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Phosgene in the UTLS: vertical distribution from MIPAS observations using new spectroscopic data

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Phosgene in the UTLS region

Phosgene ($COCl_2$) was mainly used in the 20th century by chemical industry for the preparation of insecticides, pharmaceuticals and herbicides. Its usage has been reduced over the years due to its high toxicity.

In the troposphere:

- phosgene is formed by OH-initiated oxidation of chlorinated hydrocarbons (e.g. $CHCl_3$, CH_3CCl_3, C_2Cl_4 and C_2HCl_3);
- its lifetime is about 70 days because it is rapidly removed by water droplets or by deposition in the oceans.

In the stratosphere:

- phosgene is formed by oxidation of its tropospheric source molecules and also by the photochemical decay of CCl_4;
- it is a weak absorber in the UV region and has a long lifetime (several years); however it is slowly oxidized to form ClO_X (Fu et al., 2007).

Previous studies

First studies about atmospheric phosgene:

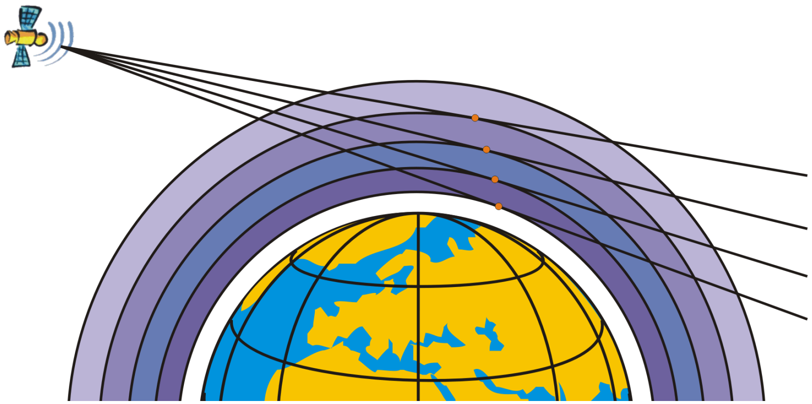
- Singh (**1976**) studied the **surface distribution** of phosgene using data from six stations in California.
- Wilson et al. (**1988**) measured phosgene at various altitudes during an **aircraft** flight over Germany.
- Toon et al. (**2001**) used the Jet Propulsion Laboratory - MkIV Interferometer, onboard **stratospheric balloons**, to retrieve different VMR profiles of phosgene from 1992 to 2000.

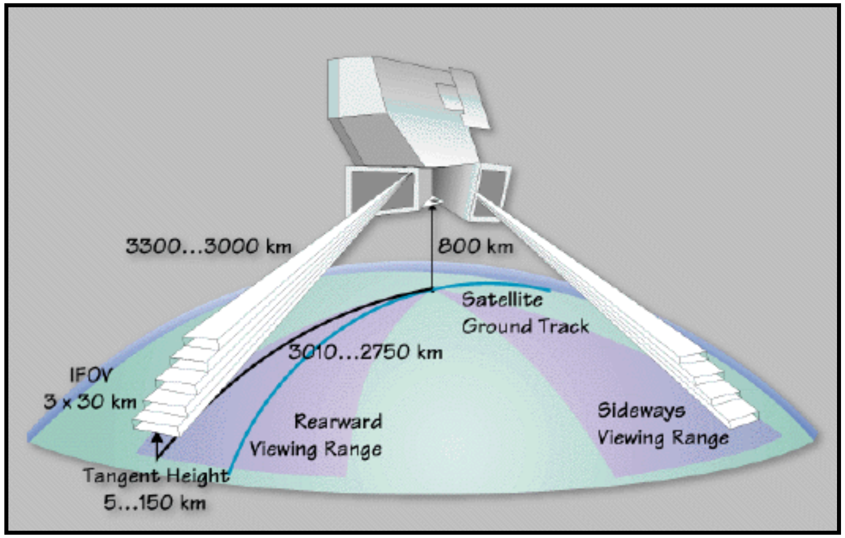
First **satellite** measurements of stratospheric phosgene:

- Fu et al. (**2007**) made the first analysis of the global distribution of phosgene using **ACE-FTS** measurements (February 2004 to May 2006).
- Brown et al. (**2011**) studied the phosgene **inter-annual variations** from **ACE-FTS** data in the years from 2004 to 2010.

Michelson Interferometer for Passive Atmospheric Sounding

Band	Spectral range (cm^{-1})
A	685 - 970
AB	1020 - 1170
B	1215 - 1500
C	1570 - 1750
D	1820 - 2410





The MIPAS measurements considered in this work refer only to the nominal operation mode of the **Optimized Resolution** (0.0625 cm^{-1}) mission:

- 6 - 71 km altitude range with 27 sweeps.
- 1.5 km vertical sampling step in the UTLS region.

Phosgene in MIPAS data

In the validation of MIPAS version 6 products, CFC-11 VMR profiles showed a positive bias. Checking the atmospheric molecules absorbing in the same spectral range, it was found that $COCl_2$ had not been included among the interfering species, and therefore its contribution was neglected.

A preliminary test including $COCl_2$ interference in the simulated spectra, using:

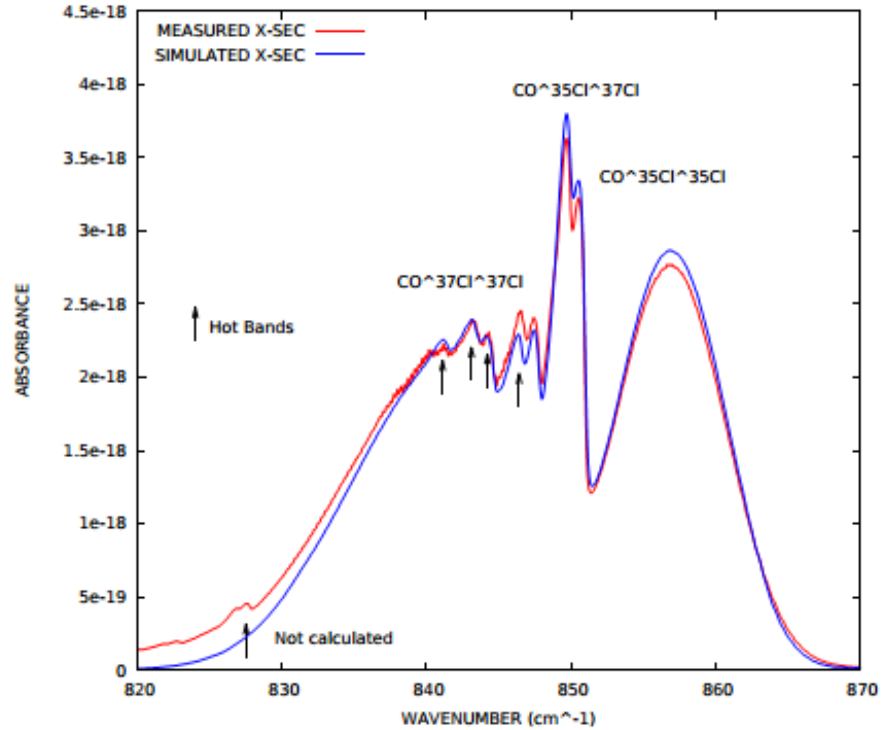
- the vertical distribution retrieved by ACE-FTS (Fu et al., 2007),
- $COCl_2$ cross-sections recorded at 25°C (Sharpe et al., 2004).

Showed that the differences in the retrieved CFC-11 with and without $COCl_2$ were of the order of the bias found in the CFC-11 profiles.

The clear interference of phosgene into CFC-11 retrieval suggested that MIPAS measurements could be exploited to retrieve phosgene global distributions.

