Reactive bromine chemistry in the Rann of Kachchh salt desert

Jonas Kuhn[1,2], Vinod Kumar[1], Simon Warnach[1,2], Ulrich Platt[1,2], and Thomas Wagner[1]

[1] *Max Planck Institute for Chemistry, Mainz, Germany*

[2] *Institute of Environmental Physics, Heidelberg University, Germany*

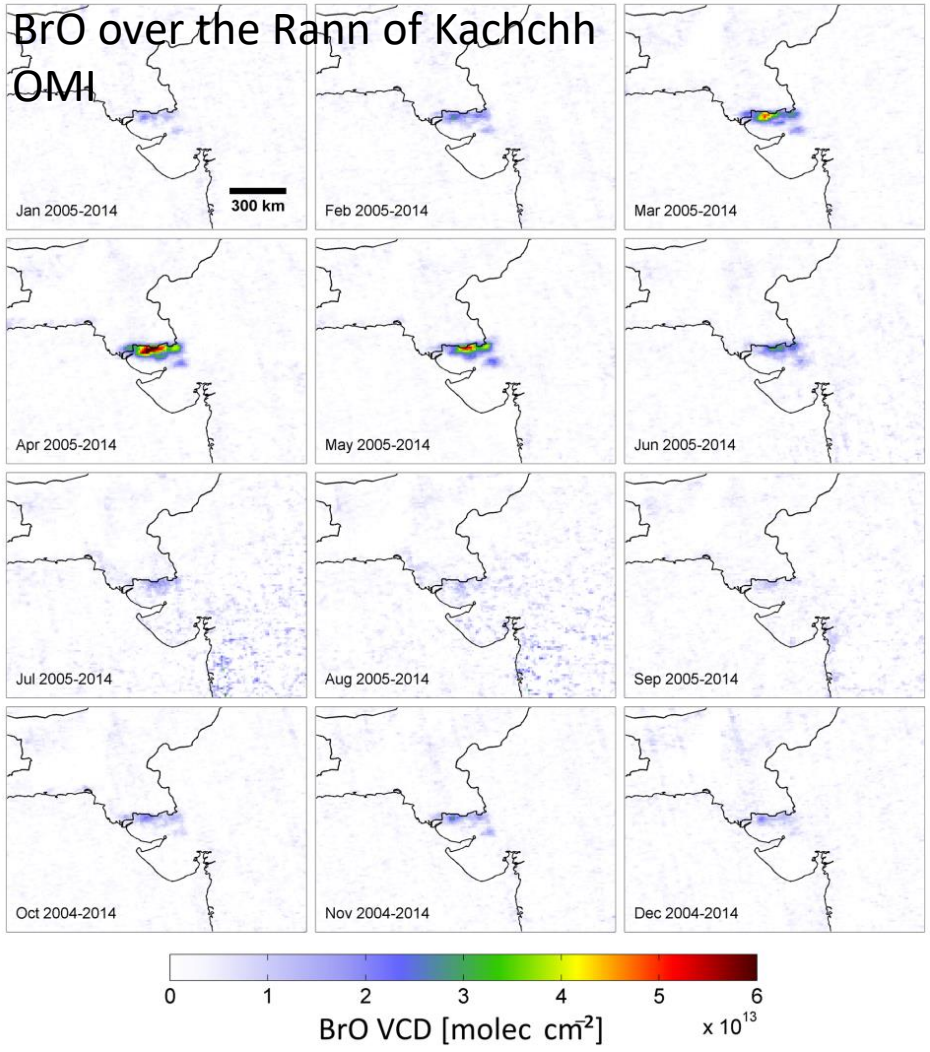
EGU General Assembly Online 2020
AS3.20 Halogens in the Troposphere

Introduction

Previous observation of BrO from Sattelite

Hörmann et al., 2016

BrO over the Rann of Kachchh
OMI



Seasonal variation of tropospheric bromine monoxide over the Rann of Kutch salt marsh seen from space

Christoph Hörmann[1], Holger Sihler[1,2], Steffen Beirle[1], Marloes Penning de Vries[1], Ulrich Platt[2], and Thomas Wagner[1]

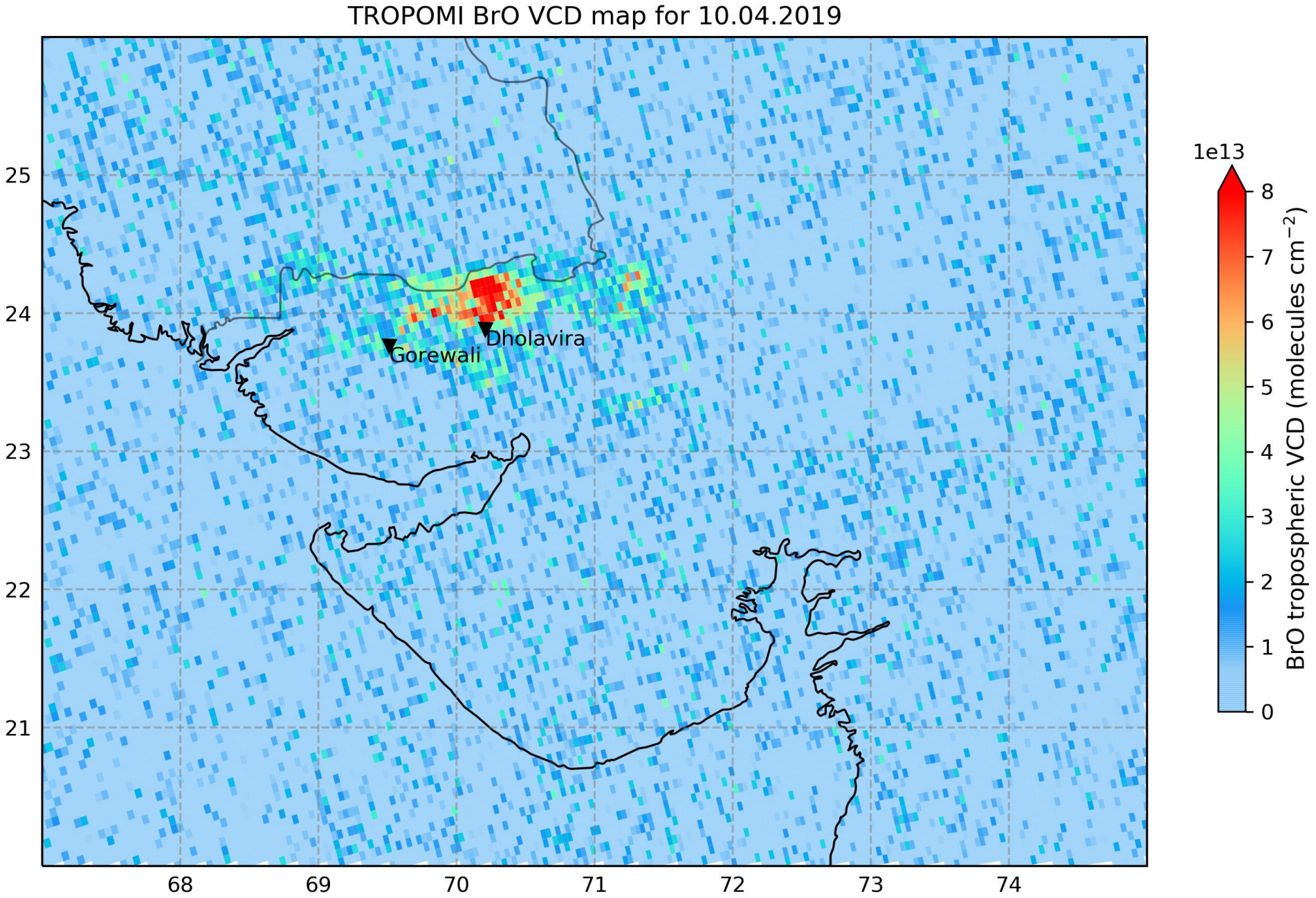
[1]Max Planck Institute for Chemistry (MPI-C), Mainz, Germany
[2]Institute for Environmental Physics, University of Heidelberg, Heidelberg, Germany

Present satellite observations:

- overpass once per day at a fixed time of day
- limited spatial resolution: ~5km (TROPOMI), no vertical resolution

