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Bromine Nitrate ($BrONO_2$) derived from MIPAS to test our understanding of Stratospheric Bromine Chemistry

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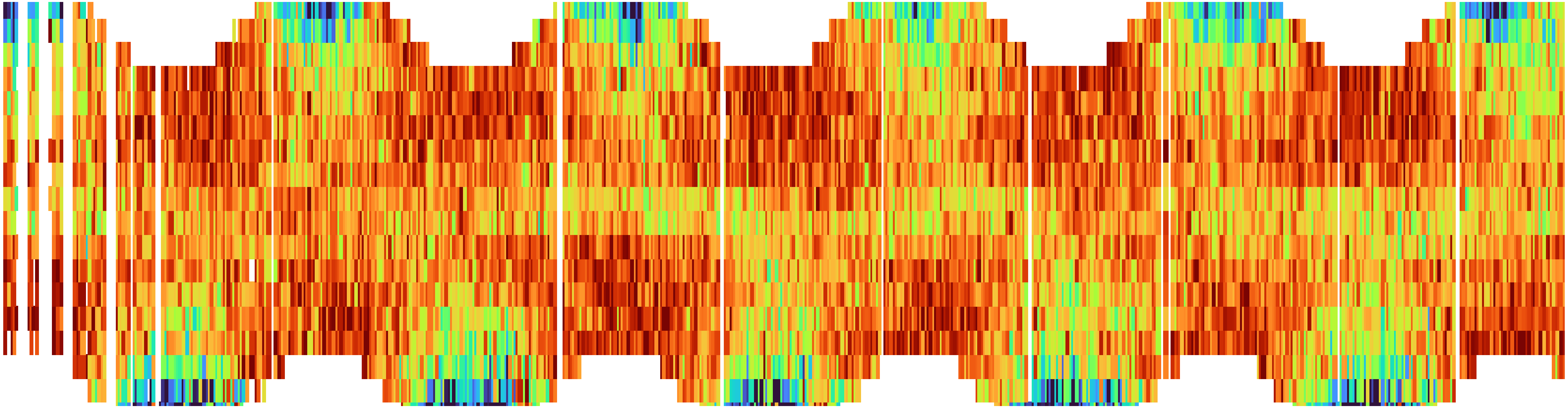

Why bromine? Why $BrONO_2$?

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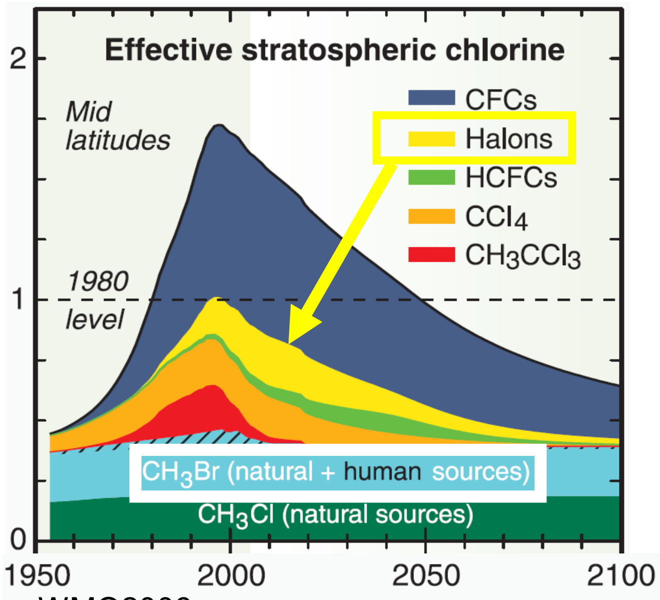
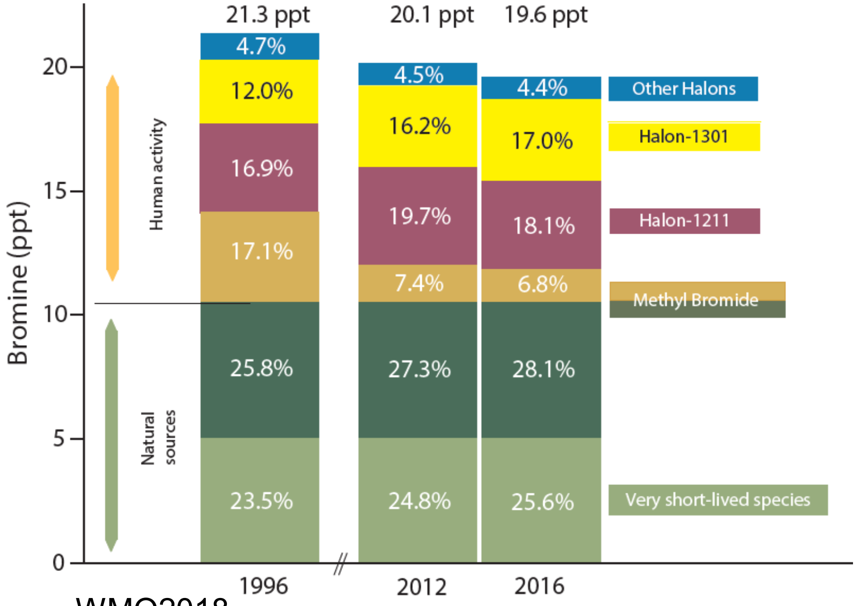
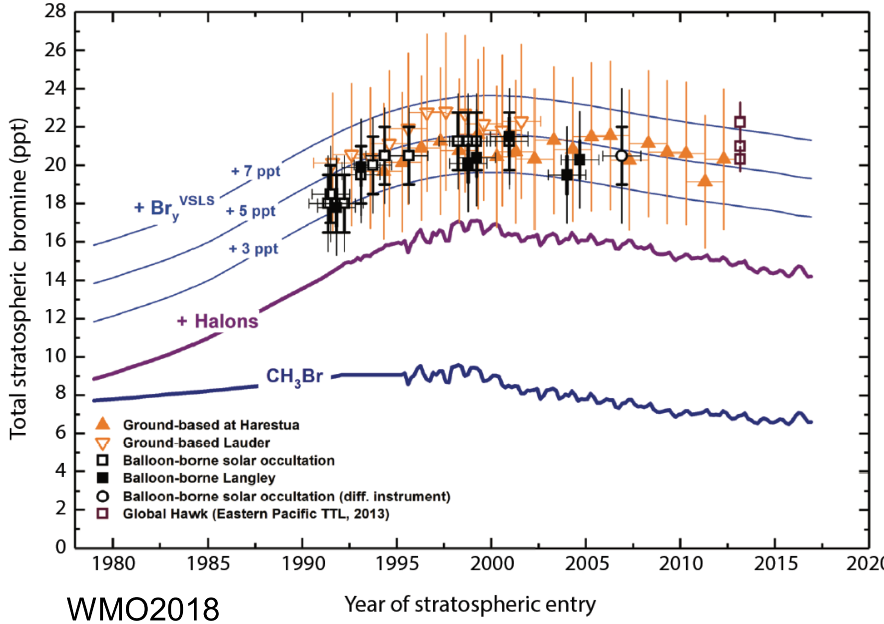
- Ozone depleting potential of bromine ~60 times greater than of chlorine due to faster photolysis of the reservoir species $BrONO_2$ compared to $ClONO_2$
- Bromine couples with chlorine cycles (ozone hole chemistry)
- Anthropogenic bromine content decreases but large natural sources which may be influenced by climate change
- $BrONO_2$ is the most abundant stratospheric bromine species during night (up to > 95% of total Br_y) and, therefore, well suited to derive Br_y



WMO2006

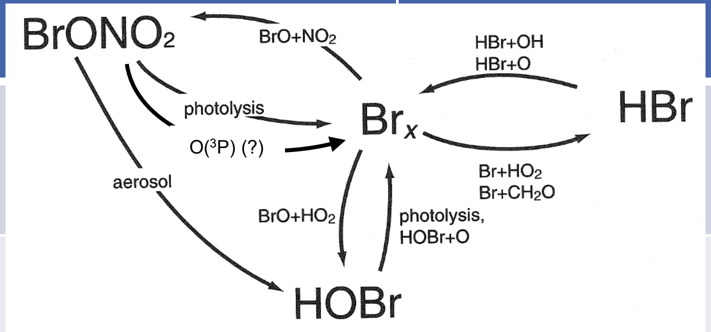


WMO2018



WMO2018

Reactions and their uncertainties determining $BrONO_2$



Reaction	1σ uncertainty factor (JPL2019) @220 K
Gain:	
$BrO + NO_2 \xrightarrow{M} BrONO_2$	1.9
Loss:	
$BrONO_2 + h\nu \rightarrow Products$	1.1 (UV x-sections)
$BrONO_2 + O(^3P) \rightarrow BrO + NO_3$	1.3 (but only one publication on this reaction)
$BrONO_2 + H_2O(s,l,H_2SO_4 \cdot nH_2O) \rightarrow HOBr + HNO_3$	2-4 (reaction probability)

First $BrONO_2$ observations

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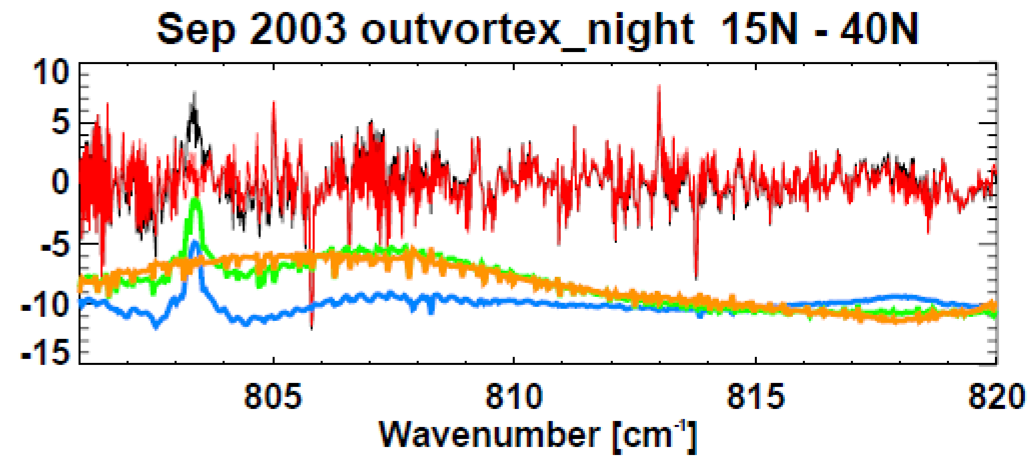
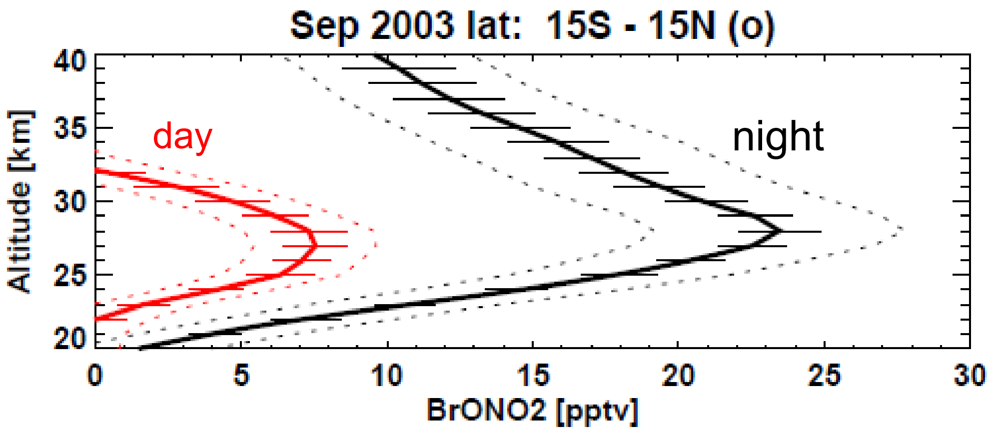
MIPAS/Envisat