New spectroscopic database

- The ν_5 band of Phosgene falls in the **830 - 860 cm^{-1}** spectral region.
- To accurately measure phosgene distribution, cross sections measured at only one temperature/pressure value are not accurate enough
- Therefore new spectroscopic data were needed.
- A **detailed and extensive analysis** of $COCl_2$ spectrum in this region has been performed by Kwabia Tchana et al. (**2015**).
- These data have been used to retrieve $COCl_2$ from MIPAS spectra



Retrieval method

Phosgene contribution in MIPAS spectra is extremely weak and hidden underneath CFC-11 spectral features.

For its retrieval we used the **Optimized Retrieval Model** (Ridolfi et al., 2000; Raspollini et al., 2006, 2013) that is the scientific prototype of MIPAS level 2 ESA processor upgraded with:

- the **Multi-Target** Retrieval functionality (Dinelli et al., 2004) using optimized microwindows for the joint $COCl_2$ and CFC-11 retrieval,
- the possibility to use the **optimal estimation** (or maximum a-posteriori likelihood) approach (Rodgers, 2000).

A-priori profile

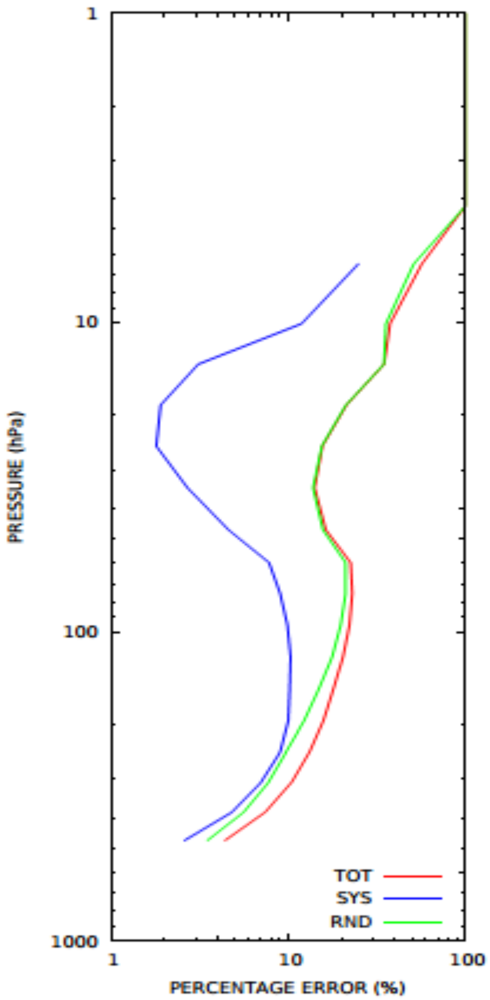
In order to highlight the observed latitudinal and seasonal variations of the retrieved $COCl_2$ VMR, we decided to use the same a-priori profile (an average of the $COCl_2$ IG2 profiles for the different latitude bands) and covariance matrix for all the retrievals.

A weak vertical regularization (5 km correlation length) has been applied to both CFC-11 and phosgene.

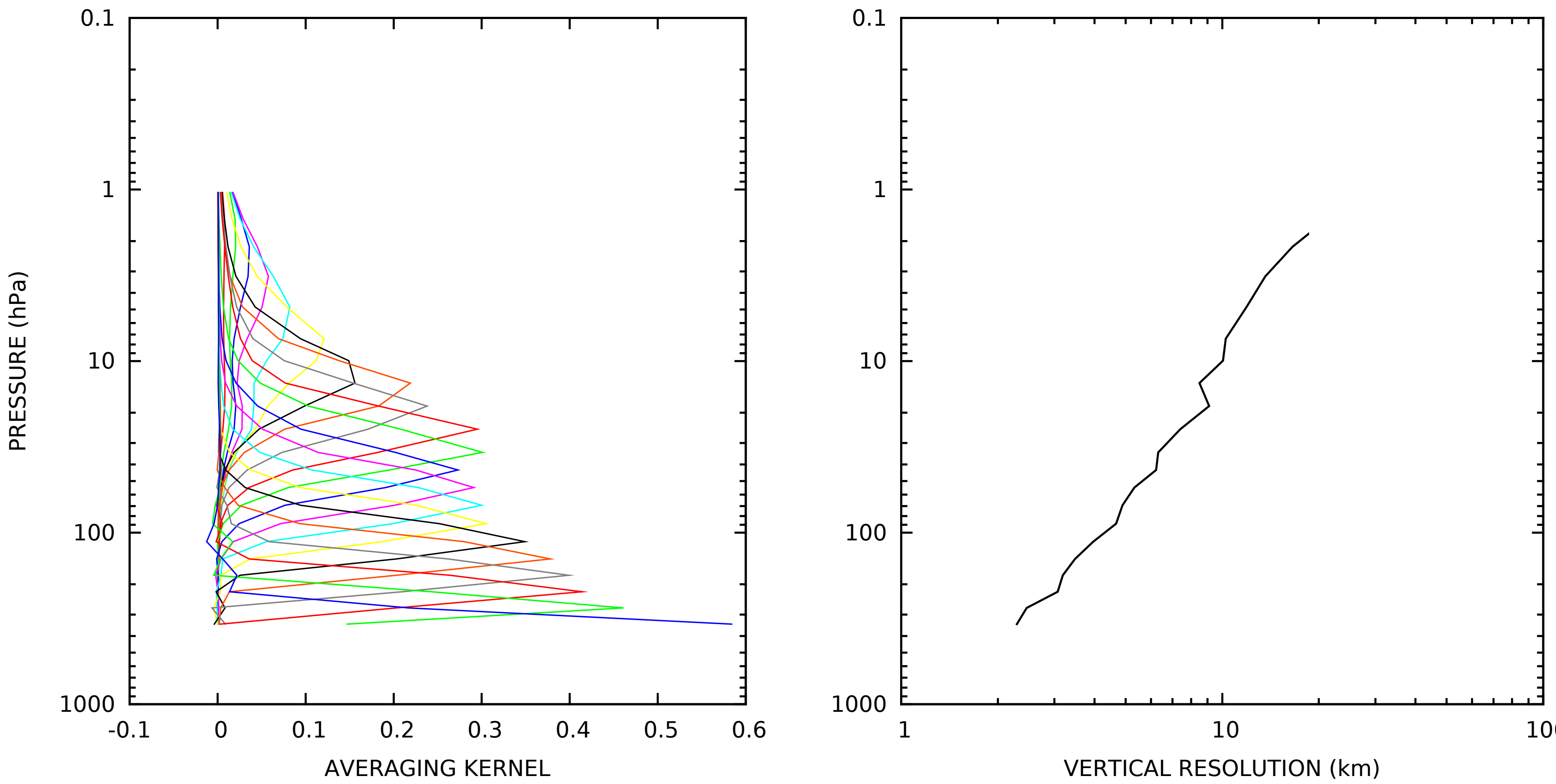
Since we have averaged the retrieved profiles using pressure as vertical coordinate, the phosgene a-priori profile used for the retrievals has been tabulated on a **fixed pressure grid**.

Error analysis

- MWs for the joint retrieval of COCl2 and CFC-11 were selected using MWMAKE (Dudhia et al. 2002)
- MWMAKE enables to estimate the total error affecting the retrieval products
- The total error (TOT) was calculated by summing in quadrature the total **systematic** (SYS, e.g. uncertainties in the spectroscopic database, in spectral intensity and frequency calibration, and in the parameterization of the width of the ILS) and **random** (RND, e.g. uncertainties in temperature, pressure and interfering species that are not retrieved) error components.
- Random components are reduced averaging over a large number of measurements.