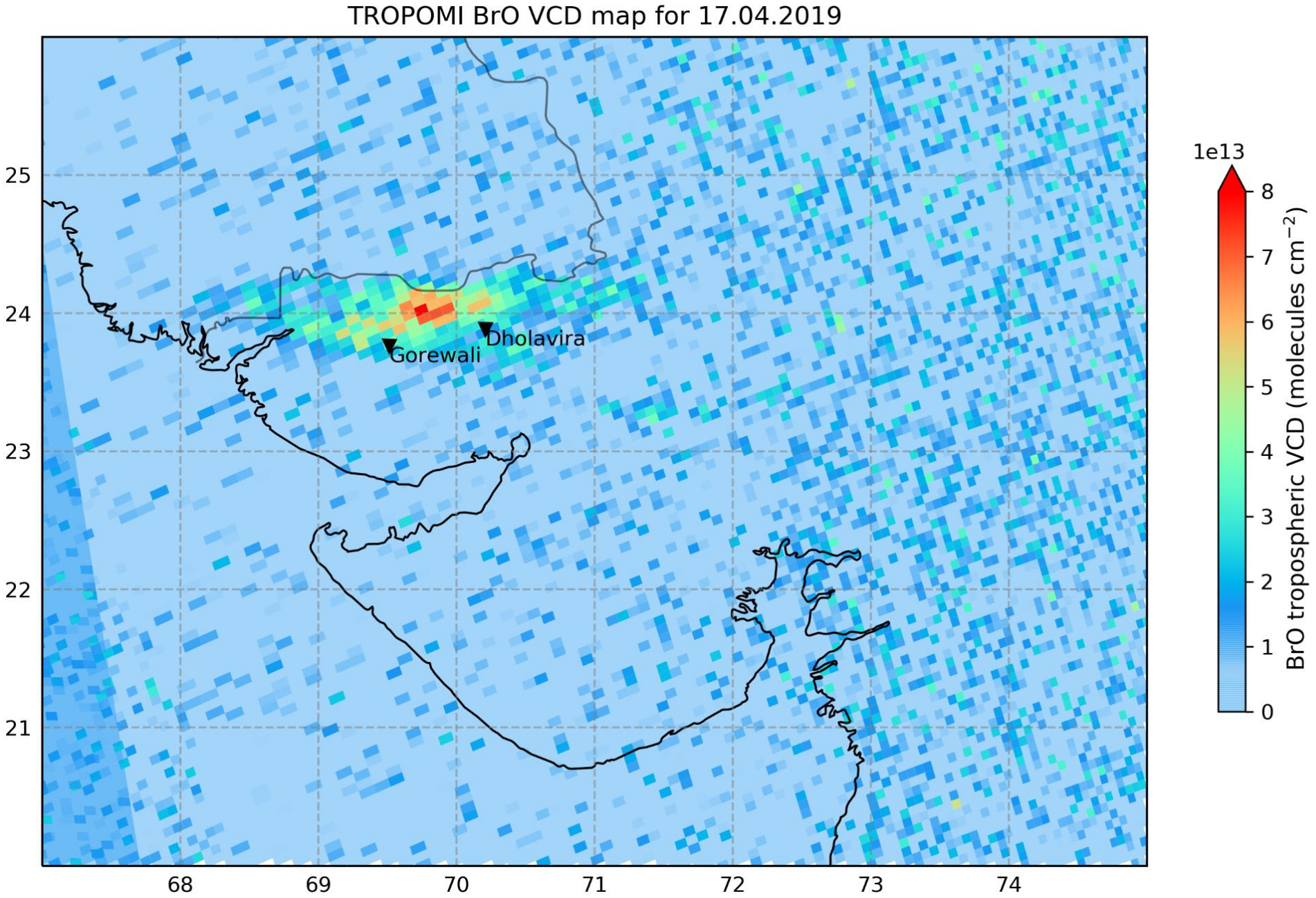
highly dynamic chemistry is expected
→ **ground based measurements!**

TROPOMI measurements



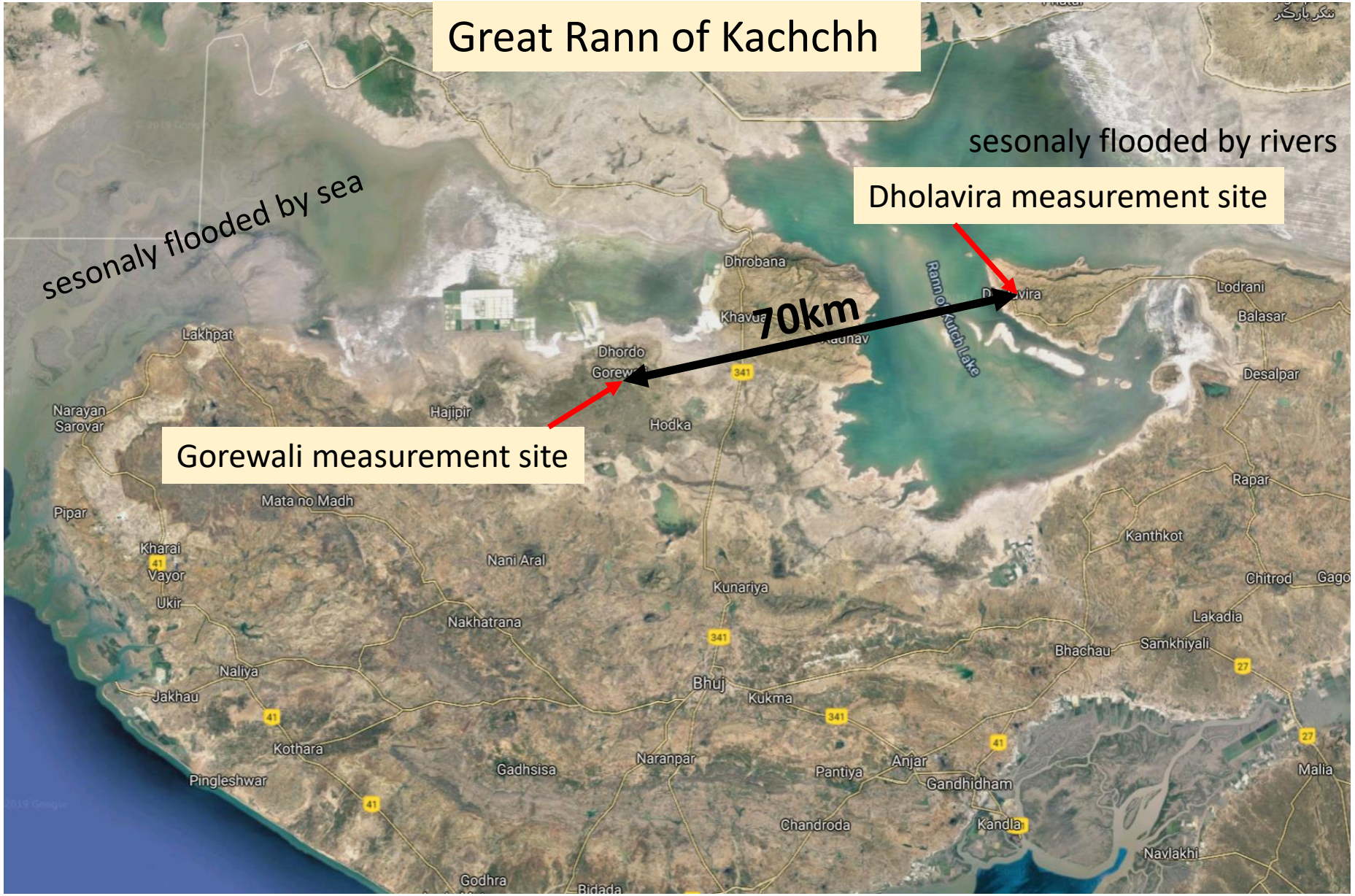
Much higher spatial resolution (~5km) than OMI,
BrO limited to the Rann, spatially variable daily observations, overpass ~13:30 local time,
Chemistry on a time scale in the range of seconds to hours, can not be resolved

TROPOMI measurements



Much higher spatial resolution (~5km) than OMI,
BrO limited to the Rann, spatially variable daily observations, overpass ~13:30 local time,
Chemistry on a time scale in the range of seconds to hours, can not be resolved

Measurement campaign Rann of Kachchh, 26 Mar – 18 Apr 2019



Both sites are located ~ 10km from the salt surface due to logistical/organisational reasons.
Measurements directly at the salt surface show no substantial differences in trace gas amount an progression.