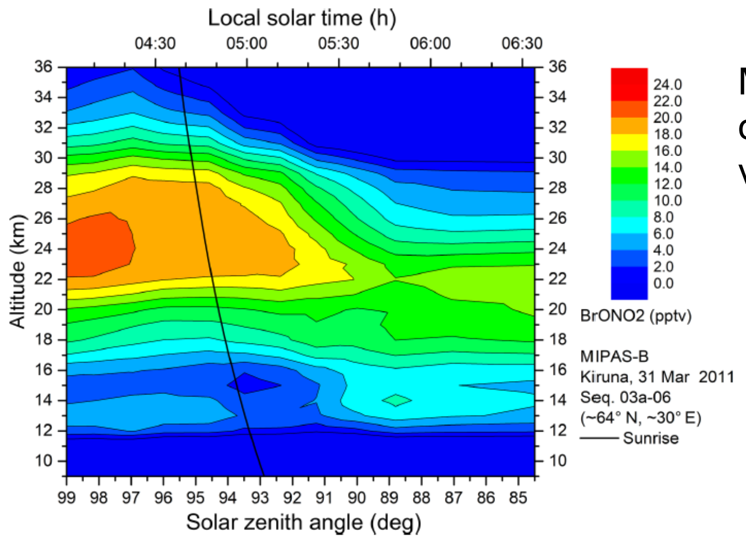
Detection of spectral signature



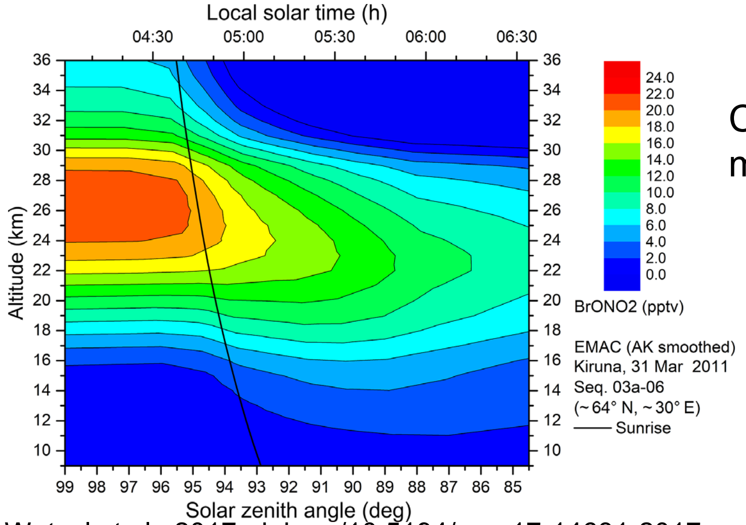
First profiles

Höpfner et al., 2009, doi.org/10.5194/acp-9-1735-2009

MIPAS-Balloon



Measurements of diurnal variation



Comparison with model (EMAC)

Wetzel et al., 2017, doi.org/10.5194/acp-17-14631-2017

MIPAS $BrONO_2$ retrieval updates

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	'Old'	'New'
MIPAS L1b spectra	4.61/62	8.03 (doi:10.5270/EN1-77pi5sd)
Data coverage/averaging	Sep. 2002 and 2003; monthly; 6 latitude bands; dark/sunlit	2002-2012; 3 day; 18 latitude bands; dark/sunlit
$BrONO_2$ x-sections	Orphal et al., 2008 (doi:10.1016/j.cplett.2008.04.089) adapted to strat. temperatures	p/T dependent by Birk et al., 2016 (doi: 10.1016/j.jms.2016.03.007)
HO_2NO_2 x-sections	220 K (May and Friedl, 1993, doi: 10.1016/0022-4073(93)90076-T)	2-point interpolation with: 298 K (Friedl et al., 1994, doi: 10.1006/jmsp.1994.1151)

Characteristics of $BrONO_2$ retrievals: error estimates and vertical resolution

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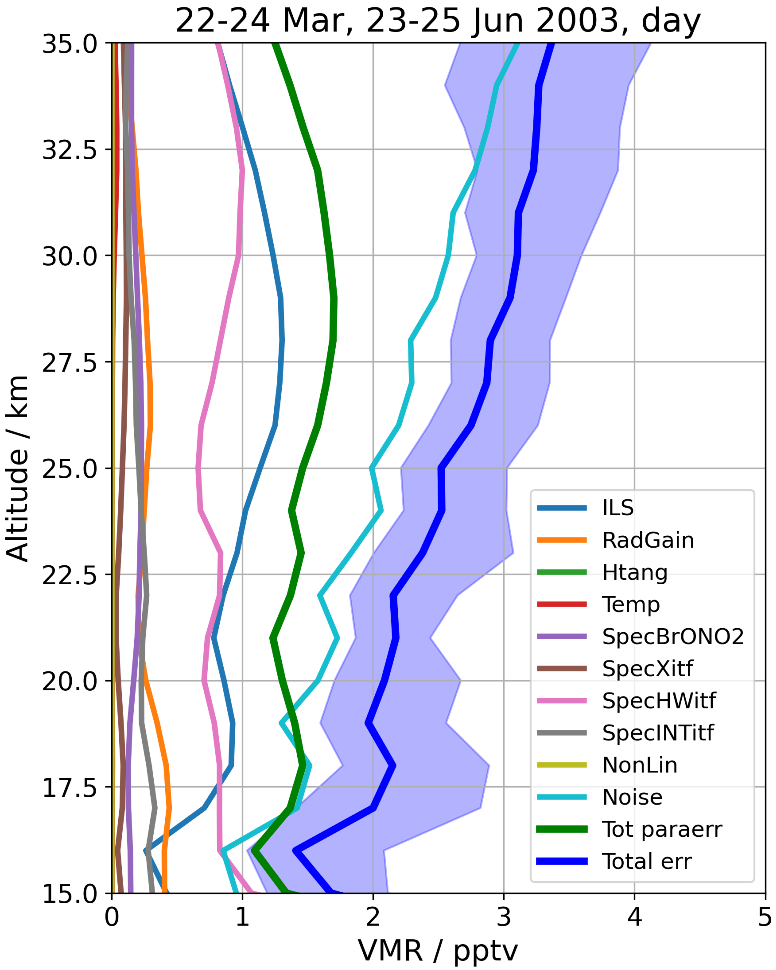
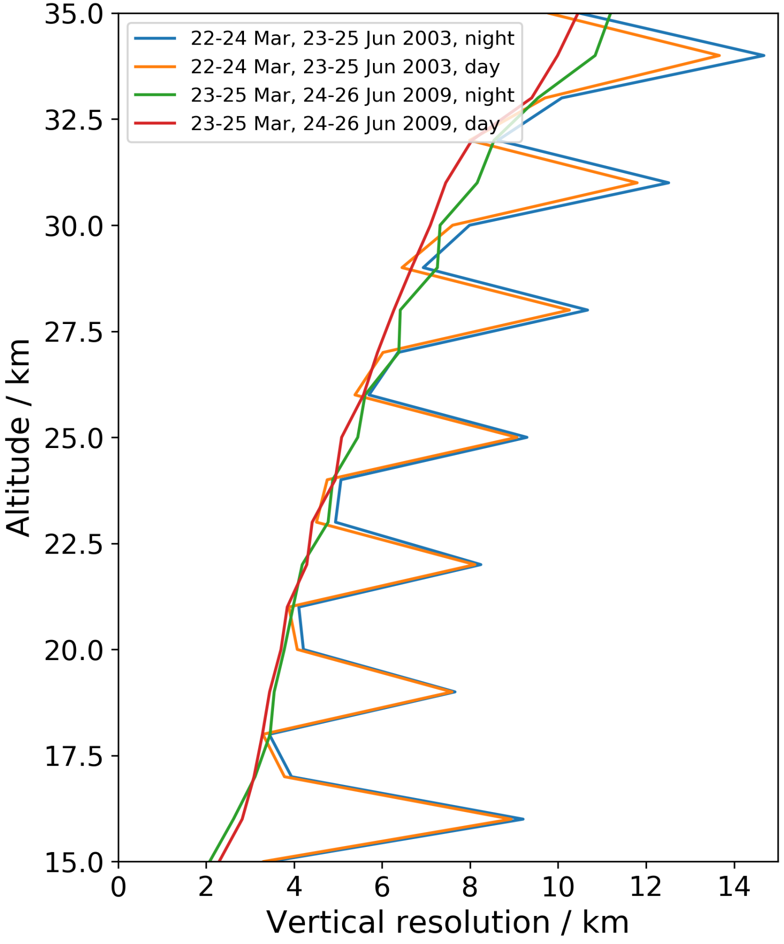
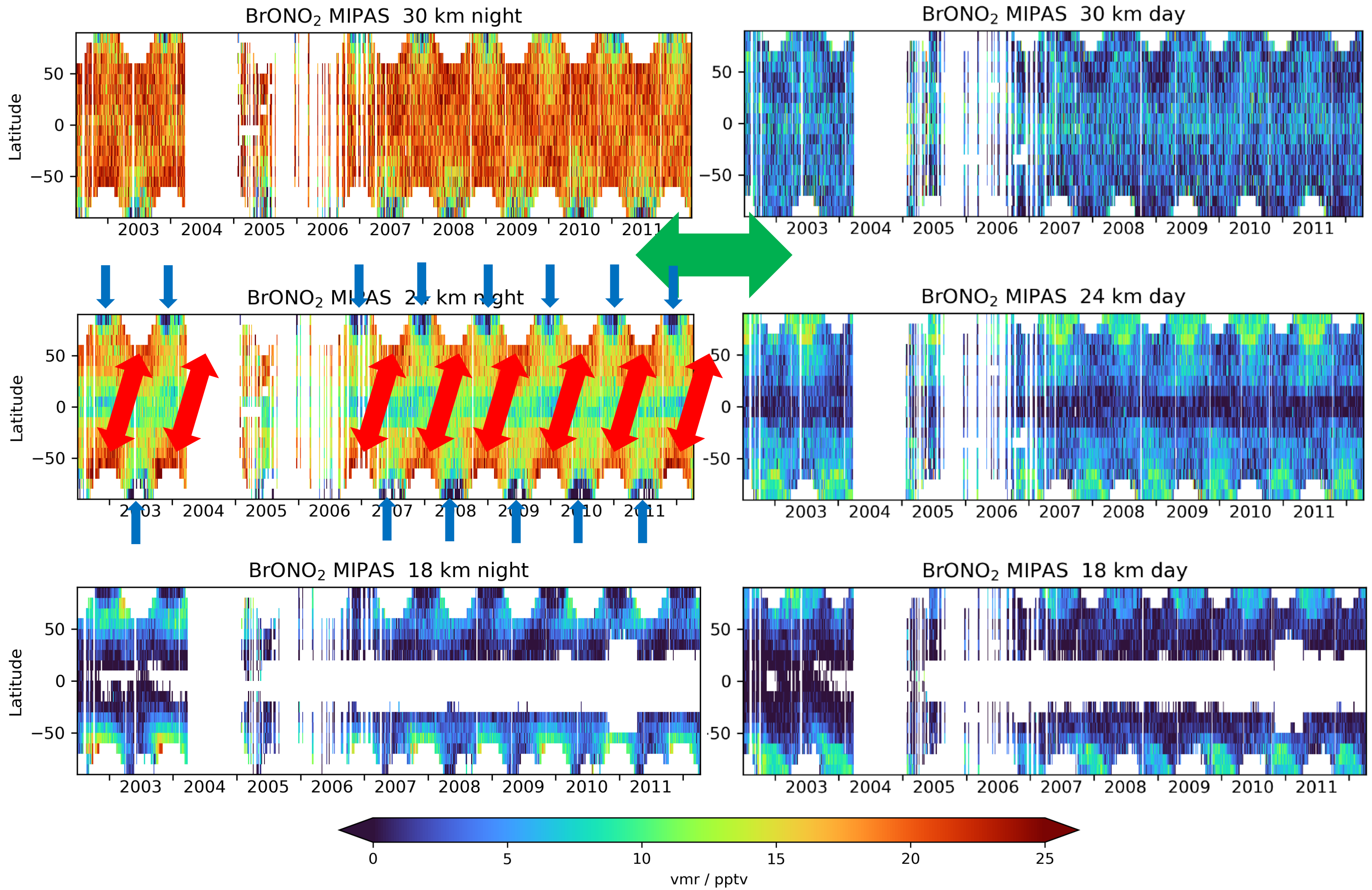
Estimated uncertainty