Averaging Kernels
Vertical resolution



Measurements

We processed all MIPAS measurements acquired in the days **18** and **20** of each month of the year **2008** (we retrieved more than 28000 profiles) to study:

- **global distribution** of the phosgene in the UTLS region
- the **seasonal variability** of this distribution.

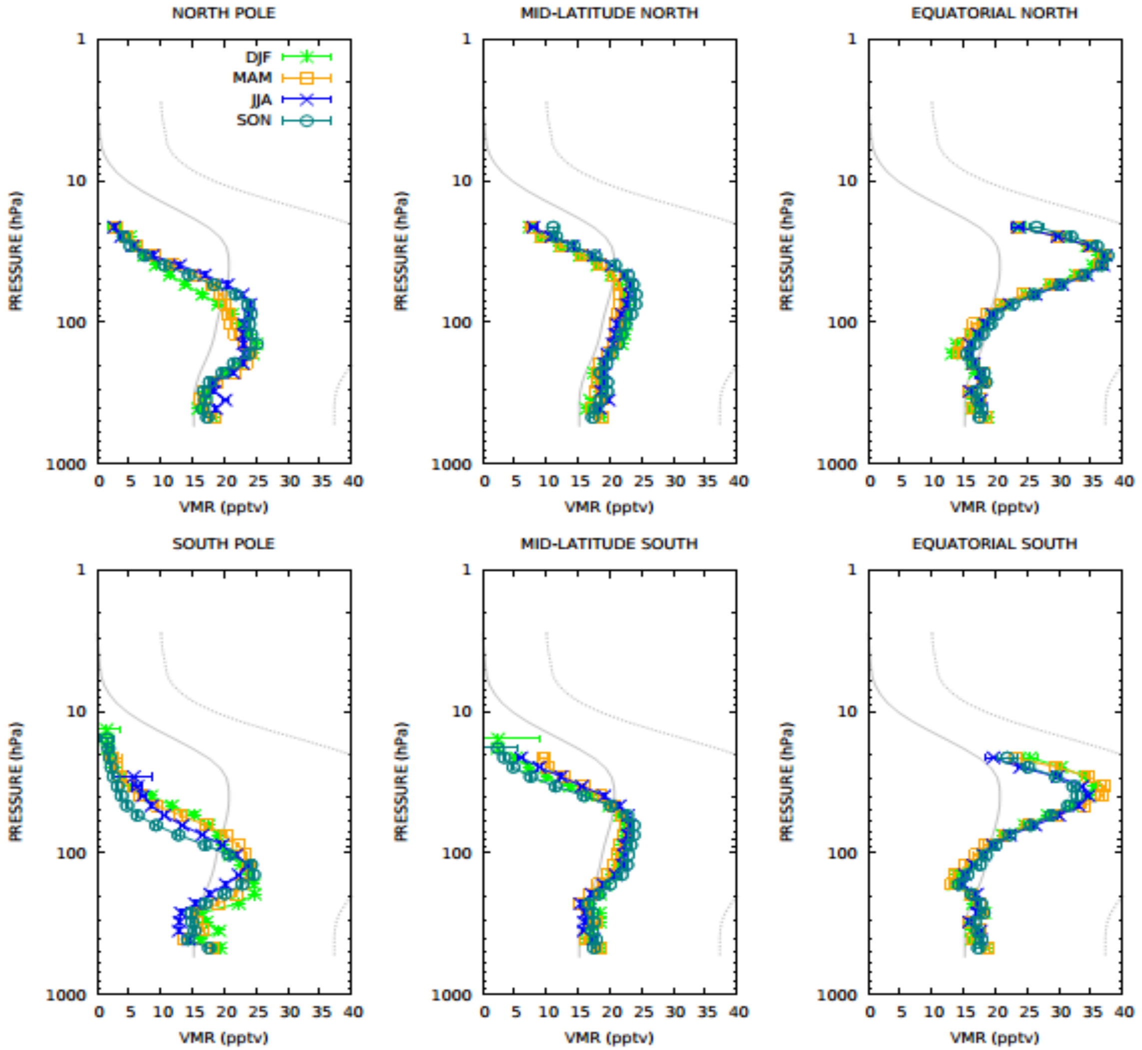
The analysis was performed using MIPAS Level 1B data version 5, where the non linear behavior of the detector, variable over the years, was not completely corrected.

Therefore the systematic errors affecting the radiometric calibration prevents the study of phosgene **inter-annual** variation.