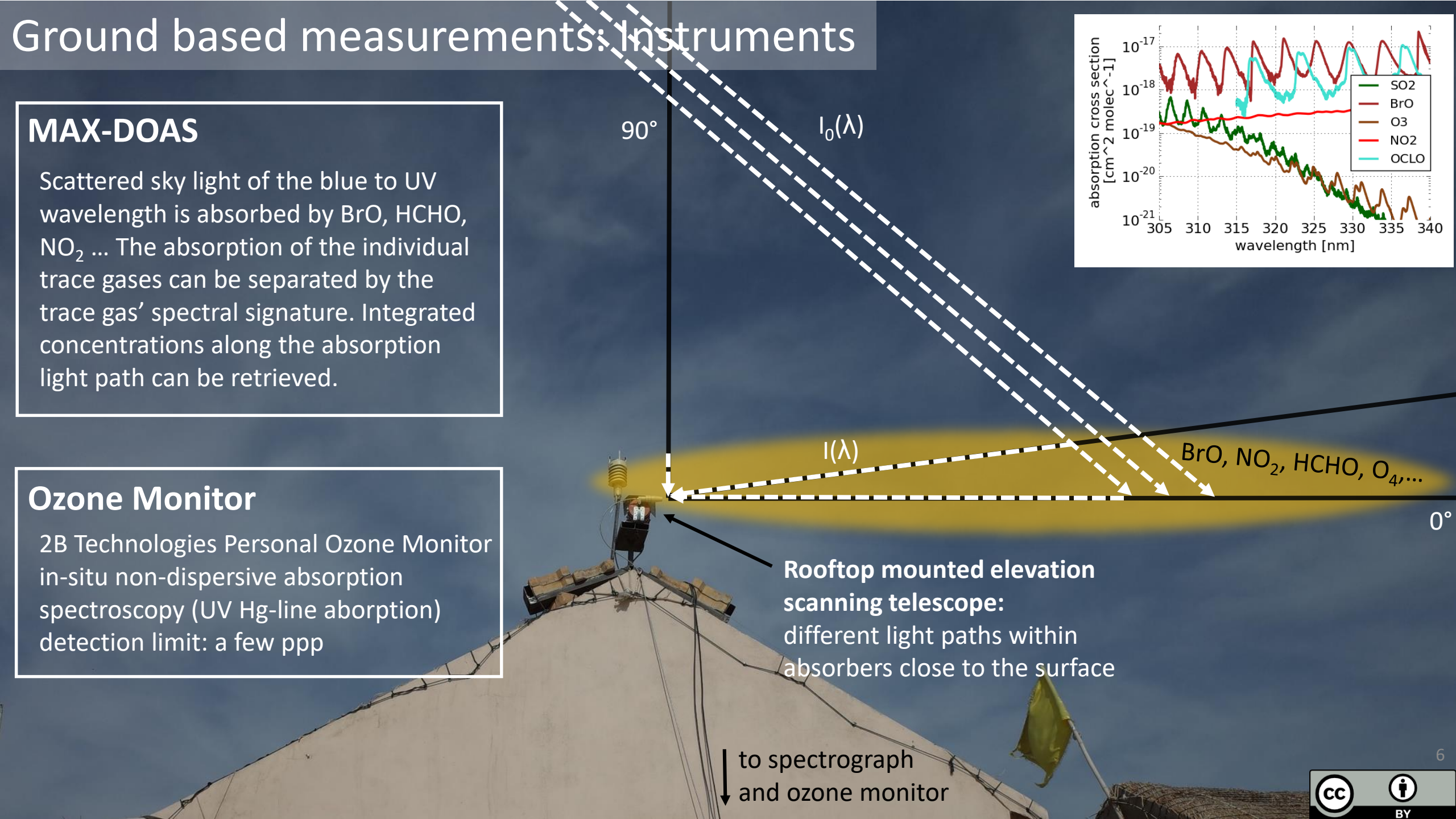
Ground based measurements: Instruments

MAX-DOAS

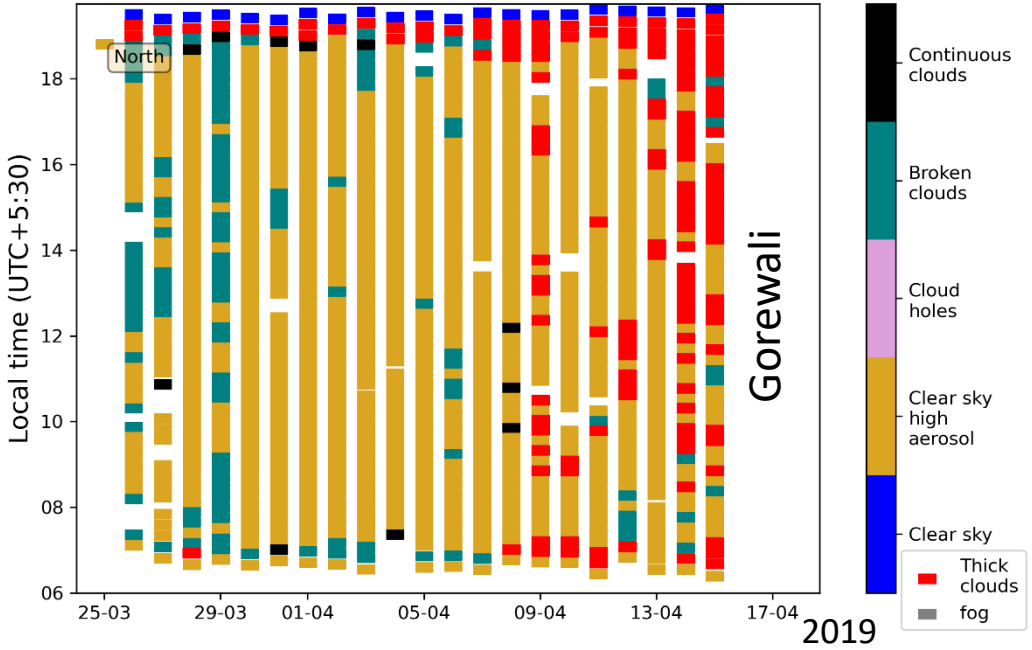
Scattered sky light of the blue to UV wavelength is absorbed by BrO, HCHO, NO_2 … The absorption of the individual trace gases can be separated by the trace gas' spectral signature. Integrated concentrations along the absorption light path can be retrieved.

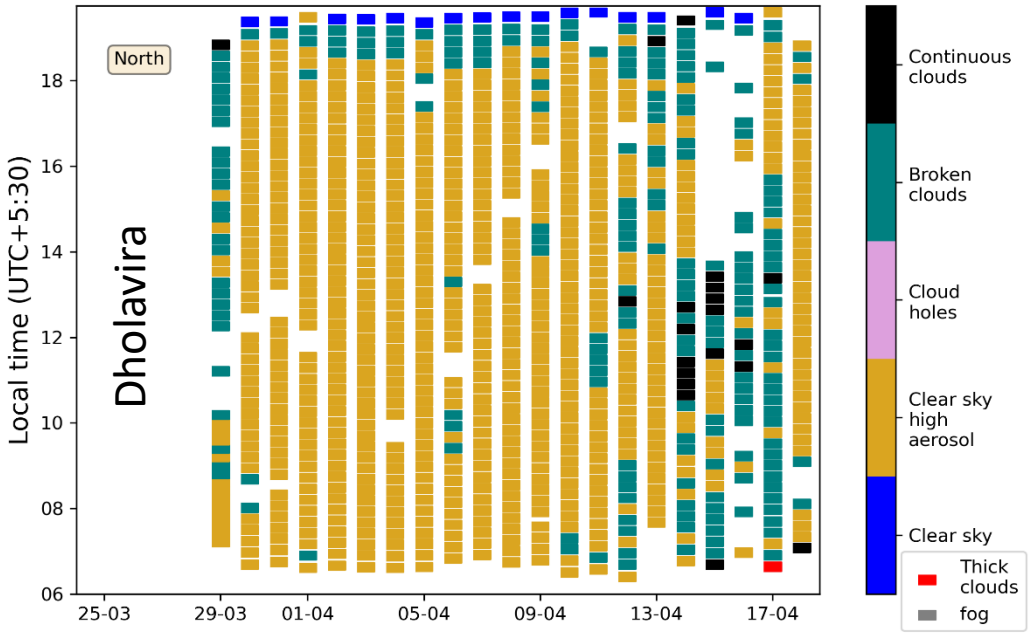
Ozone Monitor

2B Technologies Personal Ozone Monitor in-situ non-dispersive absorption spectroscopy (UV Hg-line aborption) detection limit: a few ppp