Vertical resolution



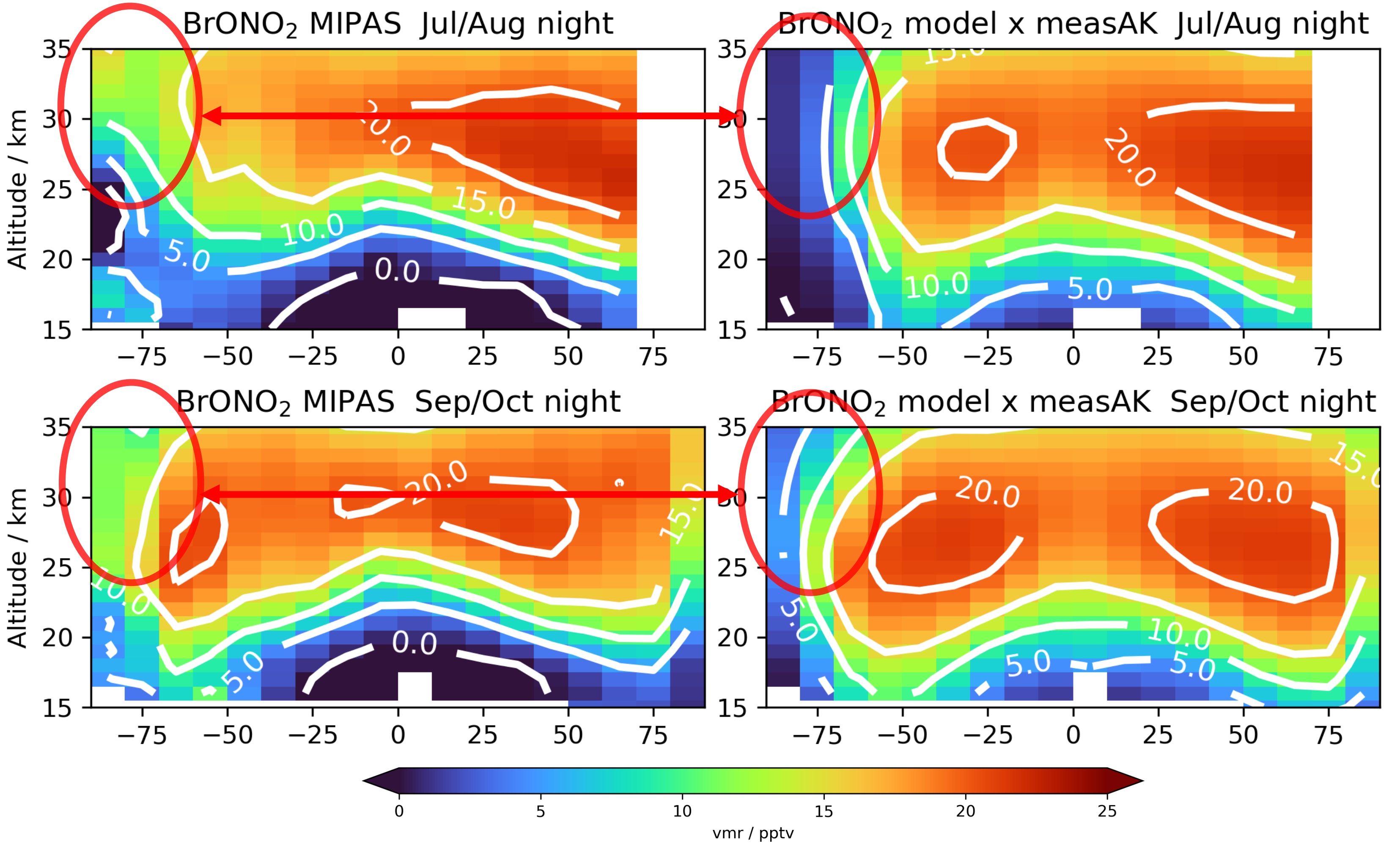
Overview of the observations



Major features of variability:

- Diurnal variability due to fast photolysis of $BrONO_2$ during day versus the production via $BrO+NO_2$.
- Annual recurrence of low values during night at high latitudes due to the lack of NO_x as supply for the production of $BrONO_2$ in combination with heterogeneous loss at PSC particles.
- Annual maxima of $BrONO_2$ volume mixing ratios at high- and mid-latitudes during day- and nighttime observations in summer caused by the annual variability of NO_2.

Comparison to model data: underestimation at high latitudes during polar night

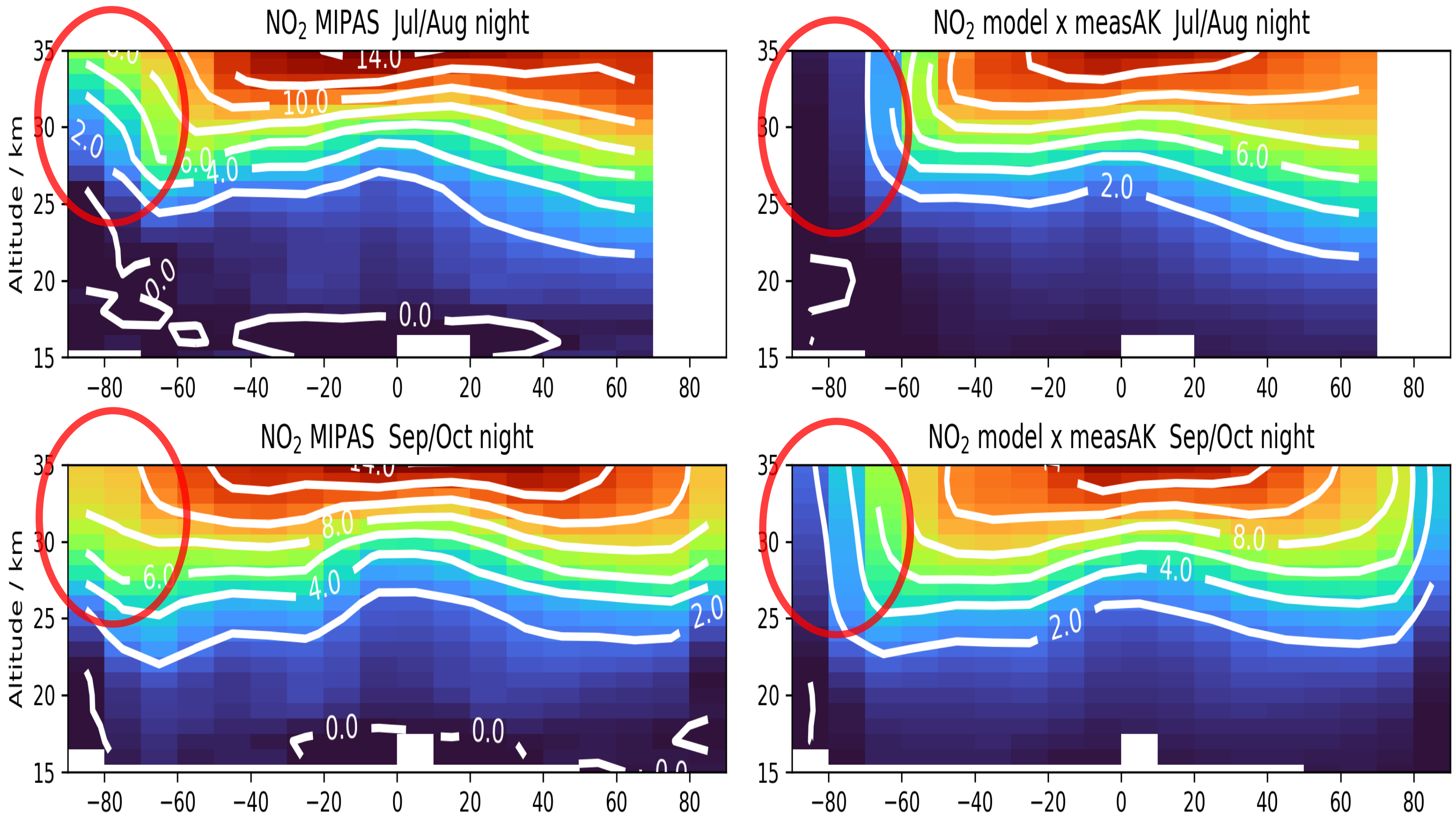


Model: EMAC (ECHAM5 version 5.3.02, MESSy version 2.52), T42L90MA-resolution with 90 vertical hybrid pressure levels up to 0.01 hPa (~80 km), horizontal resolution 2.8° x 2.8° latitude x longitude, nudged to ERA-Interim. Model results have been convolved with the vertical averaging kernel of the retrieval.

Simulations reproduce the major variabilities of the observations.

- **Model underestimation at higher altitudes during polar night**

Comparison to model data: model underestimation at high latitudes during polar night

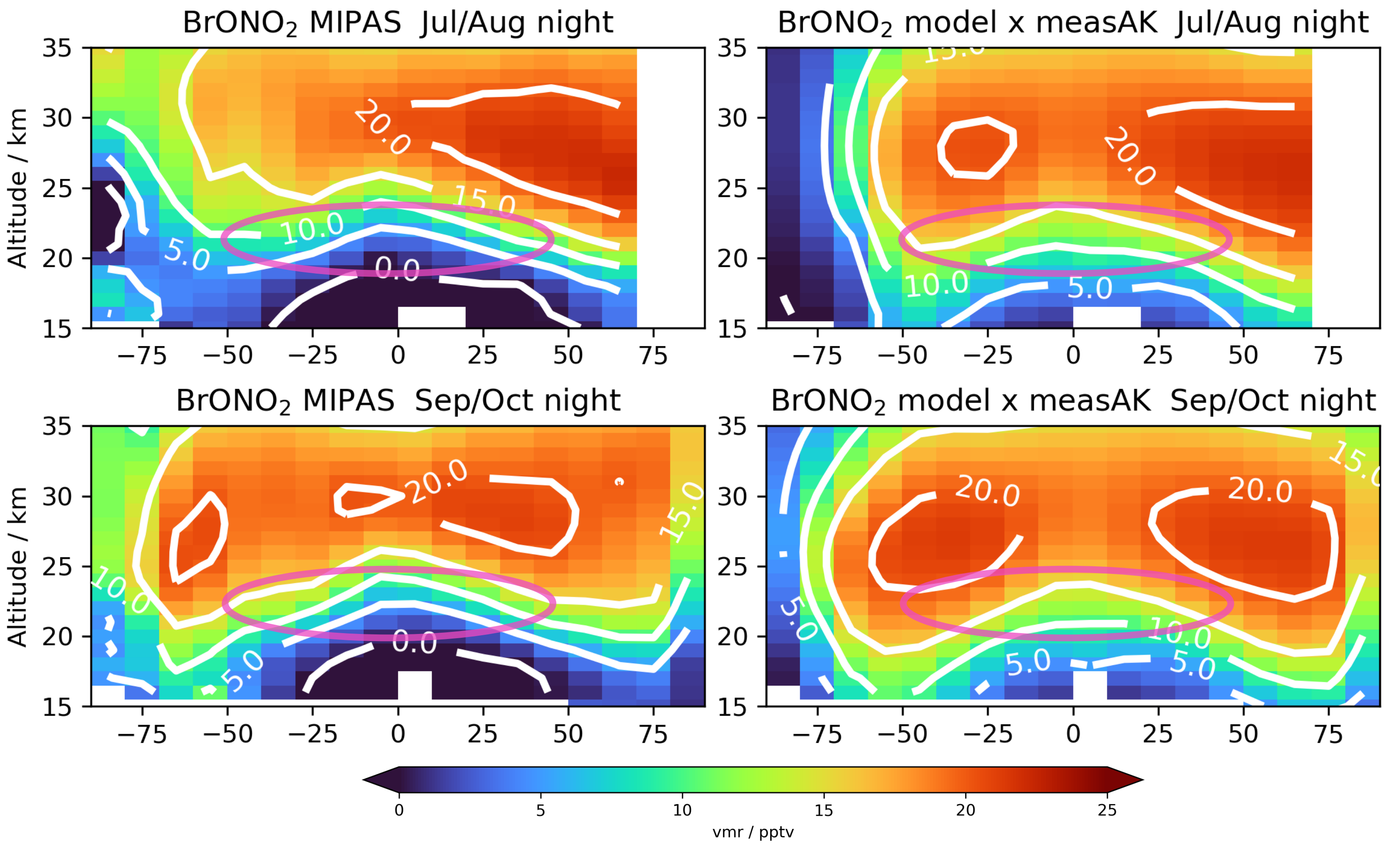


Comparison with NO_2 between model and observed by MIPAS:

- **Model underestimation at higher altitudes during polar winter → downwelling of NO_x-rich air from production by energetic particle precipitation not considered in the model.**

E.g.: Funke, B., et al.: Mesospheric and stratospheric NO_y produced by energetic particle precipitation during 2002-2012, https://doi.org/10.1002/2013JD021404, 2014.

