

General Comments

In this new study, Pettinari et al. discuss the global distribution and trends of phosgene (COCl₂) measurements by Envisat MIPAS during the years 2002-2012. A comparison of the MIPAS measurements with ACE-FTS and MIPAS balloon measurements is presented. A 10-year trend analysis is shown, and the phosgene trends found in the MIPAS data are related to different contributing factors, in particular to the distribution and trends of CCl₄.

Overall, this is an interesting and carefully conducted study, I think. The manuscript is concise and mostly clear. A few minor suggestions are listed below. In particular, it would be good to add some discussion on how the different vertical resolution of the MIPAS FR and OR modes, the ACE-FTS, and the balloon data affects the results shown here, I think. Once the comments are addressed, I would recommend the paper for publication in Atmospheric Measurement Techniques.

ANSWER: Thank you very much. we are sure that your suggestions will improve this paper.

Specific Comments

119-25: In the abstract, it would be nice to add a sentence explaining the phosgene trends observed by MIPAS, i.e., refer to the trends of CCl₄.

ANSWER: We added two sentences at the end of the abstract in the revised paper.

194-95: You might add a sentence saying how many vertical profiles are measured each day to provide a number for the "dense coverage".

ANSWER: We added a sentence with this information.

1135-136: This statement suggests the OR mode retrieval works much better and higher up than the FR mode retrieval. Is it really meaningful to say the phosgene retrieval works up to 54 km, considering the averaging kernels shown in Fig. 2 indicate a reasonable upper limit of about 25-30 km?

ANSWER: In this sentence we are just mentioning the retrieval range used for the FR and OR periods. Of course, the retrieval produces independent information only below a certain height. For this reason, this study has been performed using only data inside the so-called COCl₂ useful range, which is below 28 km. To explain this, we added a sentence citing the article where the COCl₂ useful range is defined.

1167-168: Can you please provide the actual numbers for the vertical resolution of the FR and OR phosgene retrievals?

ANSWER: Yes, the vertical resolution of FR (OR) period is about 5 km (3.5 km) below the altitude of 17 km. Then, it starts to get worse reaching 10 km at the altitude of 25 km. We added a sentence with this information in the revised paper.

Fig. 1: The OR retrievals shows a peak in "pt" errors at 25 km. What is causing this?

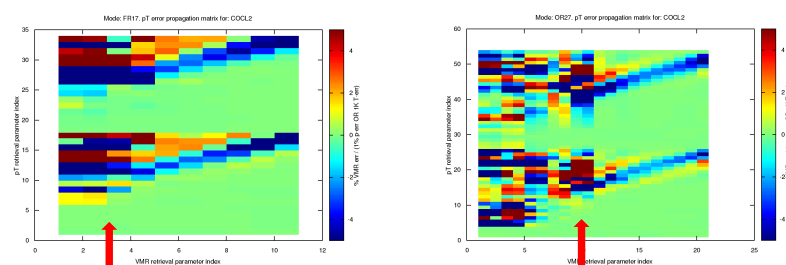


Figure A1: pT error propagation matrices for COCl₂ VMR retrieved from FR (left) and OR (right) measurements.

The green dashed lines in Figure 1 of the paper represent the profiles of COCl₂ VMR error caused by the propagation of the pT random error components. Those curves show a pronounced peak located around 27 km in the OR case, and an increase above ≈28.5 km in the FR case. Figure A1 shows the so called pT error propagation matrices for the COCl₂ VMR retrieved from FR (left) and OR (right) measurements. For each VMR parameter indexed in the horizontal axis, the color scale indicates the percentage VMR change obtained by applying a perturbation (1K variation in temperature or 1% variation in pressure) to the pT-retrieval vector element indicated in the vertical axis. The first half of the PT-retrieval vector elements refer to the tangent pressures, the second half to the temperature profile grid points. Pressure and temperature parameters are indexed starting from the top of the atmosphere. The red arrows in Figure A1 indicate the VMR parameter indices that roughly correspond to the heights of the peak (OR case, VMR parameter index #10) and of the increase (FR case, VMR parameter index #3) of the pT-errors reported in Figure 1 of the paper. Figure A1 suggests that the pronounced peak of the pT induced error observed in the OR case is caused by an increased sensitivity to pT variations of the VMR at these altitudes. Both the different microwindows used (see table 1 of the paper) and the finer limb scan pattern implemented in the OR mission can actually generate the increased sensitivity observed.

While describing the contents of Figure 1, in the revised version of the paper we added a comment on this regard.

Fig. 2: Can you please add a curve showing the integral of the averaging kernels so that it is more easy to see at which height range the retrieval results are mostly determined by information from the measurements rather than a priori data?

ANSWER:

To highlight the contribution of the actual measurements to the individual retrieved parameters we prefer to use the parameter-specific information gain q_j (first introduced in Dinelli et al. : MIPAS2D database ..., Atmos. Meas. Tech., 3, 355 - 374, 2010) defined as:

$$q_j = - \frac{1}{2} \log_2 \left(\mathbf{S}_{x,jj} / \mathbf{S}_{a,jj} \right)$$

where $\mathbf{S}_{x,jj}$ and $\mathbf{S}_{a,jj}$ denote the j -th diagonal elements of the retrieval- and a-priori- error covariance matrices, respectively. If the measurements do not contribute to determine the j -th retrieval parameter we get $\mathbf{S}_{x,jj} = \mathbf{S}_{a,jj}$, thus $q_j = 0$. On the other hand, if the actual measurements contribute to determine the j -th parameter, then we get $\mathbf{S}_{x,jj} < \mathbf{S}_{a,jj}$, thus $q_j > 0$. For example, if $\mathbf{S}_{x,jj} = \mathbf{S}_{a,jj} / 4$ (the measurements are able to halve the a-priori uncertainty), then we get $q_j = 1$, i.e. we gain 1-bit of information.