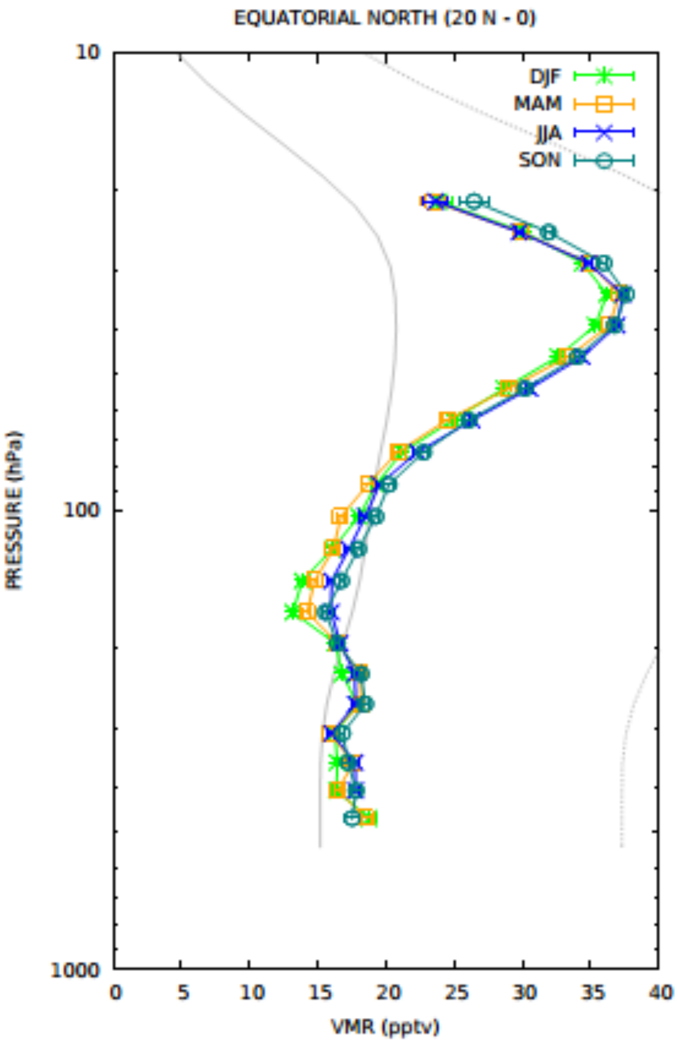
Results

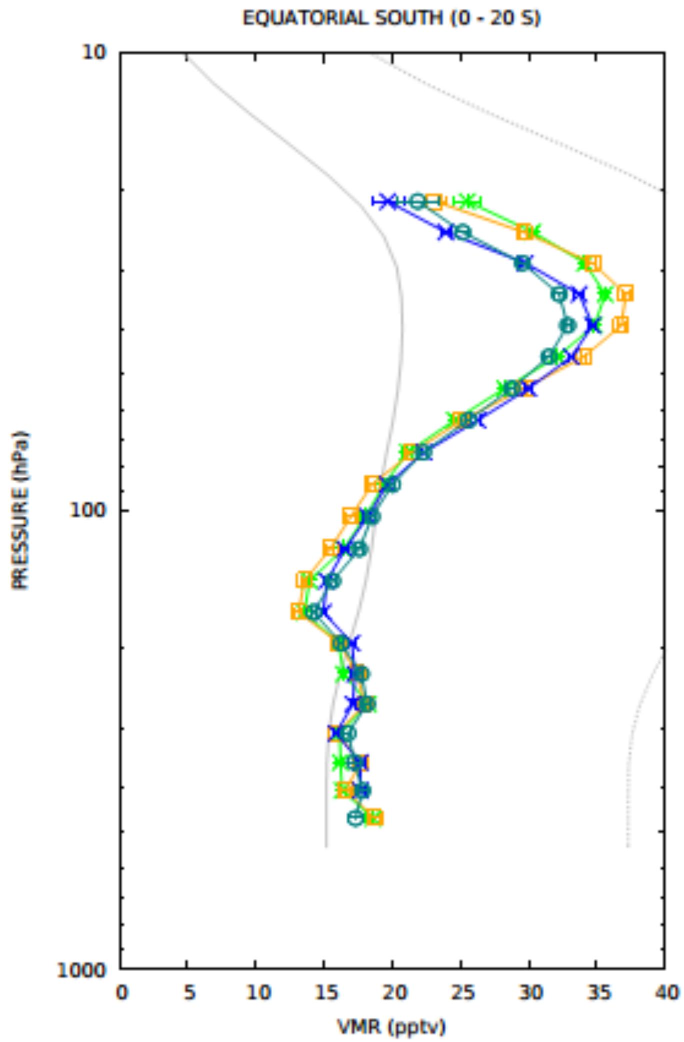
All the average profiles presented have been calculated by first interpolating the individual profiles to a **fixed pressure grid** (the same of the a-priori profile).

The average profiles show a clear **latitude dependence**.



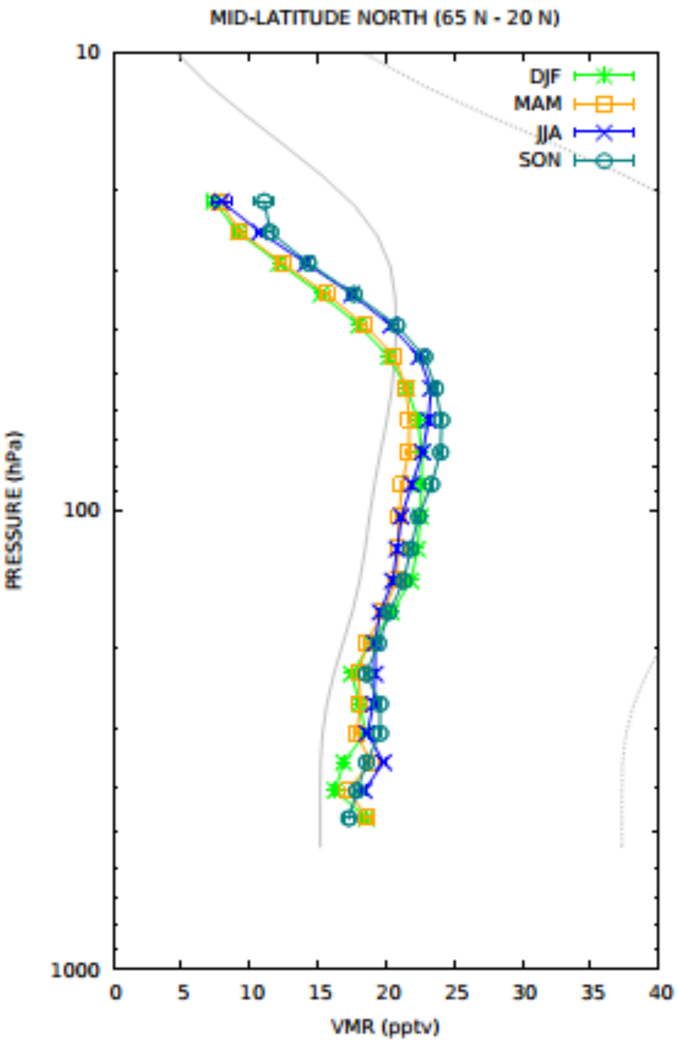
Results – Equatorial bands

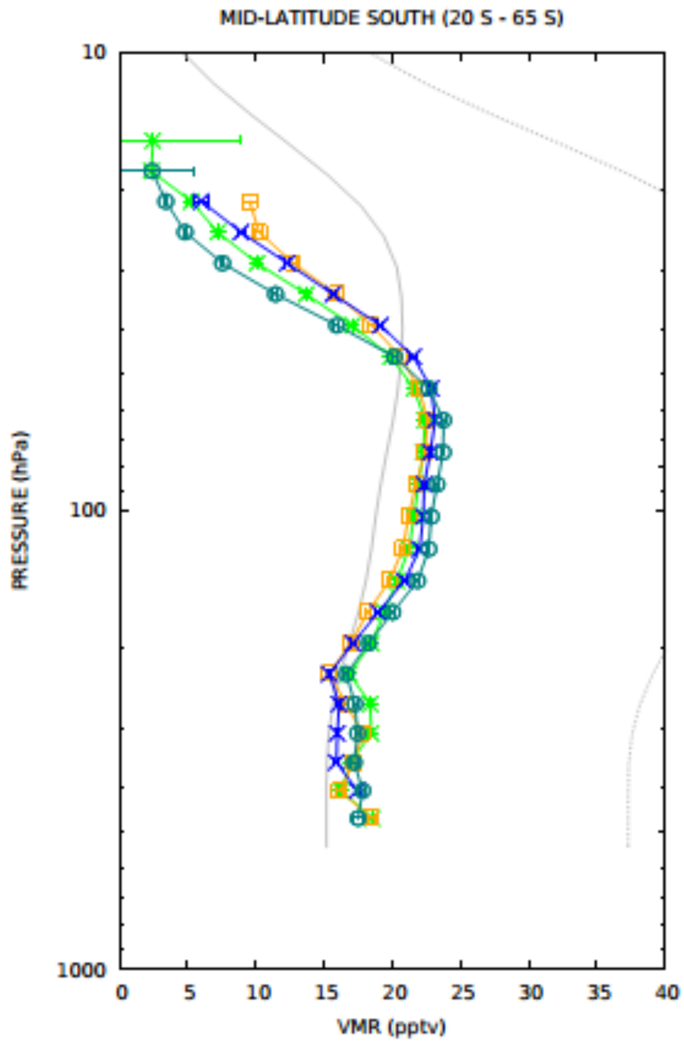




In the equatorial region (20S-20N) the vertical distributions of the phosgene VMR show peak values close to 40 pptv located at **about 40 hPa**.