Comparison to model data: overestimation at low and mid-latitudes below ~25 km

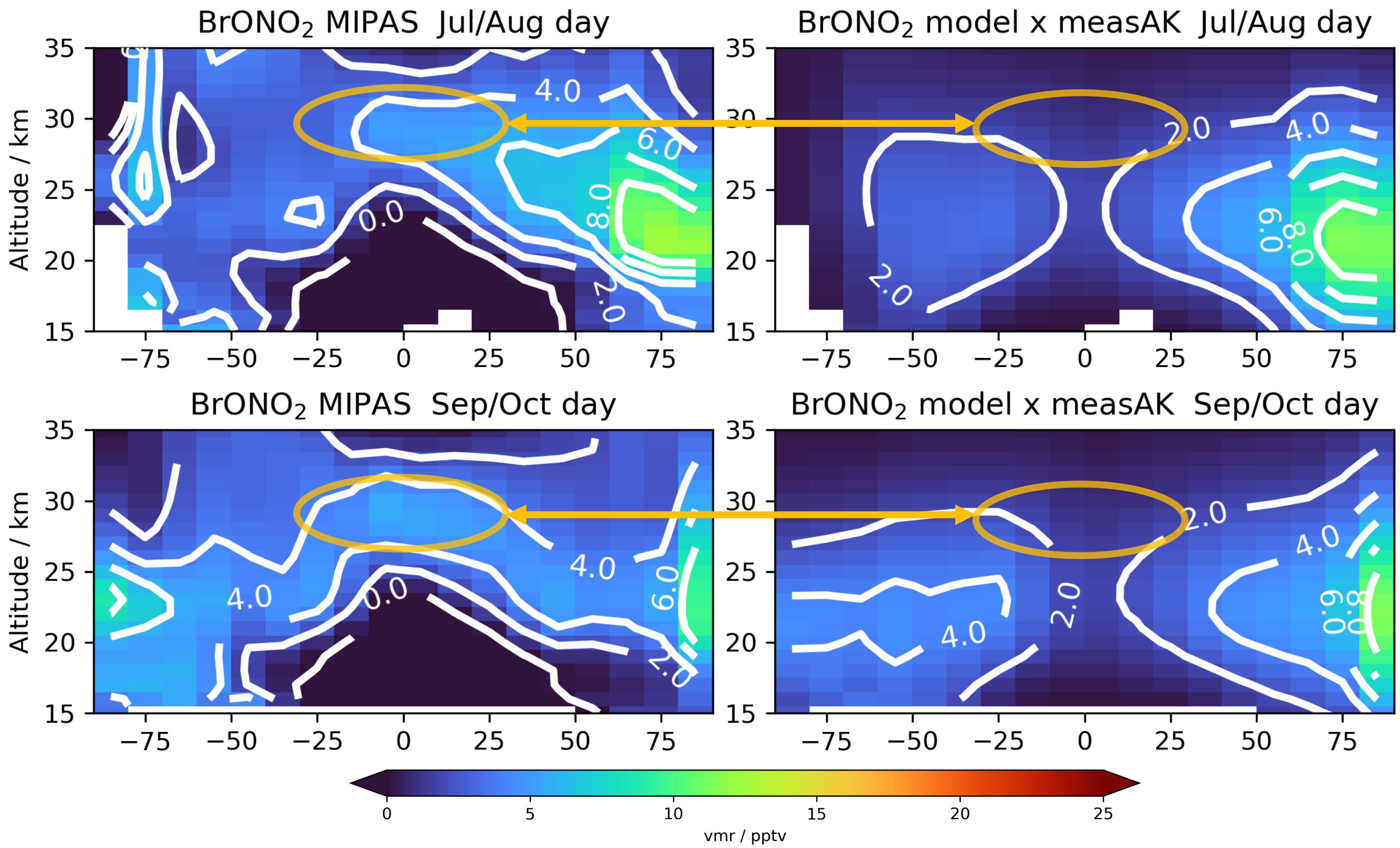


- Model overestimation at low and mid-latitudes below about 25 km.

Possible explanations:

1. Measurements uncertainty ?
2. Wrong model: NO_2 ?
3. Wrong model: release of Br_y from source gases ?
4. Wrong model: partitioning of Br_y between main constituents ?

Comparison to model data: model underestimation at low latitudes around 30 km during day



Simulations reproduce the major variabilities of the observations – also for the daytime measurements.

- Model underestimation at low latitudes around 30 km altitude.

Possible explanations:

1. Measurements uncertainty ?
2. Wrong model: NO_2 ?
3. Wrong model: reaction parameters ?

Total stratospheric bromine derived from observed $BrONO_2$

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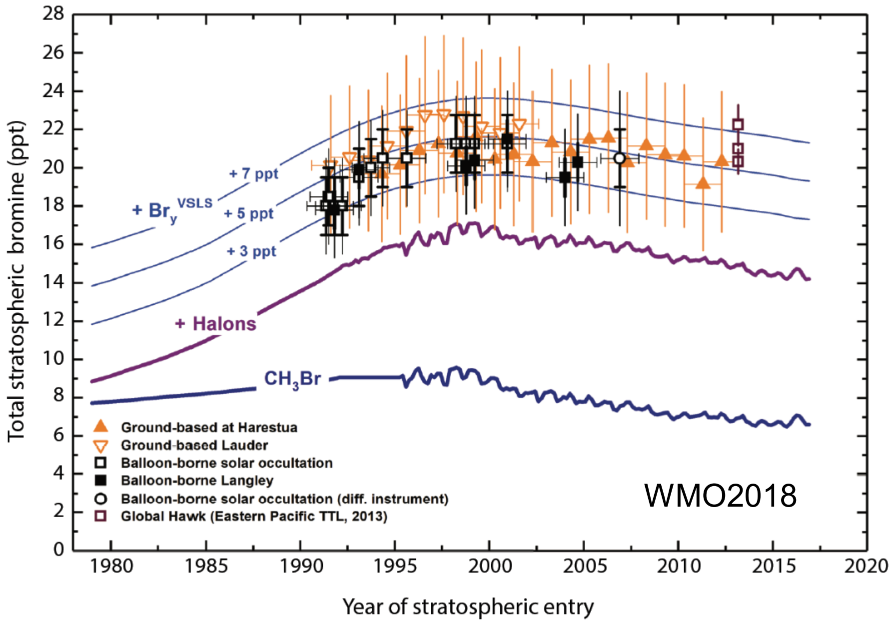
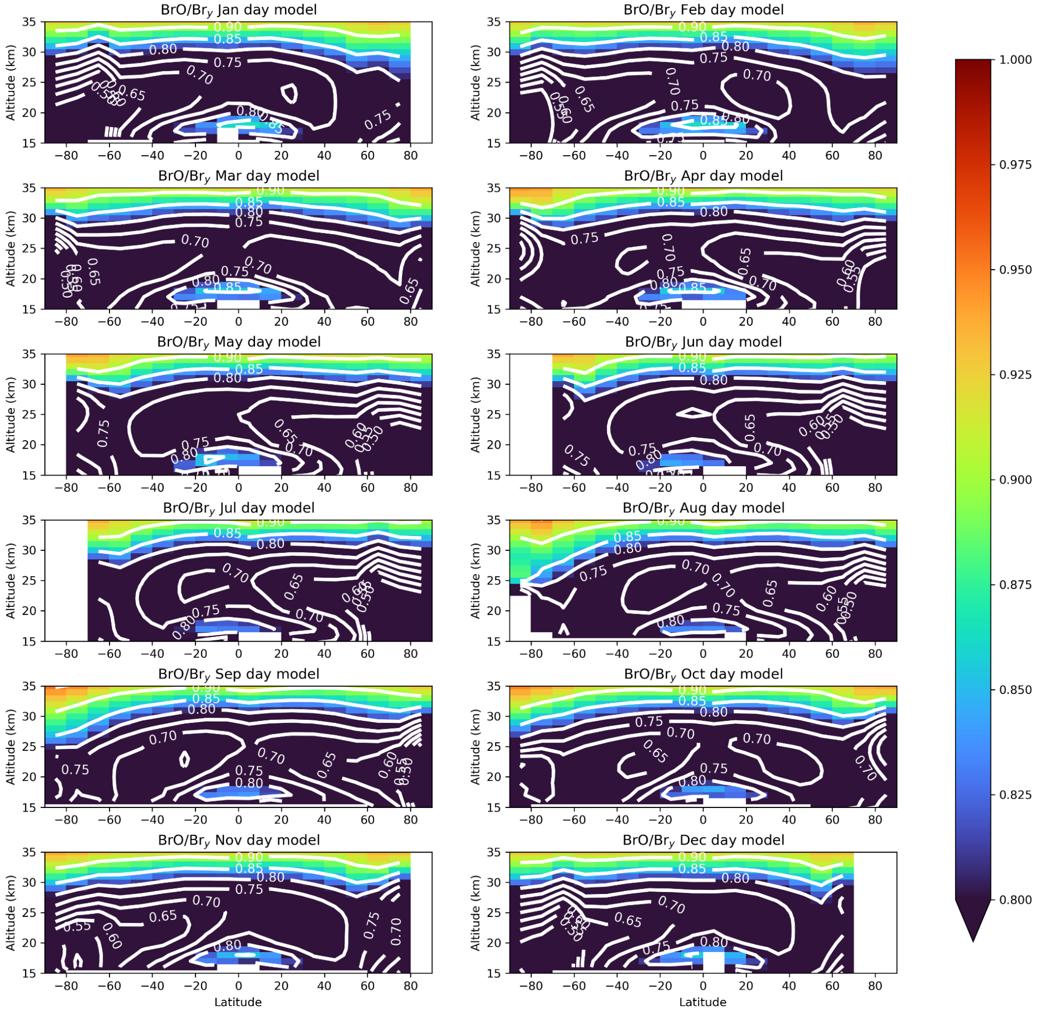