Ground based measurements: Data overview

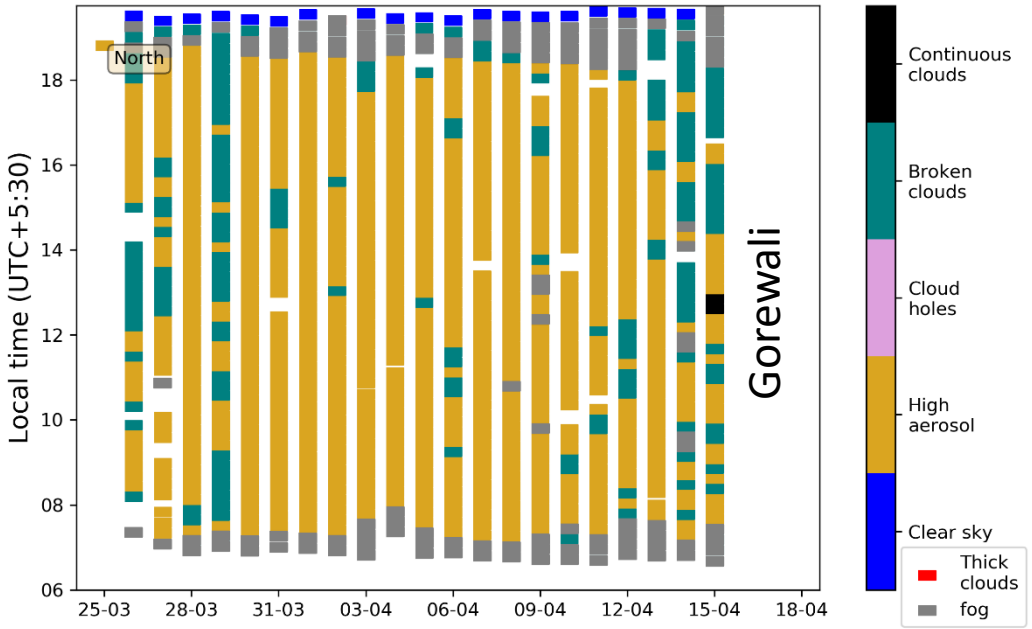


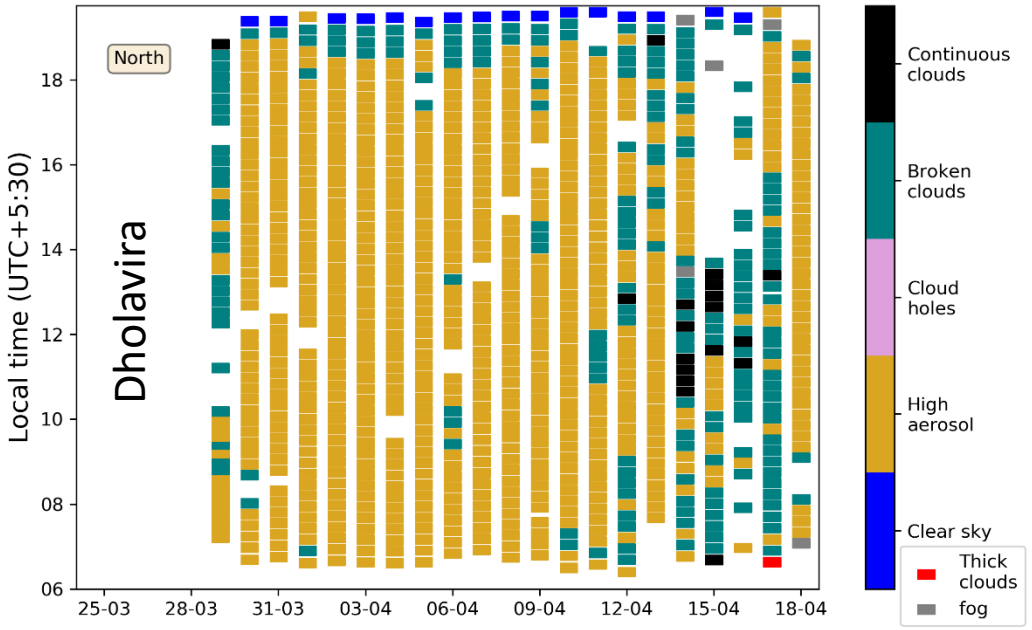


- All trace gas amounts measured with MAX DOAS are given in column density units of molec cm^{-2} and are not converted to concentrations. Assuming e.g. a 3000m light path within the boundar layer containing the absorber would mean:
  1e14 molec cm^{-2} → 13ppt
  1e16 molec cm^{-2} → 1.3ppb
- The measured ozone is given as surface mixing ratio (ppb) at the MAX DOAS location
- Due to fast chemistry and spatial inhomogeneity/mixing the data might show trage gas amounts from slightly different air masses from within a few km.
- Nevertheless, this data already allows for a multitude of important observations that will be refined in further data processing steps in the future

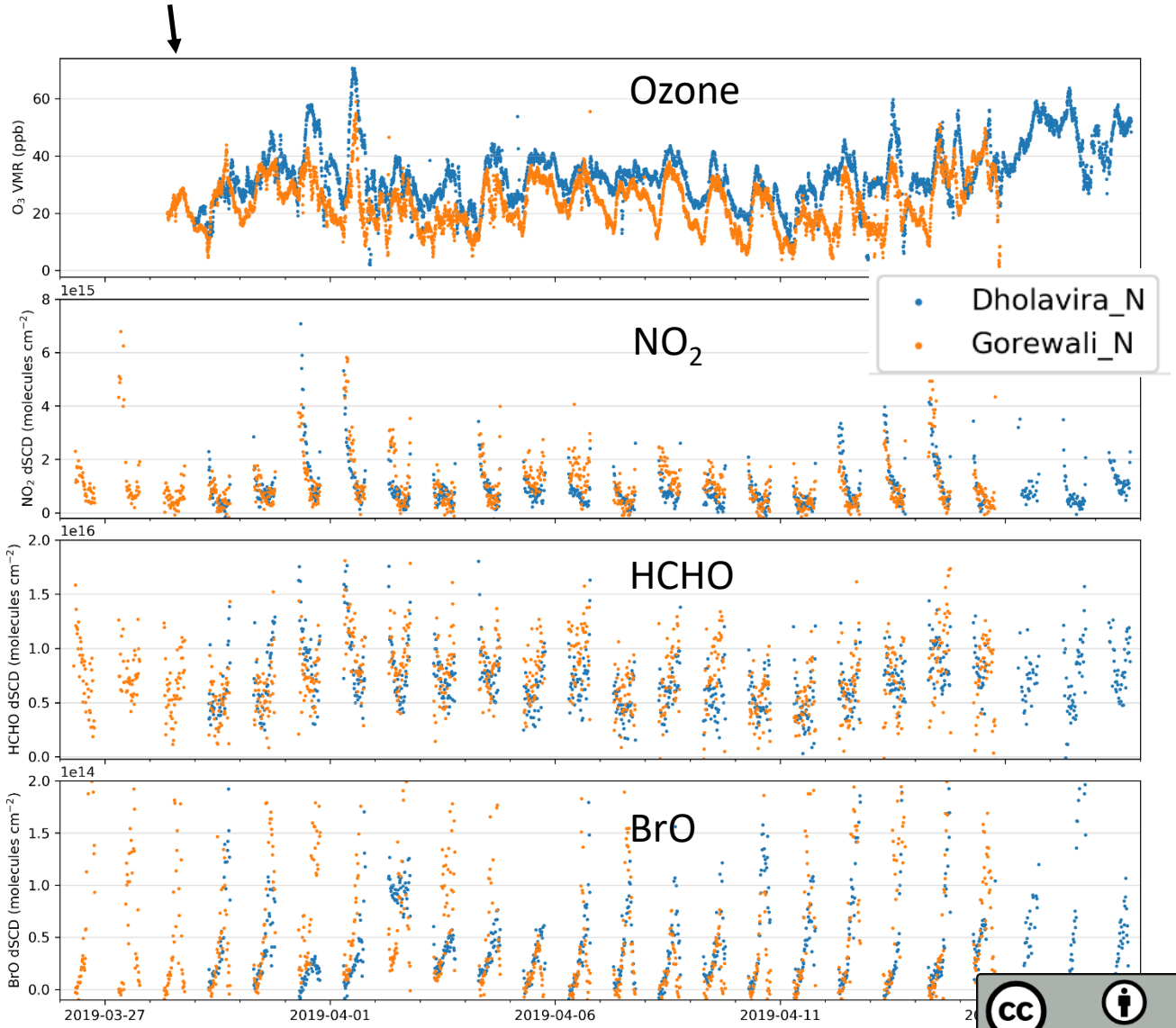
Sky conditions throughout the campaign, retrieved according to Wagner et al., 2016: **most of the time clear sky conditions**