The plots of figure 2 of the revised paper now include also the curves of $q_j = q(z_j)$. The text describing figure 2 has been modified accordingly, to include comments regarding the parameter-specific information gain.

Figs. 1 and 2: How do the phosgene retrieval diagnostics change for different atmospheric conditions (tropics, polar summer, polar winter) compared to mid-latitudes?

ANSWER:

Some differences exist. For example, in the FR polar summer scenario, the F11 interference error gives a larger contribution at high altitudes while the spectroscopic database error is smaller at low altitudes. Another example is that, in FR tropical conditions, the peak of F11 error is shifted towards higher altitudes with respect to the mid-latitude day example in figure 1. Further information can be found in the MIPAS systematic errors website maintained at the Oxford University (<http://eodg.atm.ox.ac.uk/MIPAS/err/>). Additional studies regarding the variability of the retrieval error with latitude and season were conducted during the characterization activities of Level 2 v.8 products. The Level 2 v.8 readme file (see fig. 4-121, page 154 of https://earth.esa.int/eogateway/documents/20142/37627/README_V8_issue_1.0_20201221.pdf) shows that the relative random error components due to NESR and pT error propagation actually change their value with latitude and season. The changes, however, are mainly due to the variation of the average VMR profiles in the different latitudinal / seasonal scenarios, while the absolute errors are rather constant.

In the revised text, we added a sentence citing these additional analysis that includes different scenarios. Regarding fig. 2, the showed Averaging kernels are “typical” because they change really marginally with measurement scenarios.

Fig. 4: At the 50 hPa level, a significant bias/offset seems to be present between the FR and OR measurements. Can you provide an explanation for this offset? Most likely, it is due to the different retrieval characteristics of the FR and OR mode?

ANSWER: This is a well-known offset present in most of the MIPAS products. We know that it exists and we take it into account in the trend computation. It is mainly due to the different Micro-Windows (MWs) used for the retrieval in the FR and OR periods. Minor contributions are given also by the different vertical resolution and measurement vertical step in the two mission periods. In the revised text we added a sentence explaining this.

1207-209: It would be good to mention the total number of matches/profiles that have been available for comparison.

ANSWER: We added this information.

1210-212: It is pointed out that the MIPAS and ACE-FTS vertical profiles have been interpolated to the same levels to calculate their differences. However, how did you deal with the different vertical resolution of the data sets? Presumably, the vertical resolution of the MIPAS phosgene retrieval is different from the ACE-FTS data? Did you consider that systematic biases will arise in the comparisons due to the different vertical resolution of the data?

ANSWER: We are aware of the possible systematic biases due to the different vertical resolutions of the measurements. However, we do not have and we could not find ACE Averaging Kernels. The only information we found is that the ACE vertical resolution is about 3 km. If this is a really constant value, we can say that the vertical resolution has a minor effect below 15 km because MIPAS vertical resolution is about 3.5 km, very close to the ACE's one. On the other hand, MIPAS

vertical resolution starts to degrade at higher altitudes, reaching a value of 6 km at 20 km. The lower vertical resolution of MIPAS could therefore be responsible for a negative bias above the altitude of 15 km, mainly where the COCl₂ peak is located.

We plan to include additional comments on this regard in the revised paper.

1234-238: Could the different vertical resolution of the data sets as represented by the averaging kernel also play a role in this comparison?

ANSWER: As we said in the previous answer, the contribution coming from different vertical resolutions between MIPAS and ACE is expected to be not negligible above the height of 15 km. As explanation of this point, we added a sentence in the text.

1265-273: This section looking at the comparison of the satellite data and the balloon data is also lacking some discussion regarding the (potentially) different vertical resolution of the data sets.

ANSWER: COCl₂ MIPAS-balloon has a vertical resolution between 3 and 4 km, which is insofar consistent with MIPAS-ENVISAT. In the text, we indicated the MIPAS-balloon vertical resolution.

1336: In the conclusions section, it would be nice to include a few sentences about the broader implications of the study. Since MIPAS is out of order for about ten years, are other measurements being available or becoming available sometime soon to continue atmospheric phosgene measurements? Are the MIPAS phosgene measurements particularly important for specific applications in future work, e.g., evaluation of chemistry transport models?

ANSWER: We added two sentences at the end of the paper, explaining that these MIPAS measurements can be important to improve the chemical transport models and to understand the atmospheric sources and sinks of Cl-containing species. This study also provides an independent confirmation, obtained with a better temporal and spatial coverage, of the ACE results. In the future, the continuity of this study can be provided by ACE-FTS measurements, which are still being acquired.

Technical Corrections

111-25: Merge these five paragraphs of 1-2 sentences each into just one?

185: "lies" -> "fled" or "operated"

Table 1: apply AMT/Copernicus table format

1187: "polar nights" -> "polar winter" (?)

Fig. 8: the plots are quite small

Technical corrections were implemented in the revised paper.