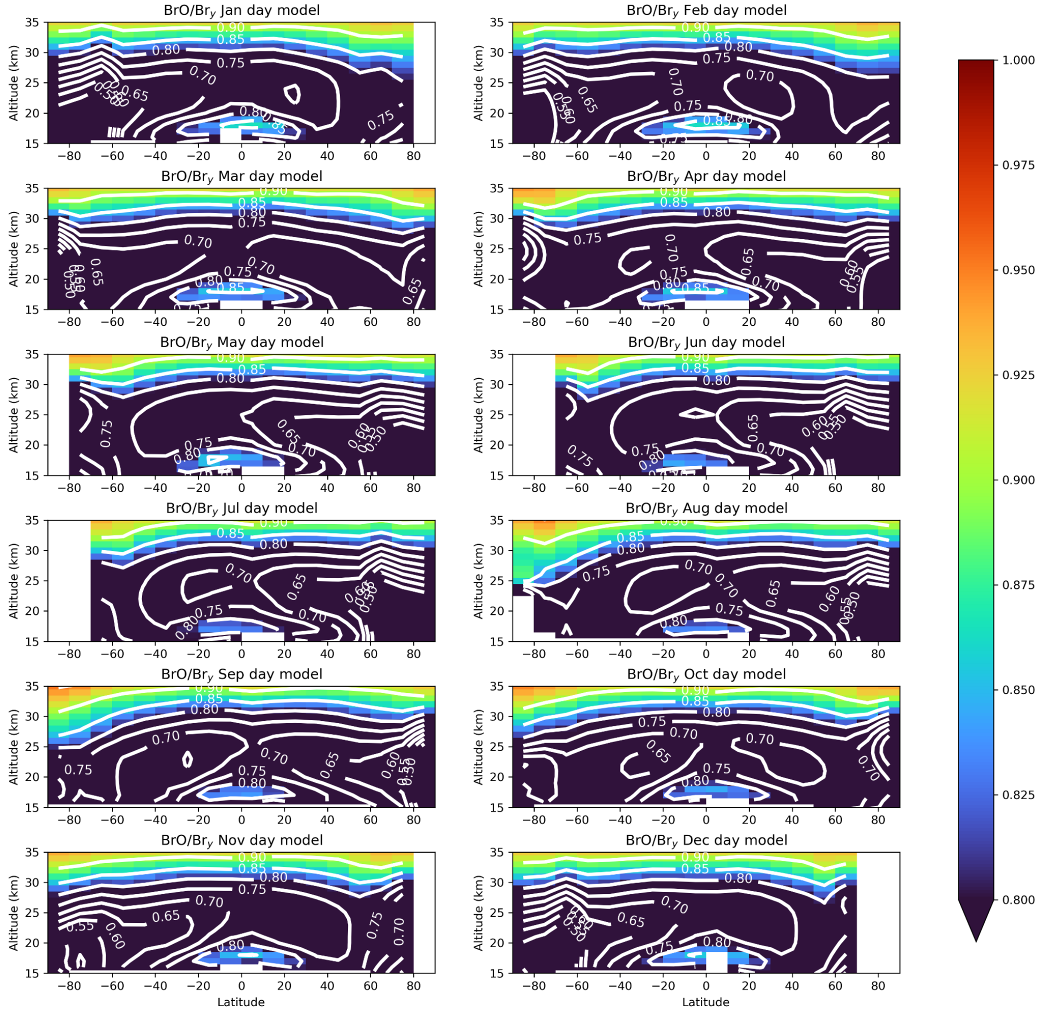
All Br_y data based on BrO measurements **but** model needed to correct for up to 40% of Br_y being not in the form of BrO.

Modelled BrO/Br_y (day)

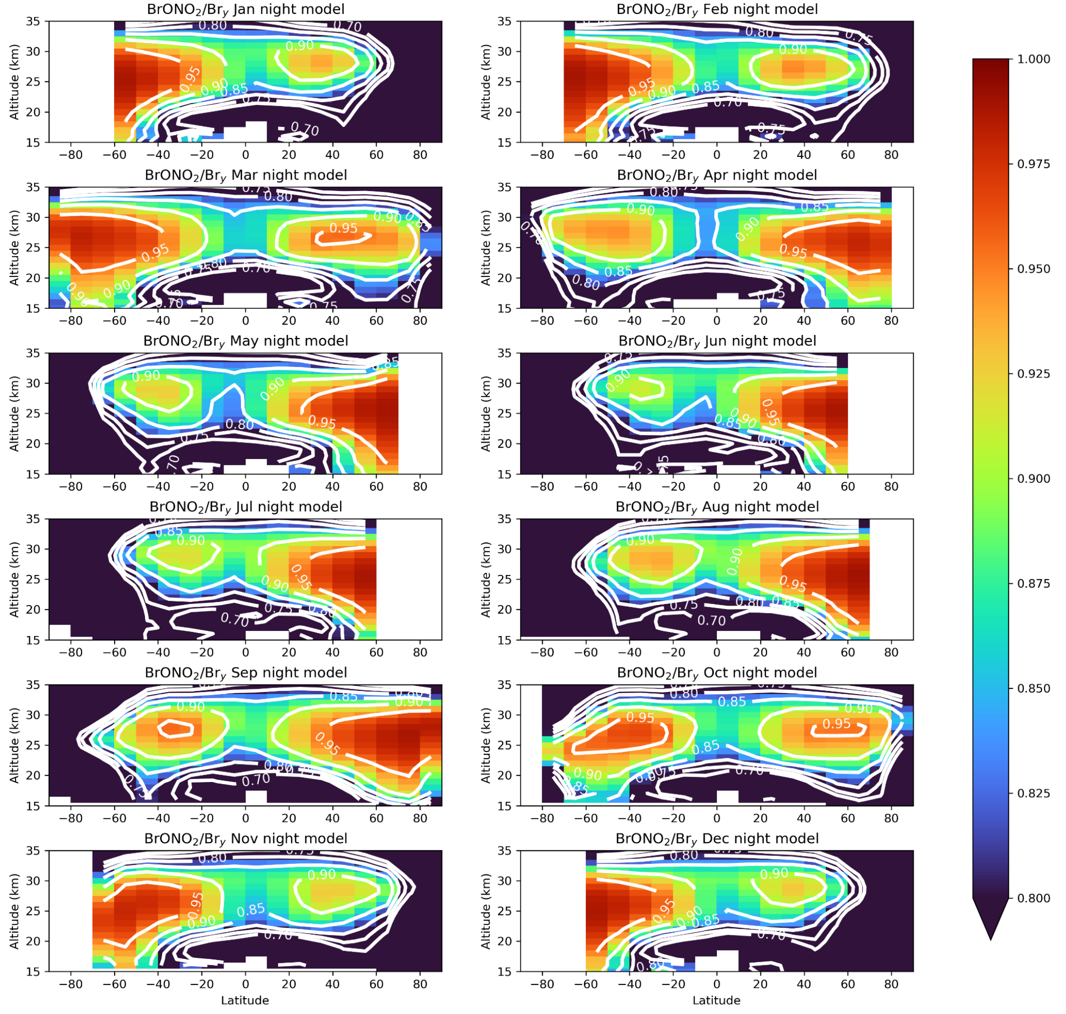


Total stratospheric bromine derived from observed $BrONO_2$

Modelled BrO/Br_y (day)



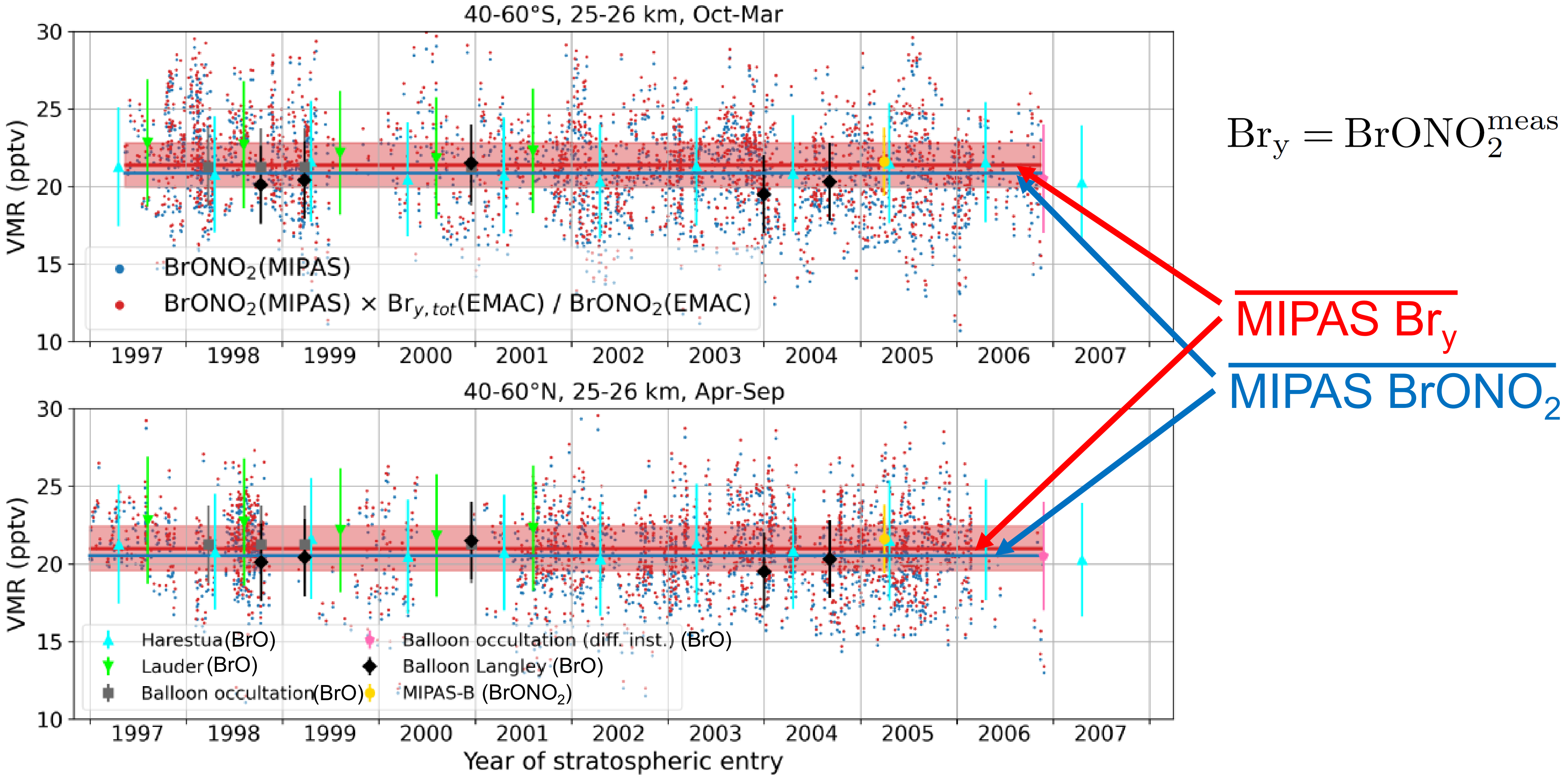
Modelled $BrONO_2/Br_y$ (night)



At certain regions >95% of Br_y is in the form of $BrONO_2$ during night
→ more independent from model corrections when calculating Br_y from $BrONO_2$ compared to determination from BrO observations