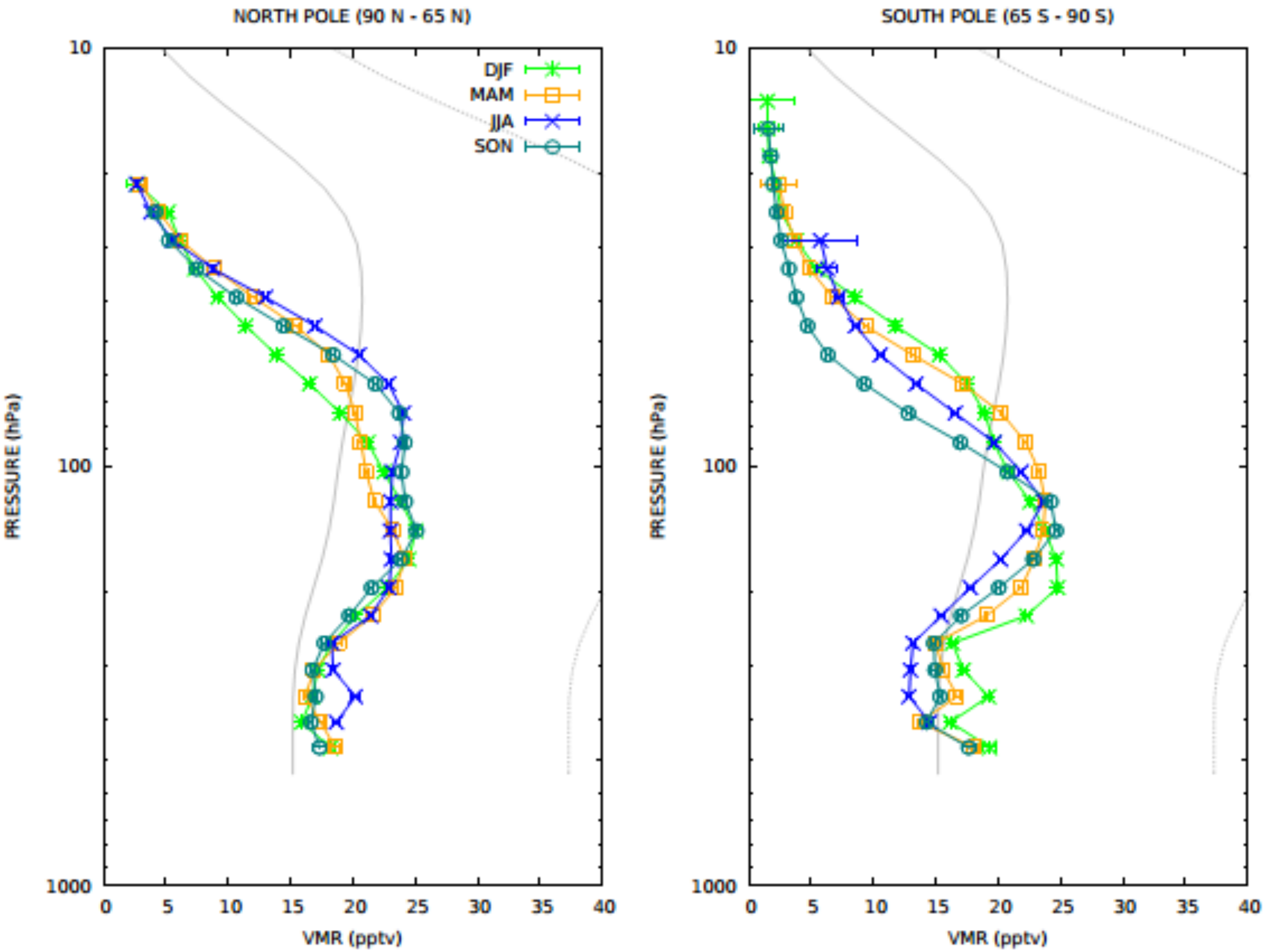
Results – Mid-latitude bands





In the mid-latitude regions (20-65) the average profiles do not exceed 30 pptv with maxima at **about 60 hPa**.

Results – Polar bands

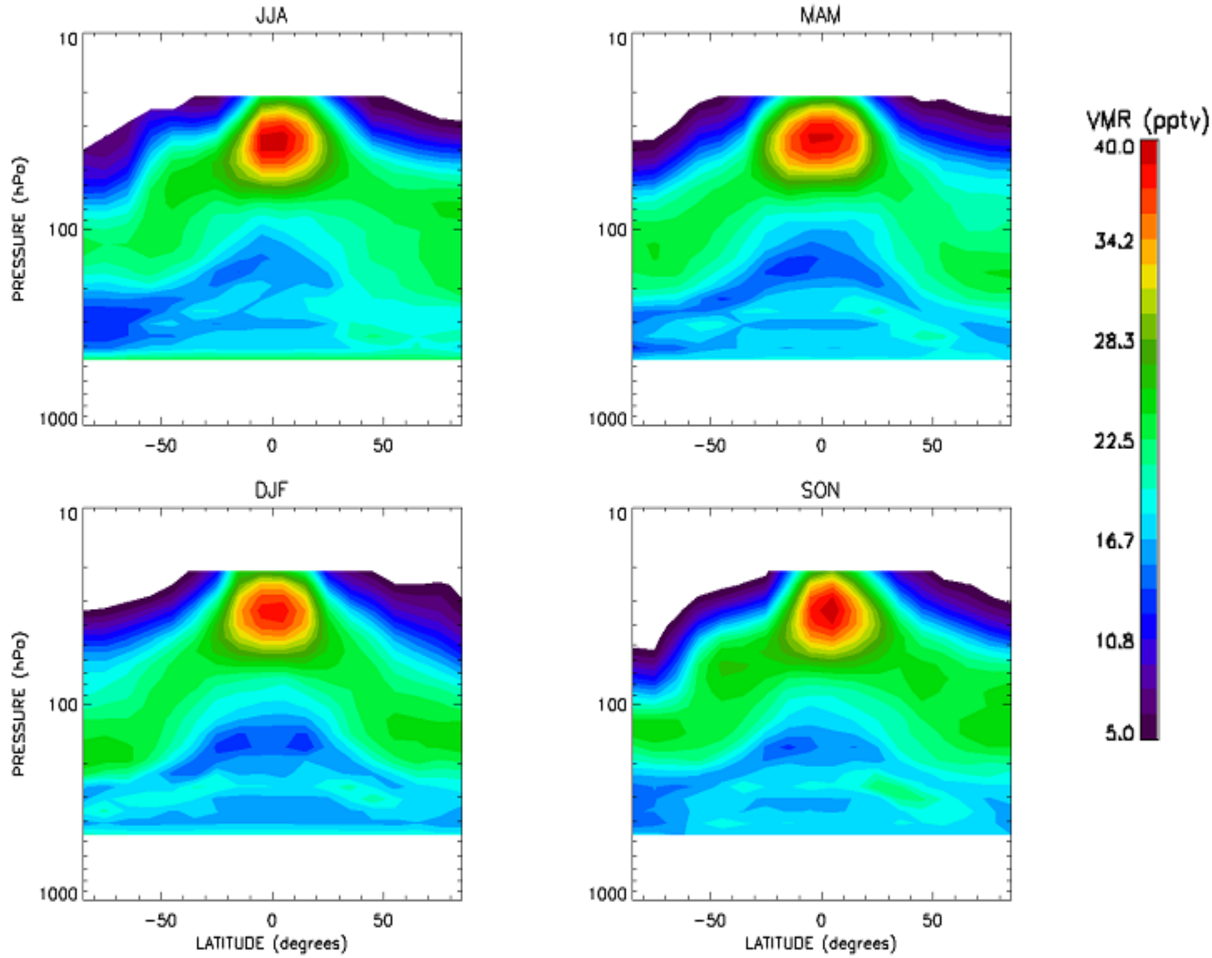


In the polar regions (65-90) the average profiles do not exceed 30 pptv with maxima at **about 100 hPa**.

Only in the polar regions we observe a **weak seasonality**, more pronounced at the South Pole.