Ground based measurements: Data overview





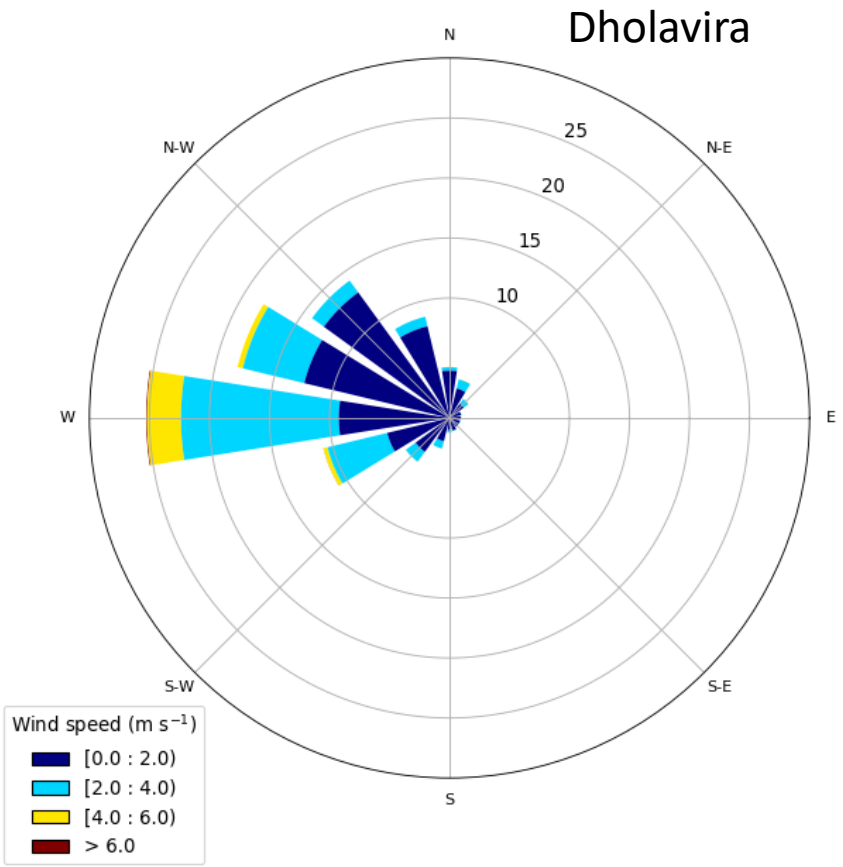
Time series of trace gases throughout the campaing for the two sites, often very similar trace gas evolution → likely chemistry driven

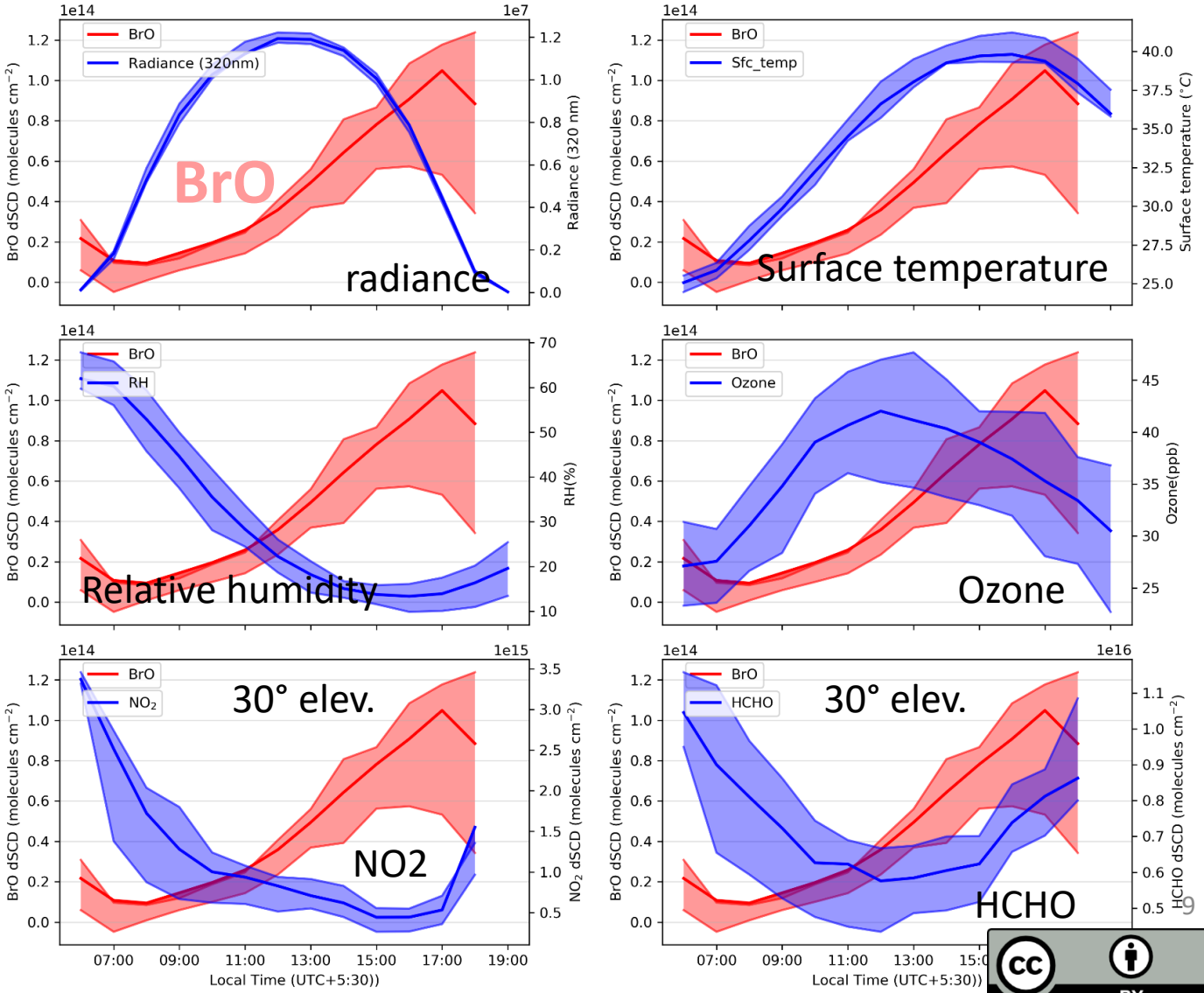


Ground based measurements: Data overview

Average values throughout the campaing
Quite **consistent diurnal patterns** are observed.