M. Höpfner et al., Institute of Meteorology and Climate Research

Total stratospheric bromine derived from observed $BrONO_2$



$$Br_y = BrONO_2^{meas} \times \frac{Br_y^{mod}}{BrONO_2^{mod}}$$

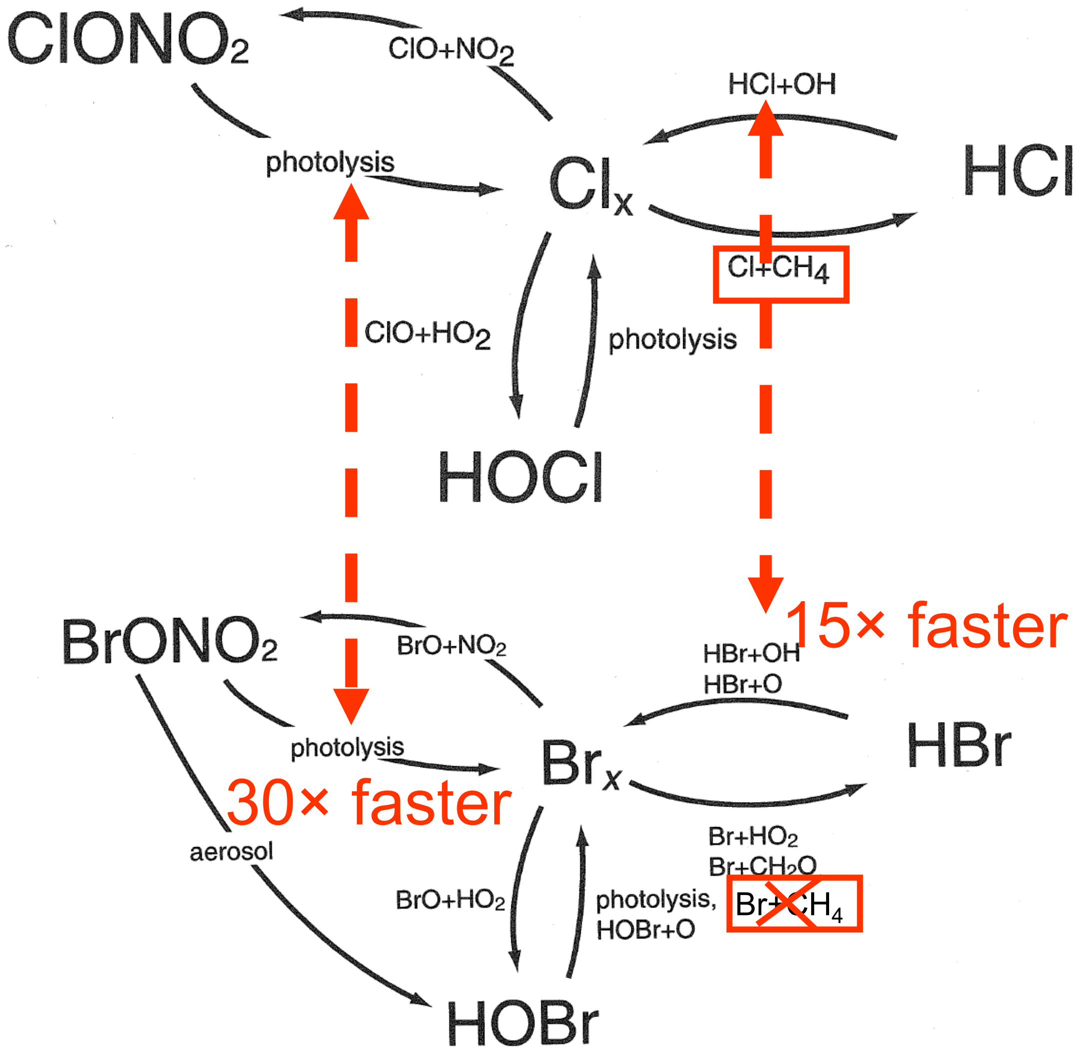
Summary

- First multi-annual observations of $BrONO_2$ profiles in the stratosphere during day and night
- Confirmation of general features as simulated by models
- First report of polar wintertime $BrONO_2$ enhancement at 30 km and above due to downwelling of NO_x – rich air from the mesosphere
- Too high modeled nighttime $BrONO_2$ at lower altitudes
- Too low modeled daytime $BrONO_2$ at 30 km over the equator
- Independent (of BrO) determination of total stratospheric Br_y confirms 21-22 pptv for years of stratospheric entry between 1997 and 2006
- Paper accepted for publication in ACP:

  https://acp.copernicus.org/preprints/acp-2021-535/#discussion

Supplementary material

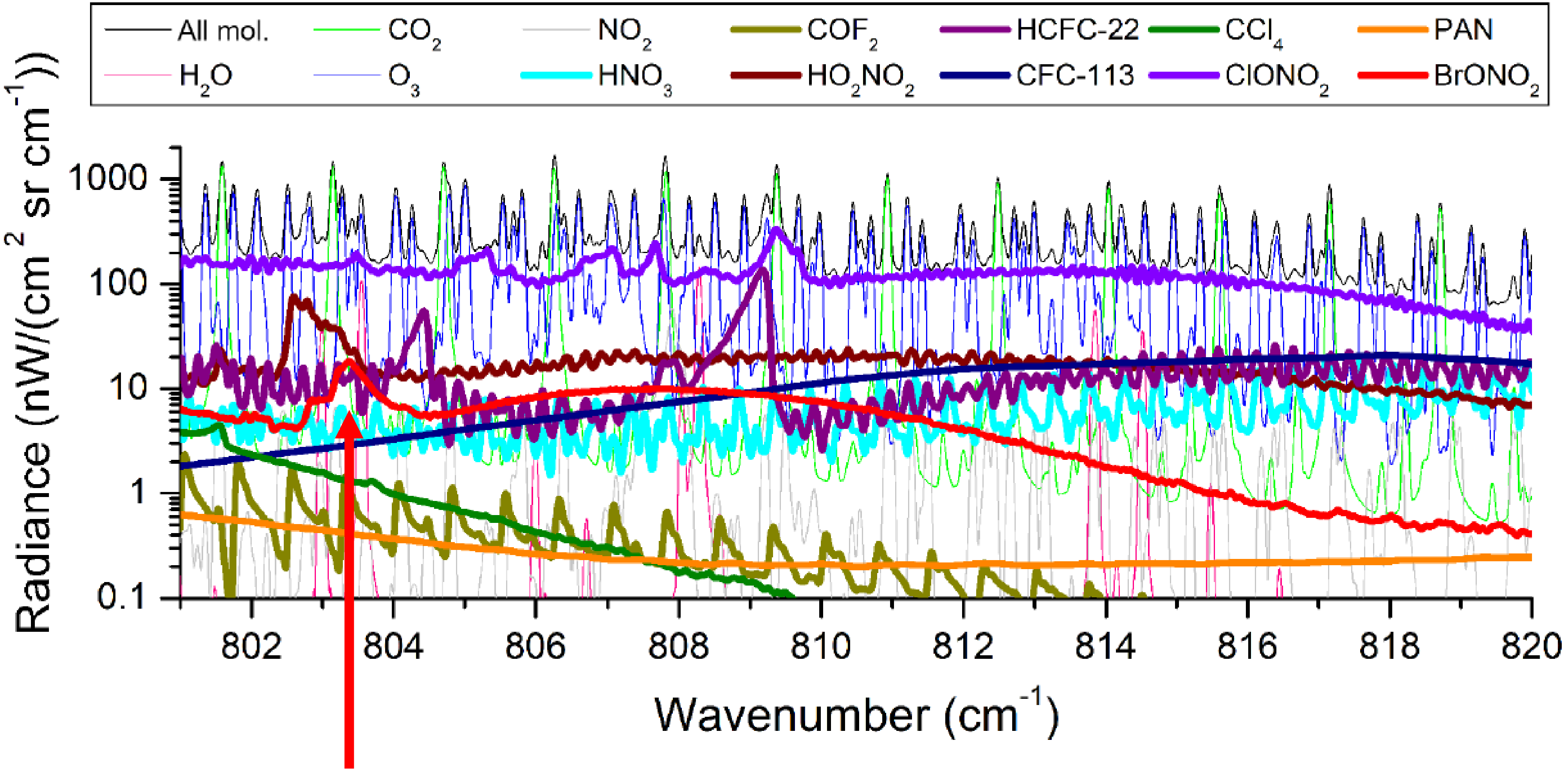
Why bromine? Why $BrONO_2$?



Concentrations:
chlorine ≈ 150 × bromine

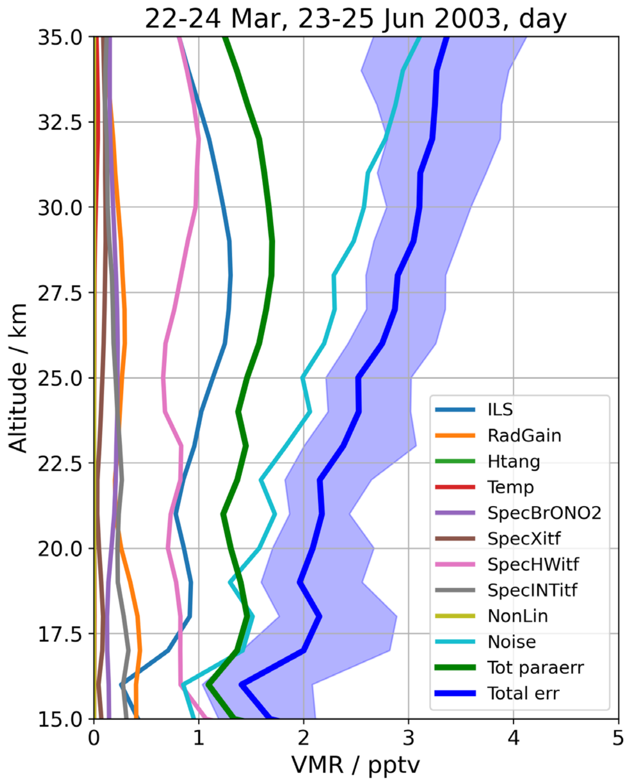
But:
ozone depleting potential per atom:
bromine ≈ 60 × chlorine