Results

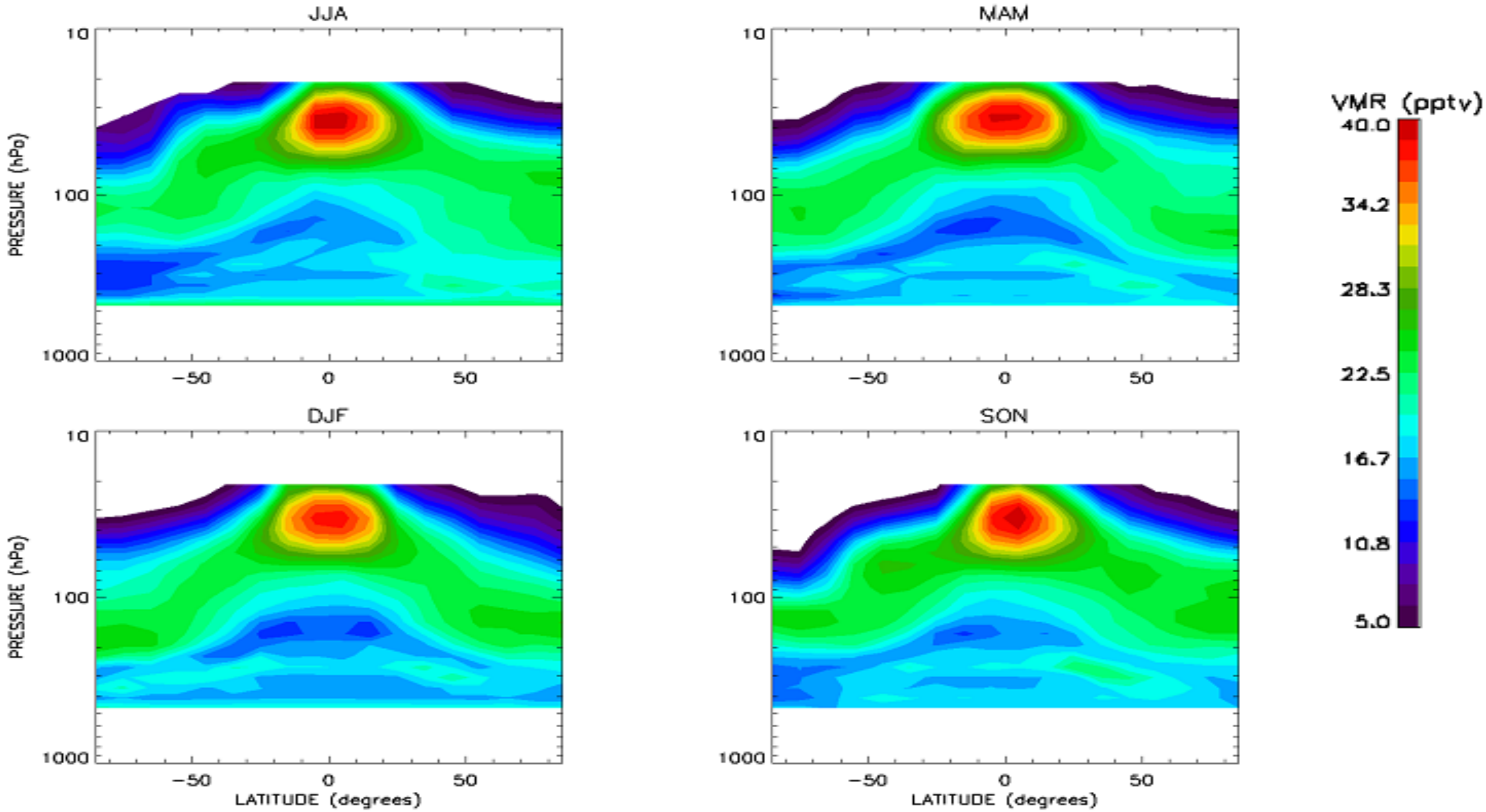
The VMR maps (averaged at **10^o latitude bins**) highlight the latitudinal dependence of the phosgene distribution in the UTLS region.



Important evidence:

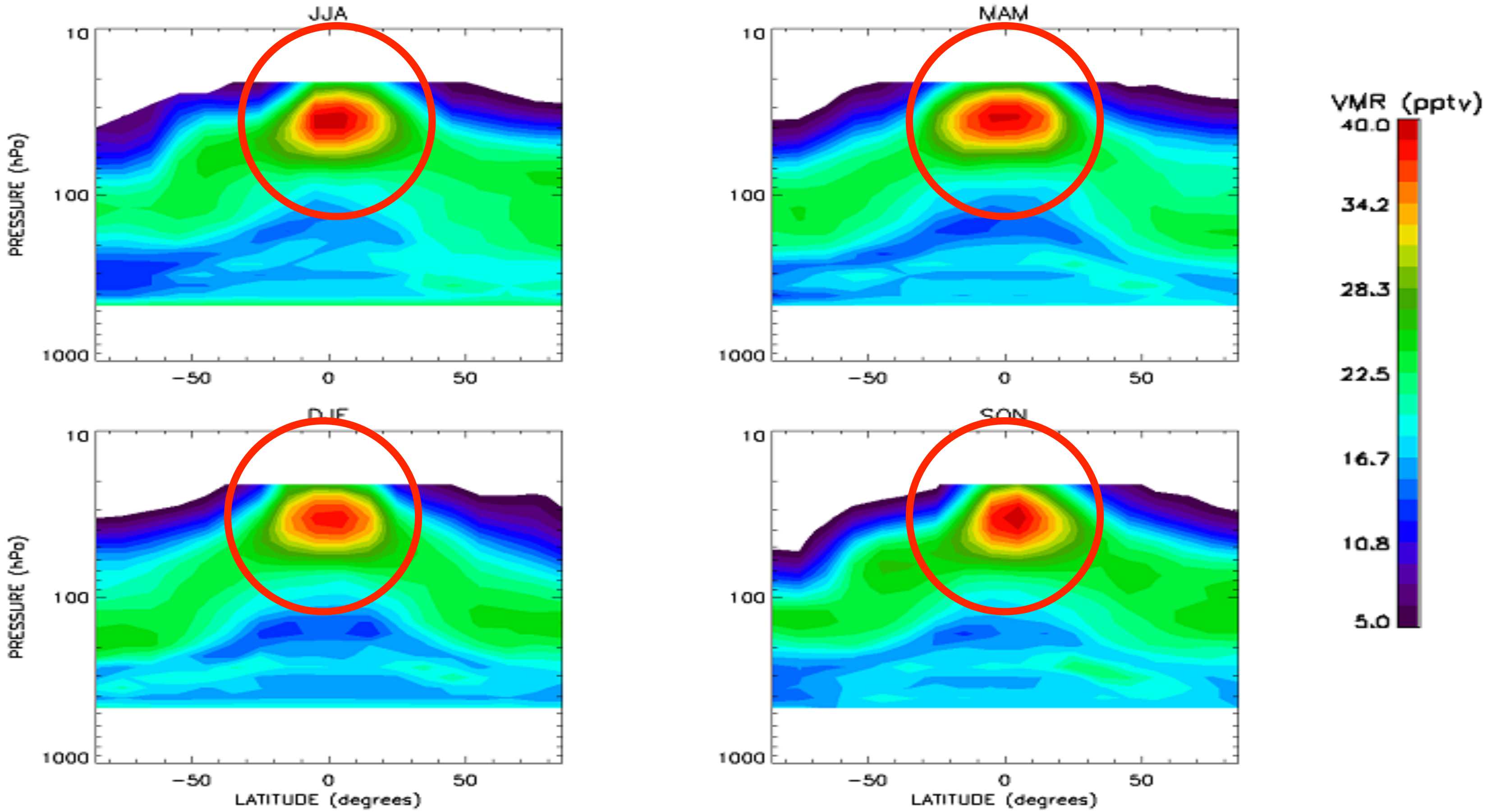
- **Equatorial bulk**
- **Quasi-symmetric pattern**
- **Low values in Antarctic Winter (JJA)**

Results



The **equatorial bulk** is caused by the **higher insulation** presents in the tropics respect to the higher latitudes (Fu et al., 2007).