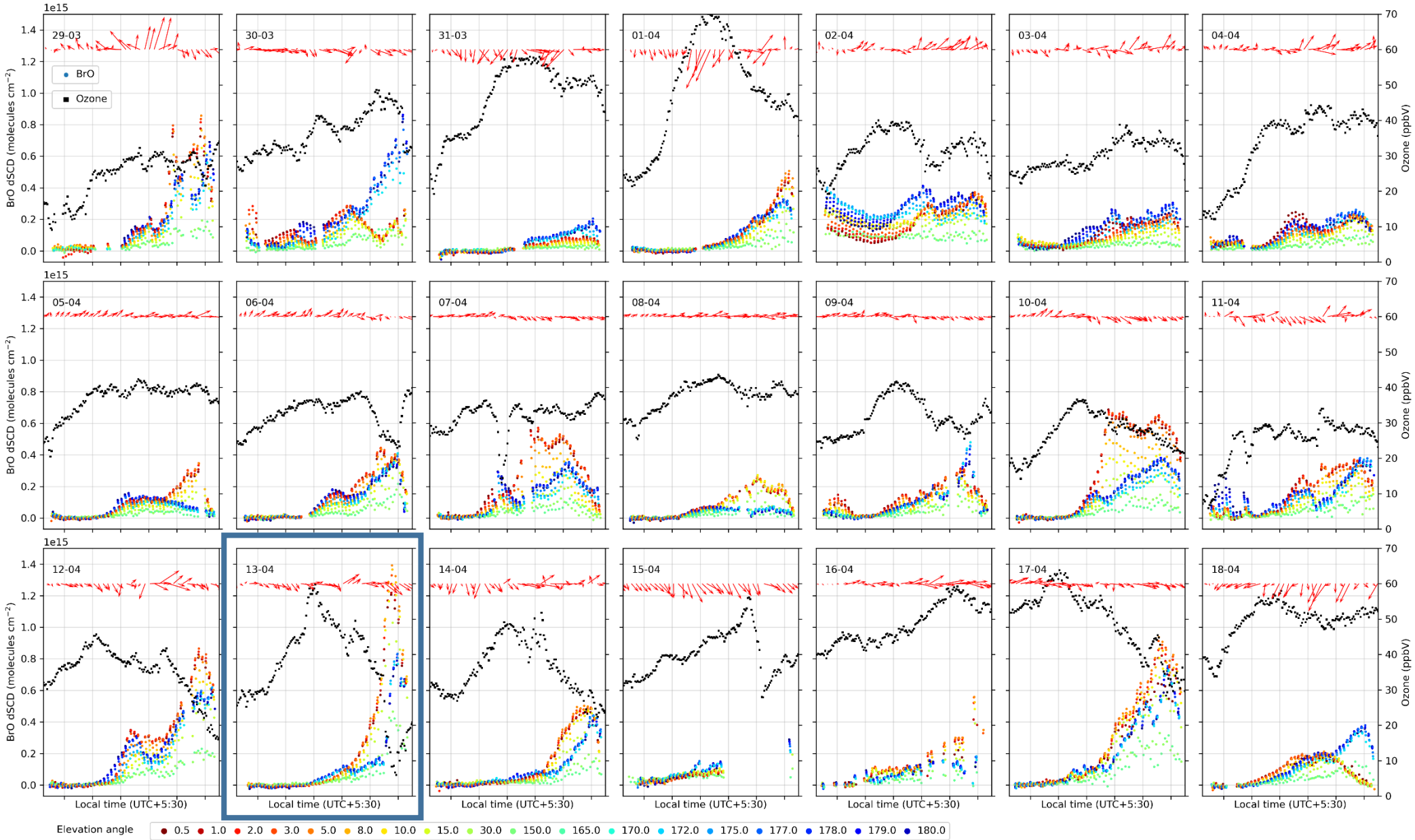
Also quite **stable wind conditions**





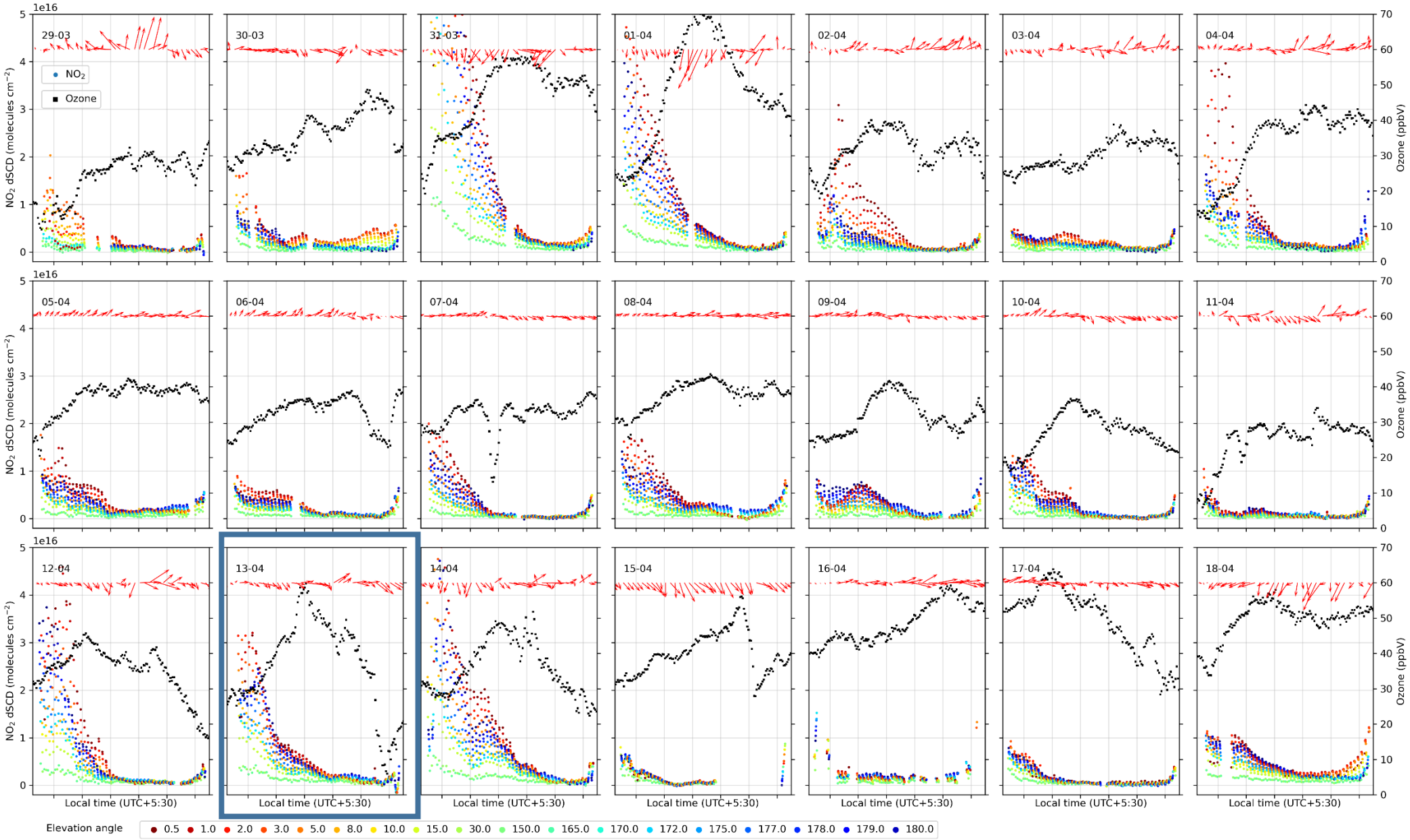
Dholavira site, 29.03. – 18.04.2019:

BrO for the individual days:
Low in the morning, rising towards the afternoon



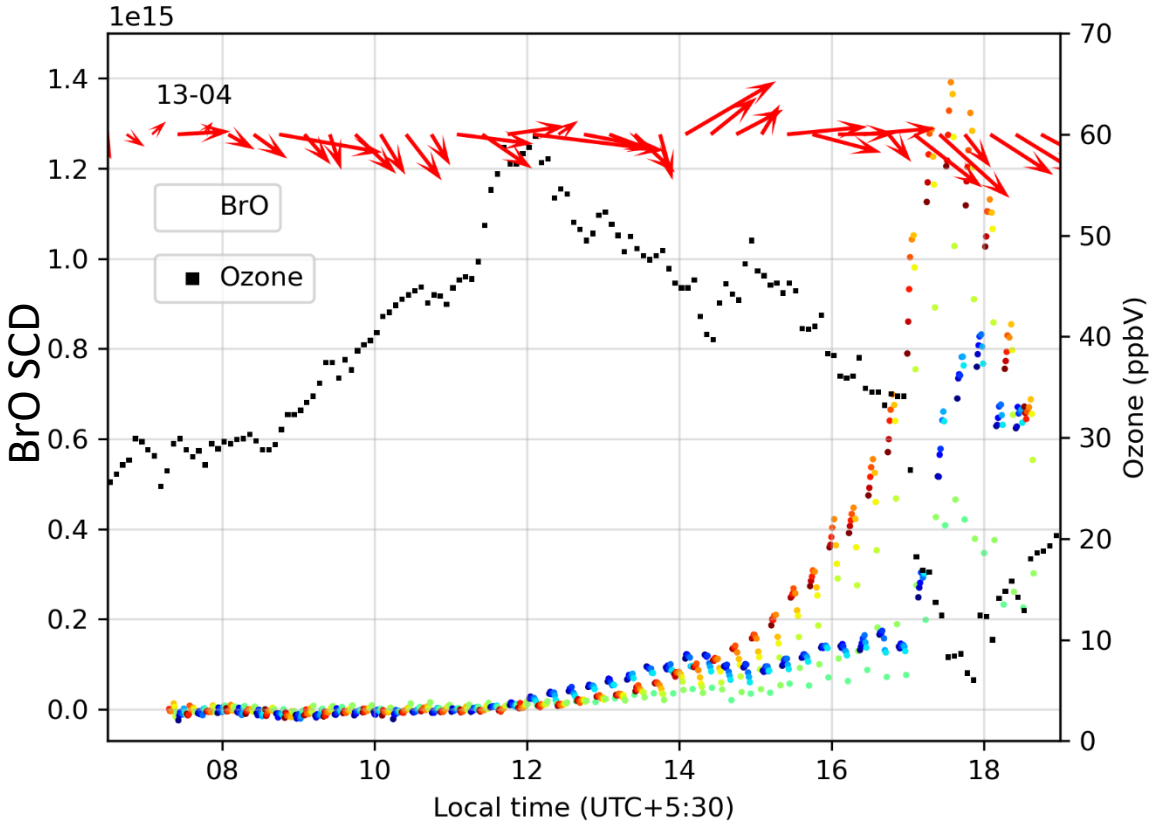
Dholavira site, 29.03. – 18.04.2019:

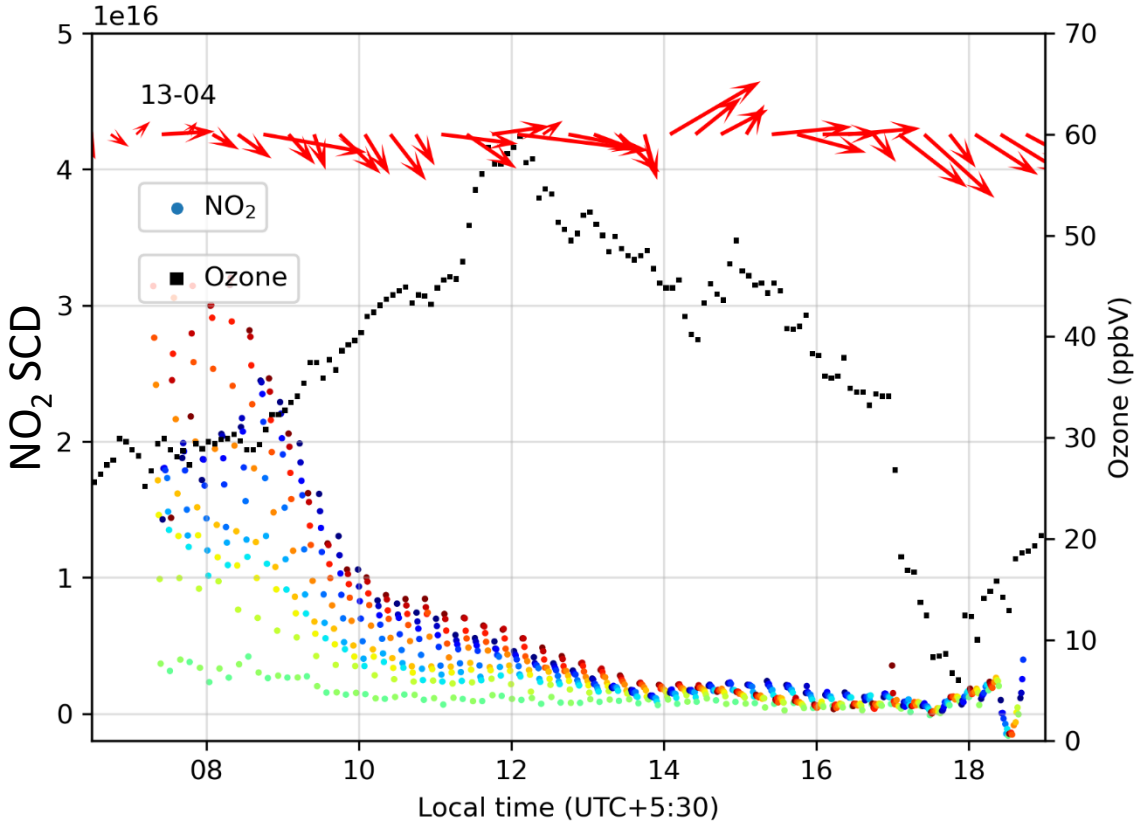
NO_2 for the individual days:
High in the morning, depleted in the afternoon



Dholavira site 13.4.2019

Blueish green dots look south, reddish yellow dots look north

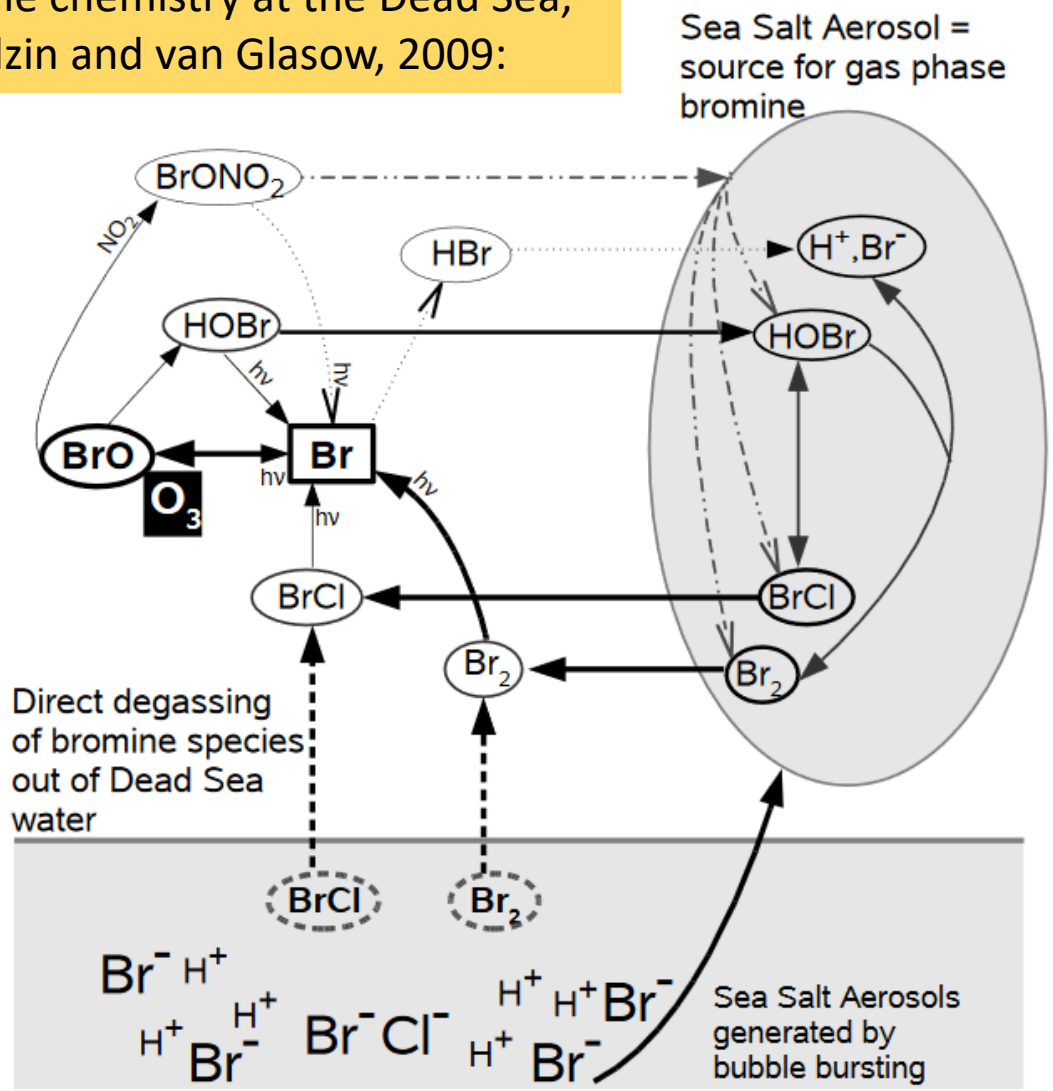




Exemplary day: BrO builds up slowly during the day, while NO_2 decreases; an air mass that is almost fully depleted in ozone moves over the measurement site at around 18:00 local time.
NO_2 concentrations fall well below 100ppt assuming a light paths of a few km. BrO concentrations then reach several tens of ppt.