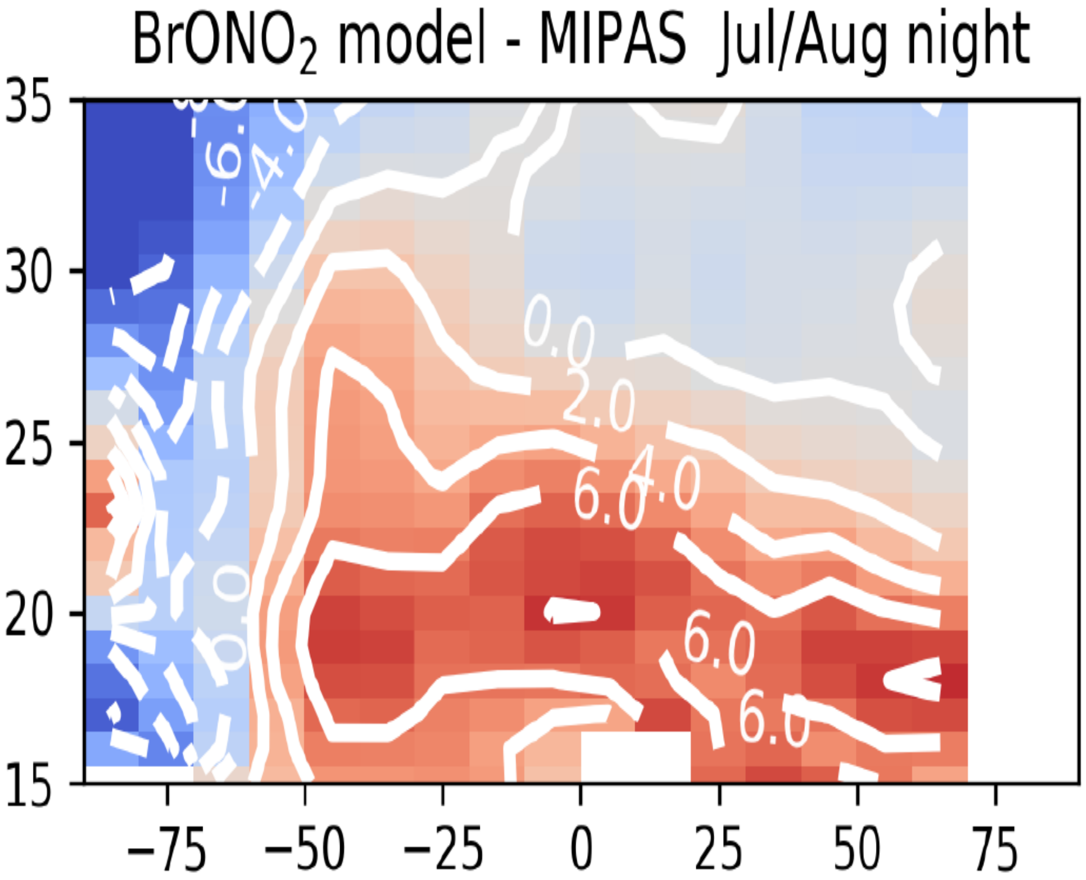
Spectral signal of $BrONO_2$



Wetzel et al., 2017, doi.org/10.5194/acp-17-14631-2017

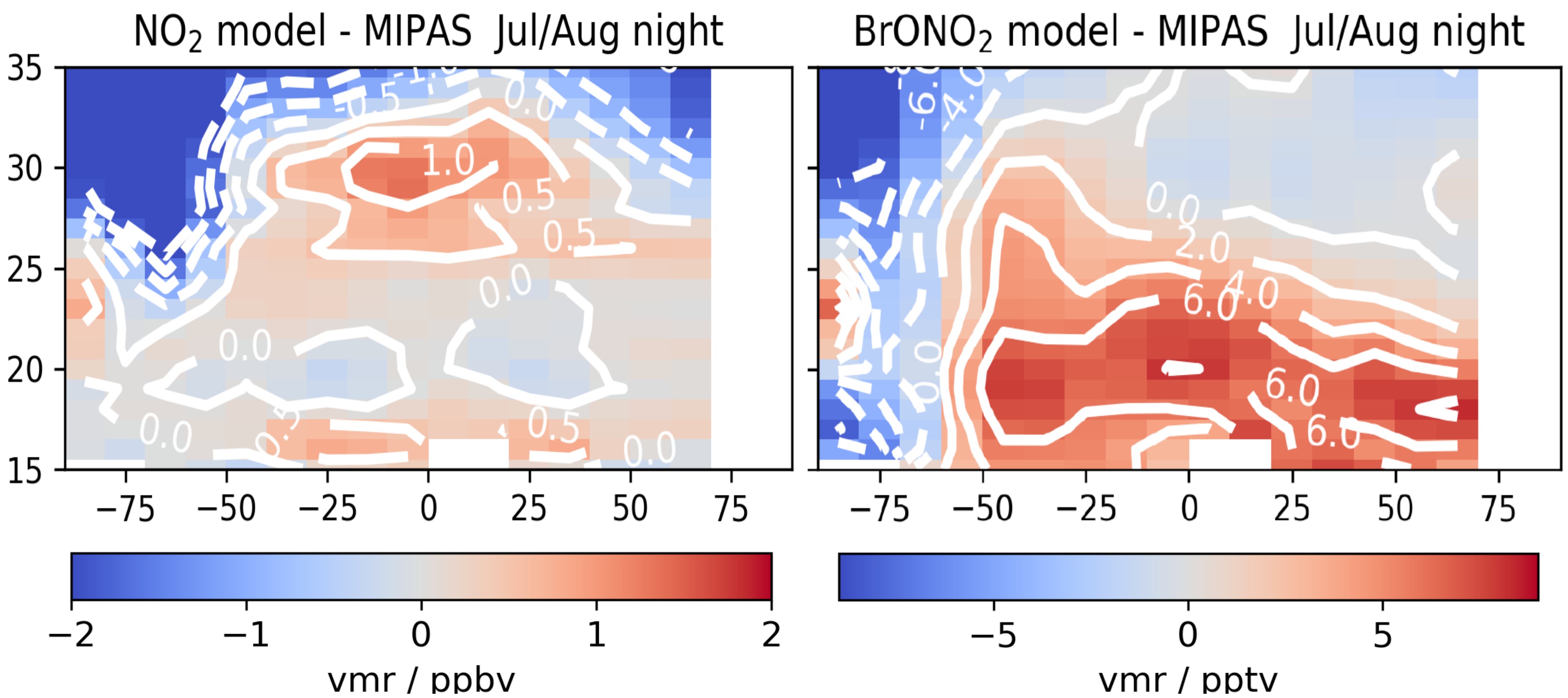
Model overestimation at low and mid-latitudes below ~25 km: (1) wrong measurements?





- Up to 8 pptv difference cannot be explained by the MIPAS error estimation.
- Any unidentified additional systematic error source cannot be ruled out.

Model overestimation at low and mid-latitudes below ~25 km: (2) wrong model: NO_2?



- NO_2 vmrs fit well between model and observation
  → explanation not probable.

Model overestimation at low and mid-latitudes below ~25 km: (3) wrong model: release of Br_y from source gases?

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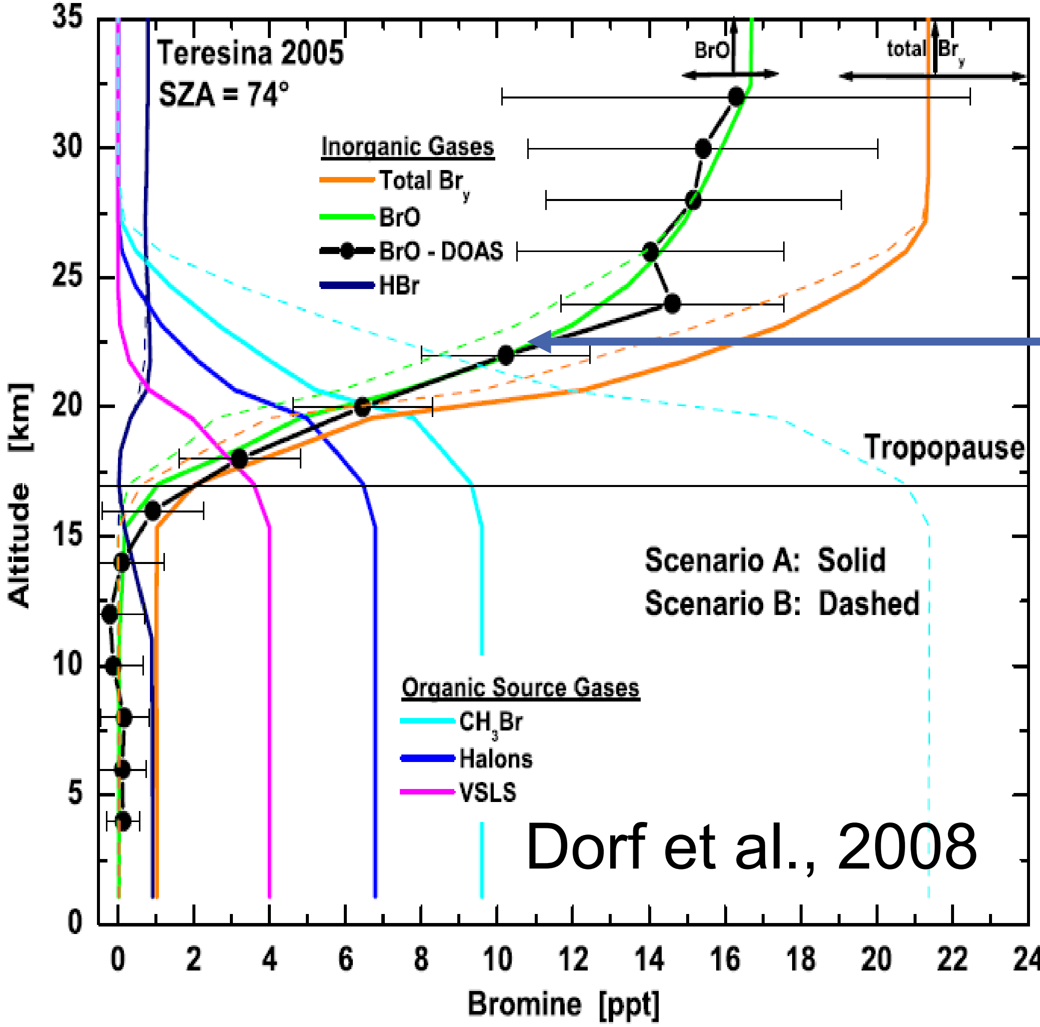
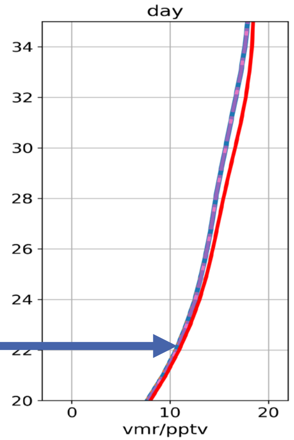




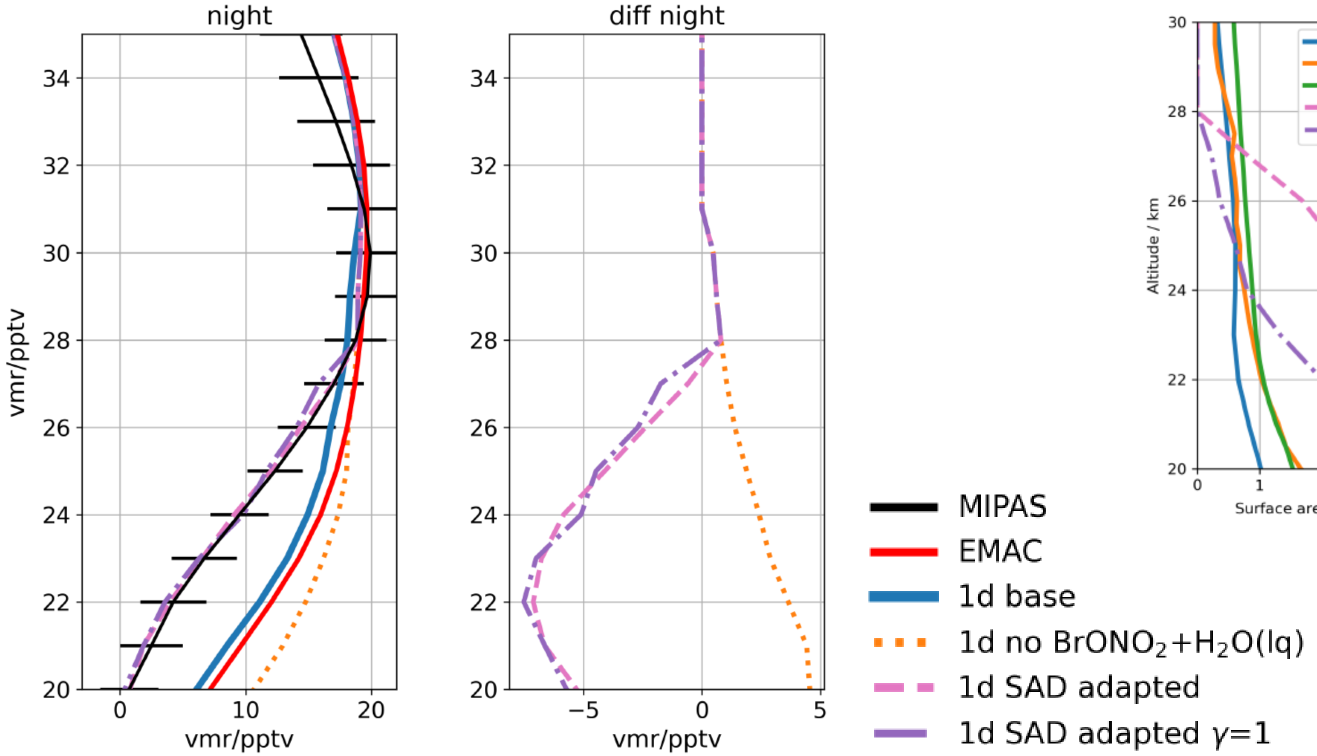
BrO models (this paper)

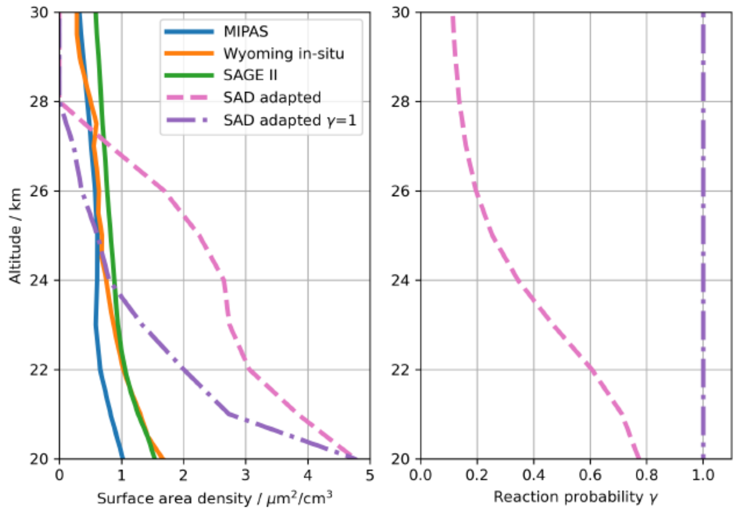
- Modelled BrO fits well to observations
→ unlikely that the inorganic bromine content at 20–25km is strongly overestimated in the EMAC model calculations

Model overestimation at low and mid-latitudes below ~25 km: (4) wrong model: partitioning of Br_y between main constituents?

