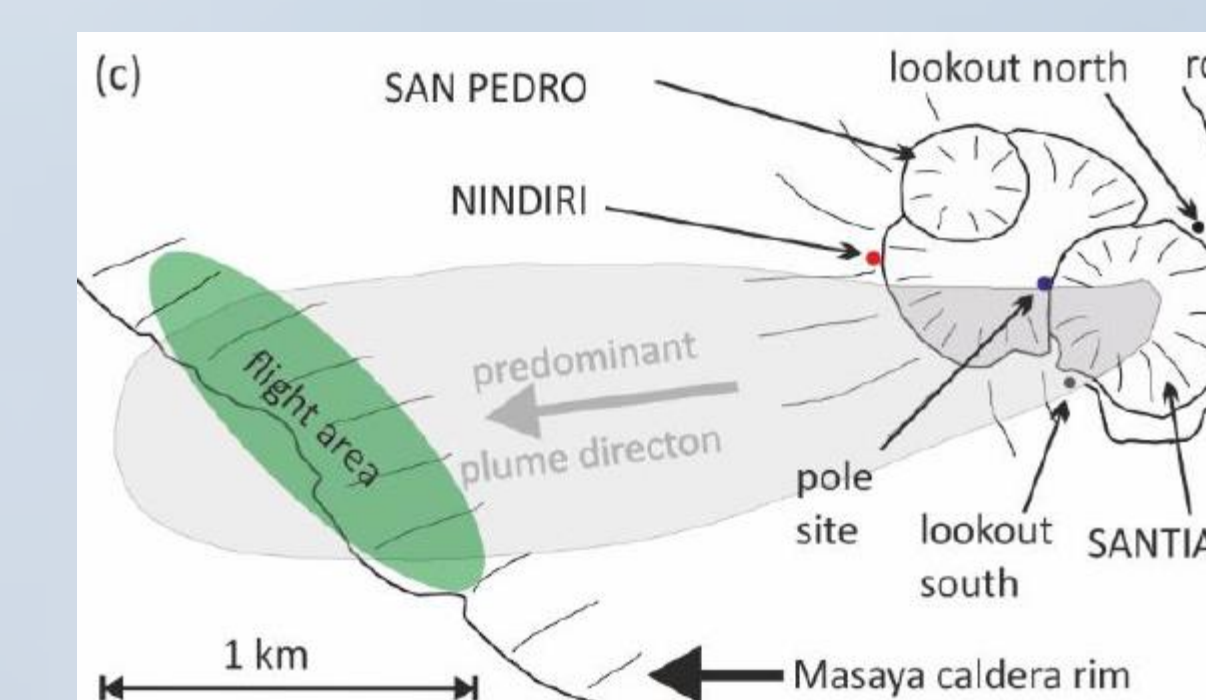


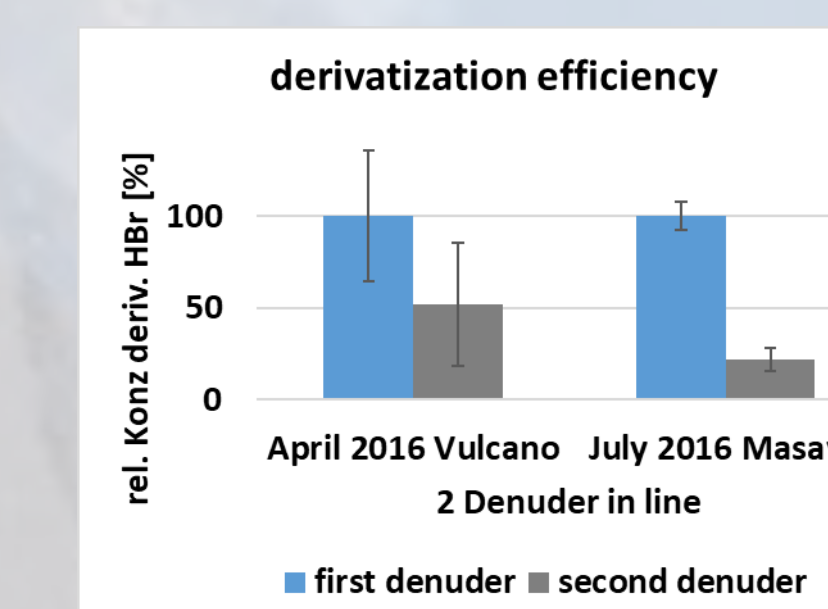
Fig. 10: Overview of Sampling Site at Masaya 2016
Data shown in Figure 9 were taken at 'Pole Site', 'Nindiri' and 'San Pedro'.^[10]

Collection efficiency

2 denuder in line ensure quantitative determination

Fig. 11: Collection efficiency dependent on coating amounts

April 2016 : 1 sample, 45 μmol EP/Denuder
July 2016: 4 samples, 90 μmol/Denuder



E Outlook

Denuder vs. Raschig tubes

- Comparison of lab samples collected by both methods simultaneously

Data sets help to gain knowledge on volcanic bromine chemistry

- Analyze collected samples
- More field applications to extent data sets

Other halogens

- Extent method for Chlorine and Iodine speciation?

Other coatings – more species

- Br radicals
- Also possible for H₂S and SO₂ distinction

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