Results



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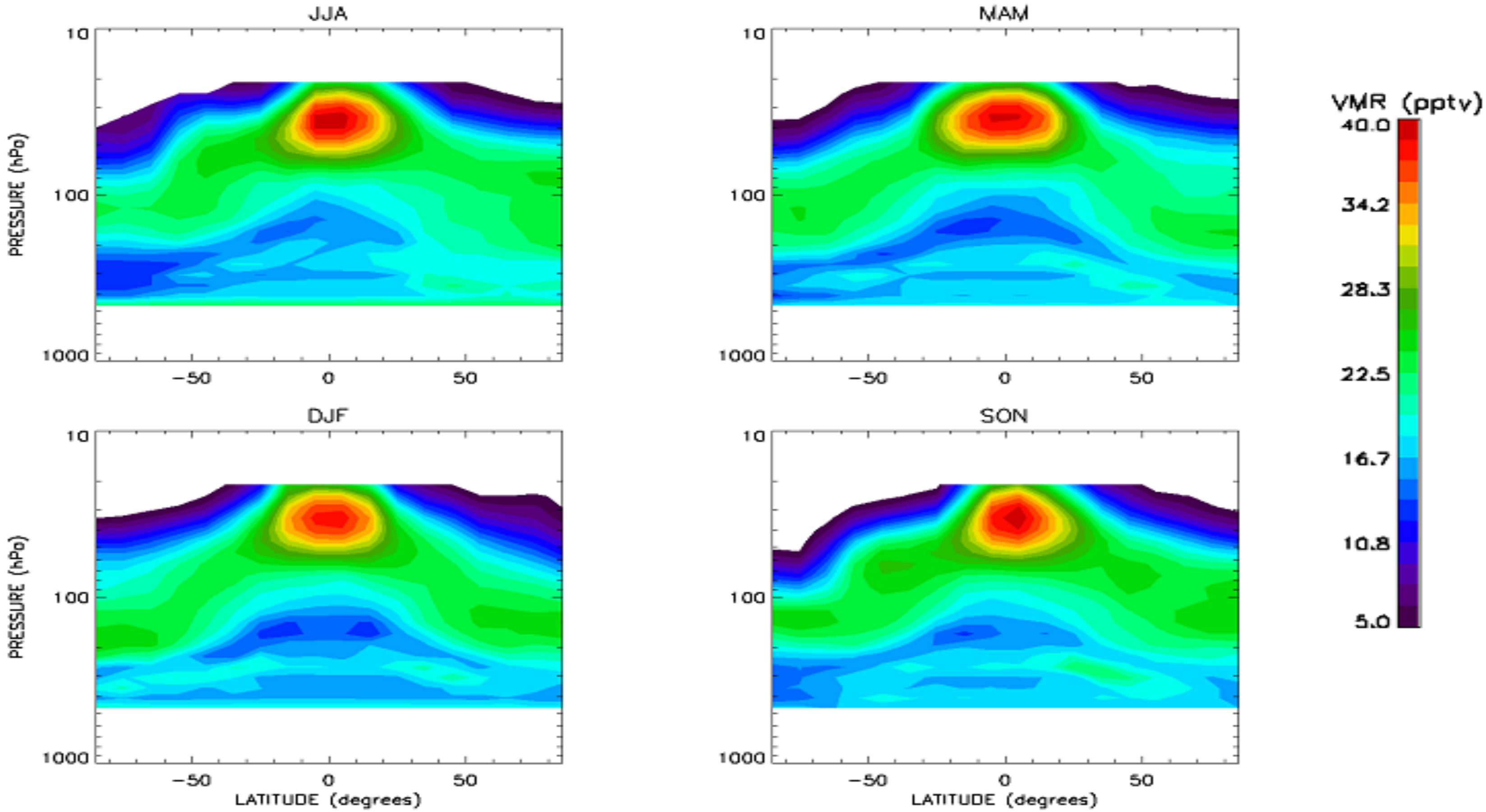
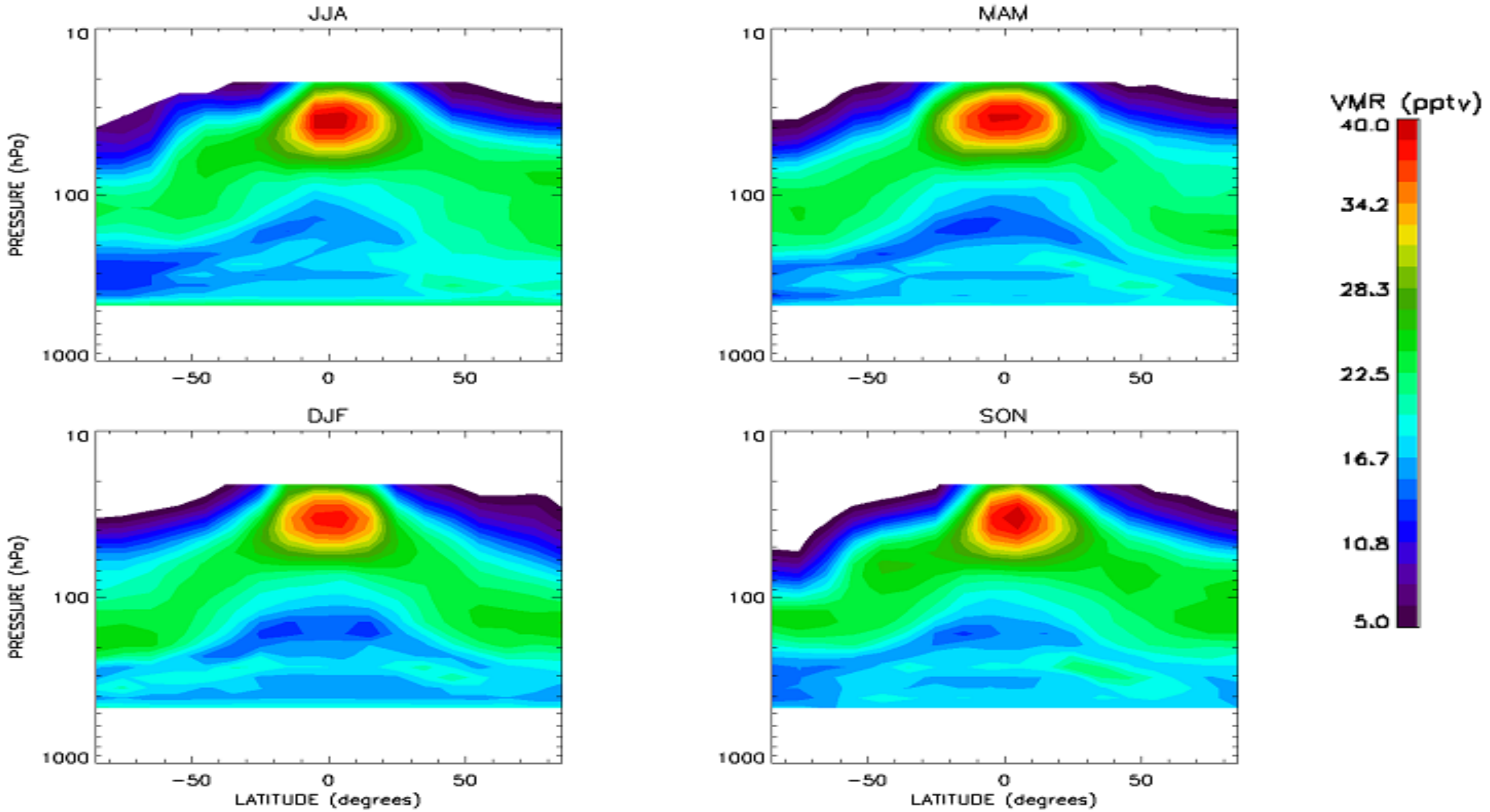