Partitioning of Br_y at around 20-25 km during night is essentially determined by the heterogeneous conversion of $BrONO_2$ into HOBr through sulfate aerosols:

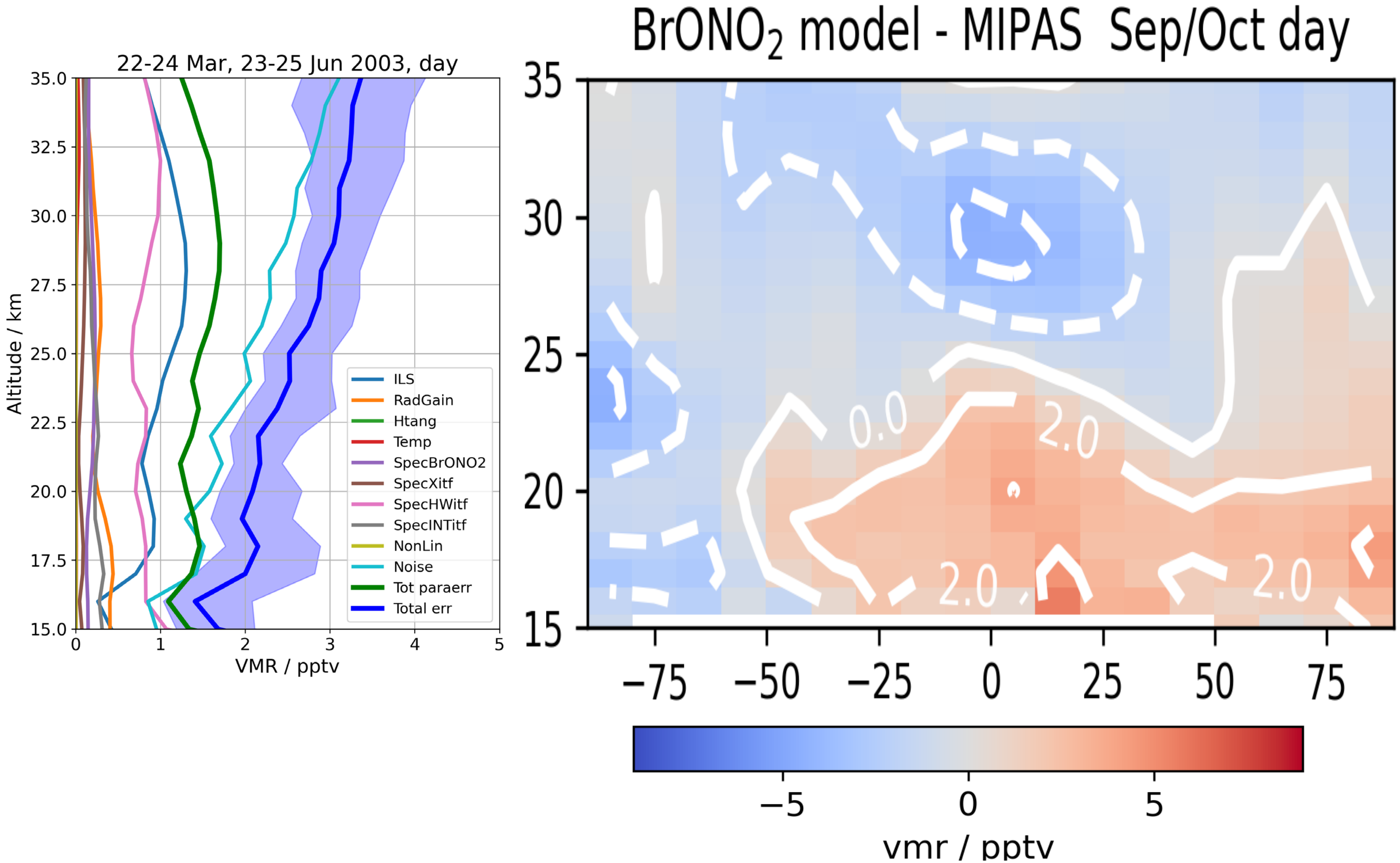
$$\mathrm{BrONO_2 + H_2O(s,l,H_2SO_4 \cdot nH_2O) \rightarrow HOBr + HNO_3}$$





- Needed aerosol surface area densities (SADs) are not consistent with observations

Model underestimation at low latitudes around 30 km during day: (1) wrong measurements?



- Up to 5 pptv difference difficult to explain by MIPAS error estimation.
- Any unidentified additional systematic error source cannot be ruled out.

Model underestimation at low latitudes around 30 km during day: (2) wrong model: NO_2?

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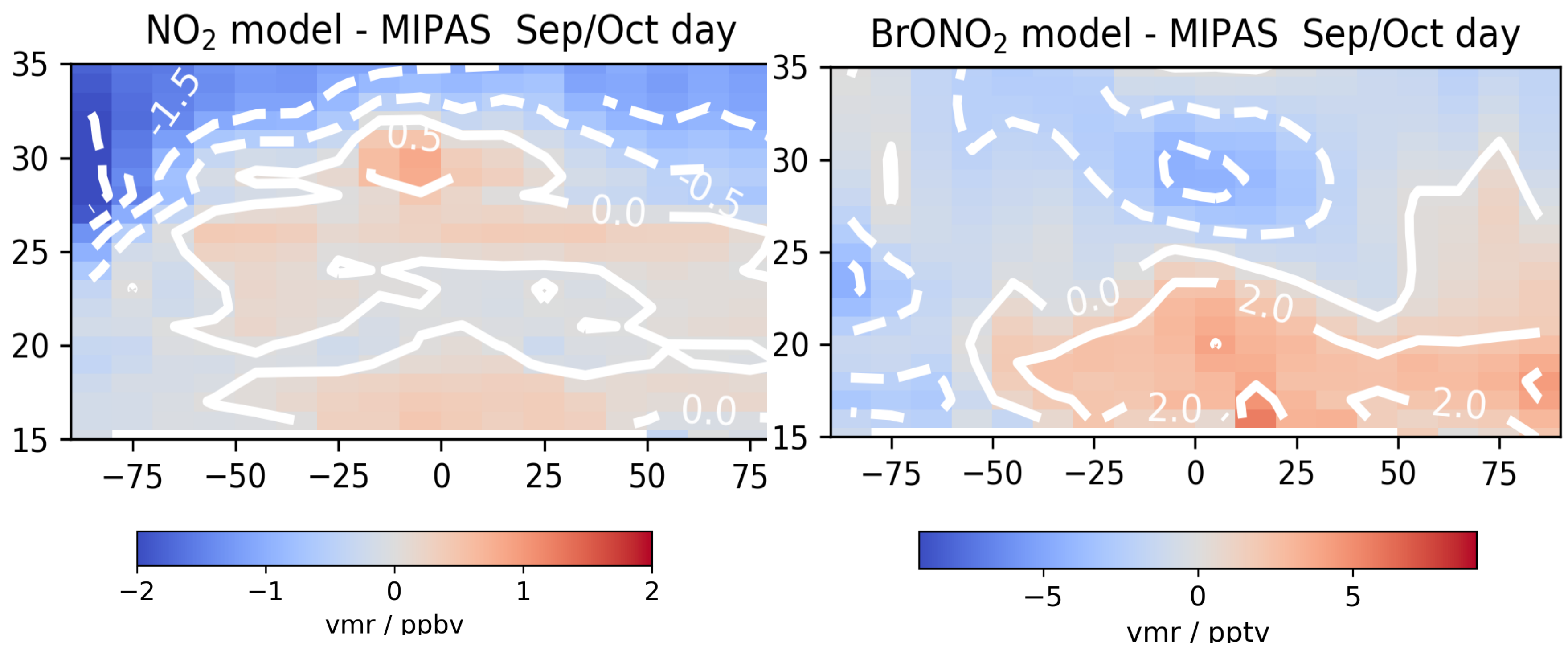

- Model overestimates NO_2 vmrs by 10-20% → cannot account for the model underestimation of $BrONO_2$ but would even imply stronger modelled production of $BrONO_2$

Model underestimation at low latitudes around 30 km during day: (3) wrong model: reaction parameters?

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Reaction	1σ uncertainty factor (JPL2019) @220 K
Gain:	
$BrO + NO_2 \xrightarrow{M} BrONO_2$	1.9
Loss:	
$BrONO_2 + h\nu \rightarrow Products$	1.1 (UV x-sections)
$BrONO_2 + O(^3P) \rightarrow BrO + NO_3$	1.3 (but only one publication on this reaction)
$BrONO_2 + H_2O(s,l,H_2SO_4 \cdot nH_2O) \rightarrow HOBr + HNO_3$	2-4 (reaction probability)

Model underestimation at low latitudes around 30 km during day: (3) wrong model: reaction parameters?

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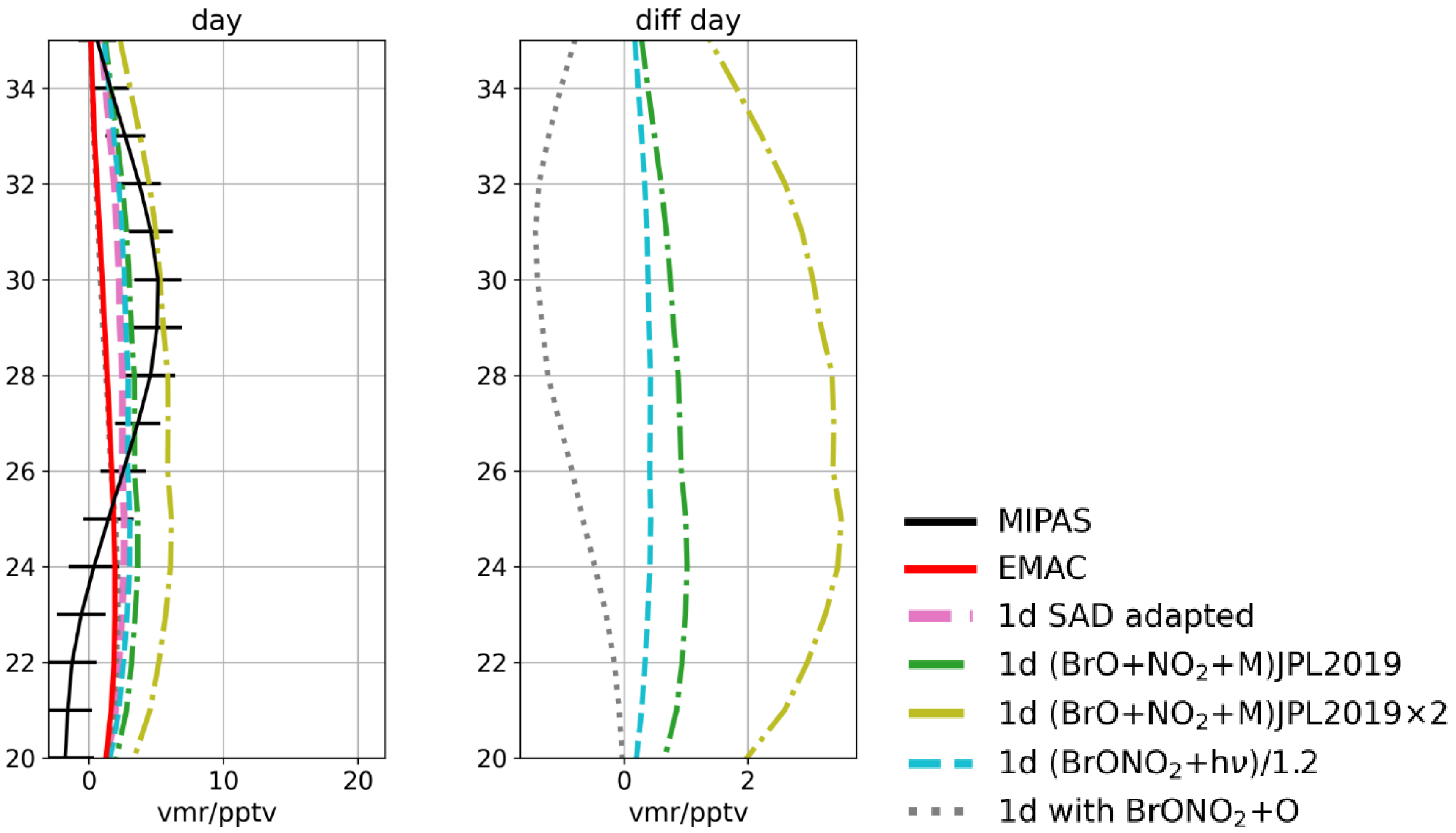

- Addition of $BrONO_2$+O(^{3}P) leads to even larger underestimation
- Increase of BrO+NO_2+M by factor 2 leads to compliance at 30 km but to overestimation below 28 km