Preliminary thoughts on chemistry:

Bromine chemistry at the Dead Sea, Smoydzin and van Glasow, 2009:



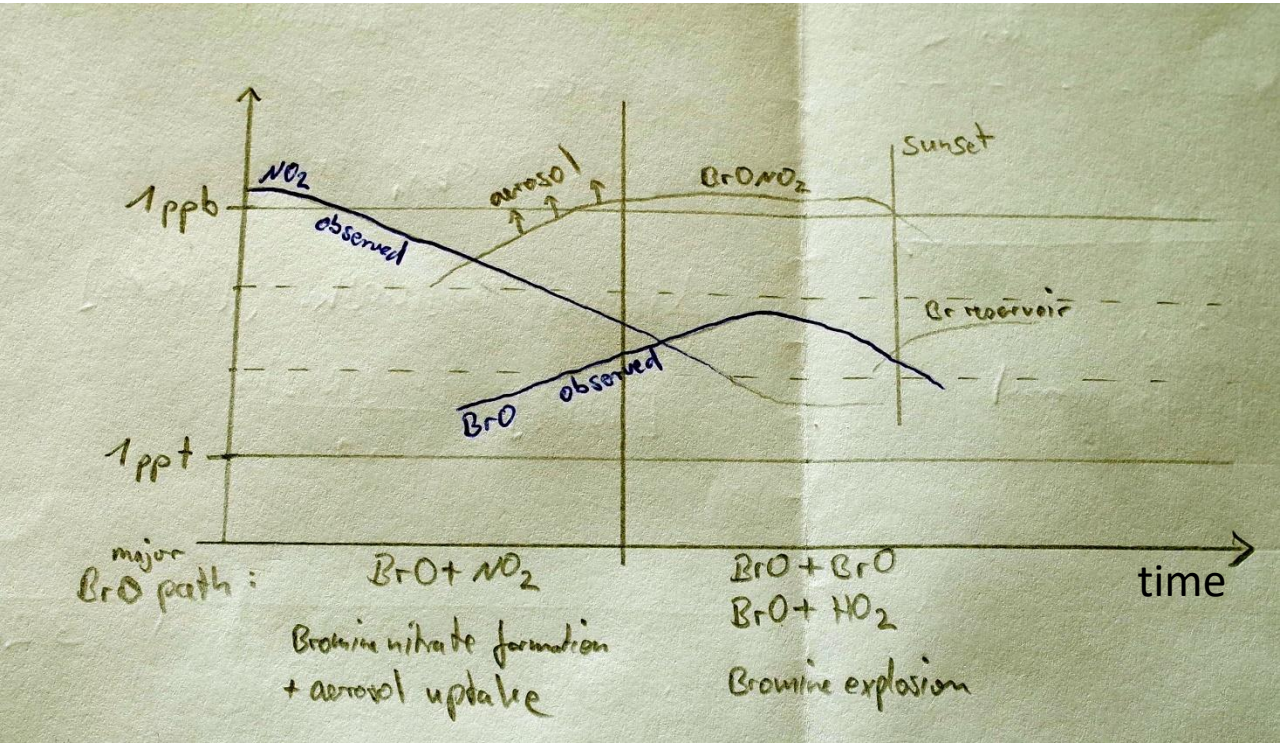
Reaction partner BrO + …	Amount [ppt]	BrO lifetime [min]
NO_2	10000	0.005
	1000	0.05
	100	0.5
	10	5
BrO	100	2
	10	20
	1	200
HO_2	10	3

Based on JPL Publication 15-10

$BrONO_2 + hv \rightarrow BrO + NO_2$ J ~ 2e-3/s (max.)
$\rightarrow$ Lifetime or $BrONO_2$ ~ 10min

NO_2 prevents BrO to accumulate, bromine nitrate is formed

Preliminary thoughts on chemistry:



Reaction partner BrO + …	Amount [ppt]	BrO lifetime [min]
NO_2	10000	0.005
	1000	0.05
	100	0.5
	10	5
BrO	100	2
	10	20
	1	200
HO_2	10	3

rate constants: JPL Publication 15-10

$BrONO_2 + hv \rightarrow BrO + NO_2$ J ~ 2e-3/s (max.)
→ Lifetime or $BrONO_2$ ~ 10min

Morning: NO_2 + BrO from night time reservoirs, released BrO is almost instantly converted into bromine nitrate ($BrONO_2$), $BrONO_2$ aerosol uptake (~20min time constant, Holla et al., 2015), probably limited by reactive bromine supply
Afternoon: NO_2 is depleted (< 100ppt) by the above process and photolysis, catalytic ozone destruction, bromine explosion results in high BrO amounts, release of Br from aerosol
Evening: Br → reservoir species, new NO_2 from pollution transport..

→ Reduction of NO2 lifetime, nitrification of aerosol, ozone destruction, reactive bromine supply by release from the salt surface?

Summary

- In a 3-weeks field campaing, atmospheric trage gases in the Rann of Kachchh salt desert were measured at two sites, separated by ~ 70km and each ~10km far from the salt surface
- High amounts of BrO were observed building up during the day, reaching a maximum in the later afternoon
- Both sites observe similar amounts and temporal progression, indicating dominace of chemical processes
- Rather low NO_2 amounts decrease further with increasing BrO and get depleted at peak BrO
- Air masses depleted in Ozone (surface point measurement) occasionally correlate with high BrO (column density) abundance

Conclusions

- Reactive bromine substantially reduces NO_2 and ozone lifetimes
- high amounts of bromine nitrate ($BrONO_2$) might be formed and taken up by aerosol
- once NO_2 is low enough, the bromine explosion causes high BrO amounts (up to ~100ppt), releasing bromine from the aerosol, destroying ozone and depleting the residual NO_2
- Nitrate might reside in the aerosol

- The preliminary data of this first exploratory campaing already allow for insights into halogen chemistry in this unique environment. For a more comprehensive study, further trace gas species need to be measured in order to model the chemistry.

References

Hörmann, C., Sihler, H., Beirle, S., Penning de Vries, M., Platt, U., & Wagner, T. “Seasonal variation of tropospheric bromine monoxide over the Rann of Kutch salt marsh seen from space.” *Atmospheric Chemistry & Physics*, *16*(20), (2016).

Smoydzin, L., and von Glasow, R. "Modelling chemistry over the Dead Sea: bromine and ozone chemistry." *Atmospheric Chemistry & Physics* 9.14, (2009).

Holla, R., Schmitt, S. , Frieß, U. ,Pöhler, D. ,Zingler, J., Corsmeier, U., and Platt, U. "Vertical distribution of BrO in the boundary layer at the Dead Sea."*Environmental Chemistry* 12(4) 438-460 https://doi.org/10.1071/EN14224, (2015).

Wagner, T. K., Beirle, S., Remmers, J., Shaiganfar, R., & Wang, Y. “Absolute calibration of the colour index and O-4 absorption derived from Multi AXis (MAX-)DOAS measurements and their application to a standardised cloud classification algorithm.” *Atmospheric Measurement Techniques, 9*(9), 4803-4823. doi:10.5194/amt-9-4803-2016, (2016).

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H. “Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies”, Evaluation No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, (2015).