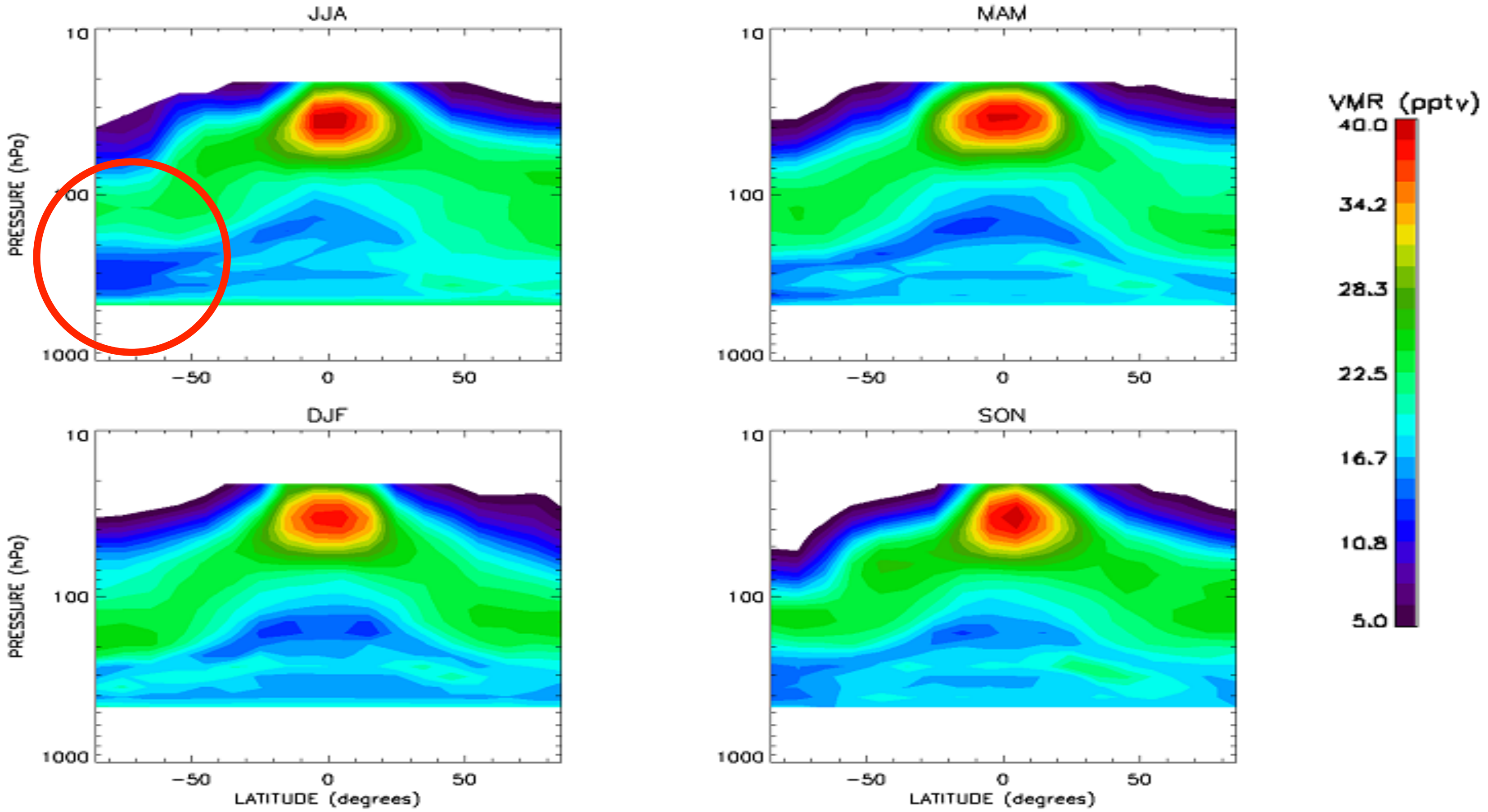
Quasi-symmetric pattern in the VMR distribution is caused by the **Brewer-Dobson** circulation that transports the tropical phosgene poleward.

Results



Low values in Antarctic Winter (June – July – August)

Results



Low values in Antarctic Winter (June – July – August)

Comparison with ACE-FTS

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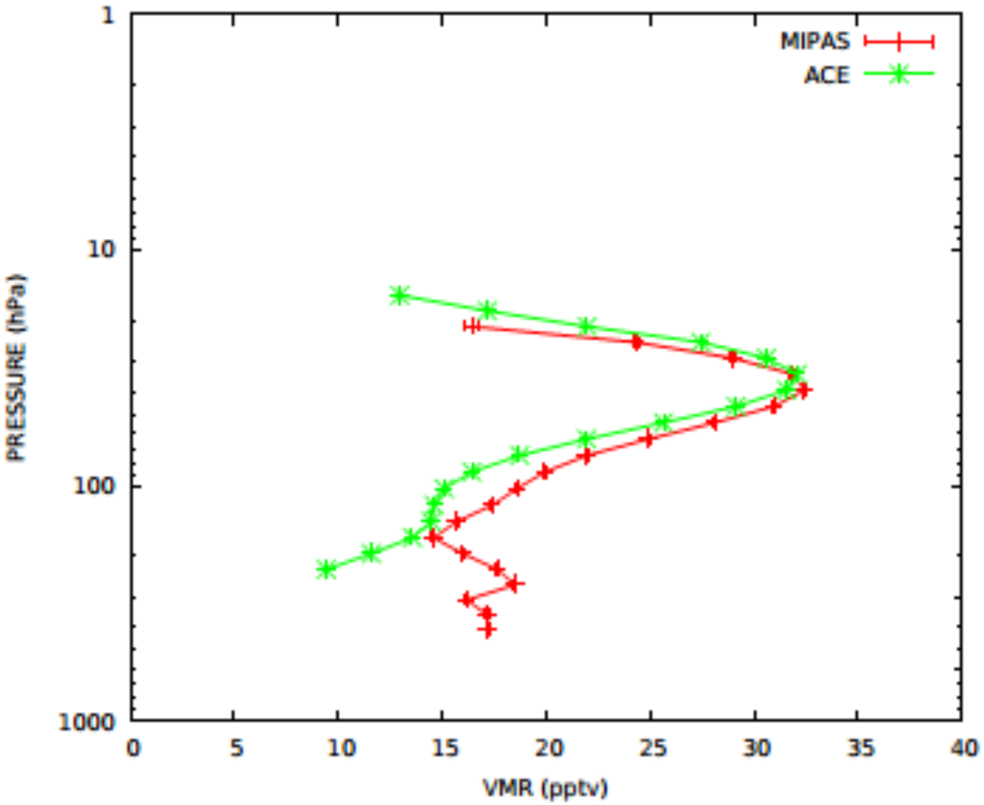
We compared our results with the average VMR profiles from ACE-FTS in the 30^{O} N - 30^{O} S region in the 2004 - 2010 period (Brown et al., 2011) .

- **good agreement at** pressure levels around the VMR **peak**,
- Differences between MIPAS and ACE-FTS at lower altitudes.



Summary and conclusions

We studied the phosgene global distribution using:

- the new phosgene spectroscopic database (Kwabia Tchana et al., 2015),
- the new MTR functionality of the ORM ($COCl_2$ and CFC-11 joint retrieval),
- more than 28000 profiles retrieved from MIPAS in the 2008.

MIPAS spatial and temporal sampling rates allowed to highlight the seasonal and latitudinal variations:

- largest values in the tropical regions,
- less peaked vertical distributions in the mid-latitude and polar regions,
- no seasonal variability in the UTLS apart for a weak seasonality in the polar regions,
- the lowest average values occur in the South Polar Winter (JJA).

With MIPAS level 1b version 7 data (see Raspollini's presentation tomorrow) the study of inter-annual variations of phosgene will be possible.