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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Partitioning and budget of inorganic and organic chlorine species observed by MIPAS-B and TELIS in the Arctic in March 2011" *by* G. Wetzel et al.

**G. Wetzel et al.**

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**Response to referee #3:**

First of all we thank the referee for his/her effort to carefully read the manuscript and for all comments.

**General comments:**

*1. The most important overall revision that I think is needed to support the analysis and the conclusions drawn is to include some discussion of how representative the chlorine budget derived from one balloon flight in the polar vortex near the end of one*

*very exceptional Arctic winter is of the "current" budget overall. The authors conclude that their results "confirm" a slightly decreasing chlorine trend in the stratosphere, but this is only the case if they can show/argue that the chlorine budget derived under these quite unusual conditions is representative of the current budget in general.*

The Arctic winter 2010/11 was characterized by a strong polar vortex. The year-to-year variability of the Arctic vortices is quite high (at least compared to the Antarctic) and therefore such a situation is expected to appear from time to time. For instance, a long-lasting spring Arctic vortex (similar to an Antarctic spring vortex) existed also in the winter 1996/97 (Coy et al., Geophys. Res. Lett., 24, 2693-2696, 1997). Anyhow, our measurements are typical for a strong late winter vortex situation. Of course, the chlorine partitioning changes, depending on the time and activation of very reactive components from their reservoir species, but the total chlorine budget remains unchanged. The amount of total chlorine is governed by the age of air entering the stratosphere which may vary slightly inside the vortex. It is difficult to assess how representative our Cl budget is on a more general view. However, if we look at the horizontal variation of Cltotal in EMAC at altitudes above 24 km we see virtually no variation inside the polar vortex. The variation inside/outside vortex is no larger than 0.1 ppbv. That is clearly smaller than the estimated Cltotal measurement accuracy of 0.3 ppbv such that the observations can be treated as representative at least for the Arctic vortex and not only for a very limited geographical region. We included some more information in the conclusions and abstract to clarify this issue.

*2. Have there been any comparisons between the MIPAS-B and TELIS measurements described here with other instruments? In particular, are there not ACE-FTS measurements in 2011 at a similar time of year that could be (or perhaps have been) used to construct a chlorine budget?*

Many species measured by the MIPAS-B instrument were involved in a large number of validation activities and cross-comparisons on satellite sensors (e.g. MIPAS-Envisat, ILAS/ILAS-II, SMILES). For species used in this work we mention for evalu-



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ation: ClONO2 (Höpfner et al., Atmos. Chem. Phys., 7, 257–281, 2007; Wetzel et al., Atmos. Chem. Phys., 8, 1119–1126, 2008; Wetzel et al., Annals of Geophysics, 56, Fast Track-1, 2013), CFC-11 and CFC-12 (Wetzel et al., Atmos. Chem. Phys., 8, 1119–1126, 2008; Wetzel et al., Annals of Geophysics, 56, Fast Track-1, 2013), ClO (Sagawa et al., Atmos. Meas. Tech., 6, 3325–3347, 2013), and N2O (Wetzel et al., Atmos. Chem. Phys., 8, 1119–1126, 2008; Payan et al., Atmos. Chem. Phys., 9, 413–442, 2009).

TELIS HCl and ClO observations have been evaluated using MLS measurements (de Lange et al., Atmos. Meas. Tech., 5, 487–500, 2012). The species ClO was additionally compared to SMILES observations (Sagawa et al., Atmos. Meas. Tech., 6, 3325–3347, 2013). This work also includes a cross-comparison to MIPAS-B ClO. We added corresponding sentences at the end of sections 2.1 and 2.2.

There are some ACE-FTS measurements (version 3.5) from 31 March 2011 available to compare with MIPAS-B/TELIS observations. However, ACE-FTS geolocations are at least 1000 km south of the balloon instrument's tangent points during this time of the year. The mean ACE-FTS profile (calculated from three closest observations) above 24 km exhibits 0.15 ppbv lower Cltotal compared to MIPAS-B. This value is clearly within the combined error limits of both instruments.

**Specific comments:**

*Page 5394, lines 1–6: It would be good to include Solomon (1999, Revgeo) here.*

Included.

*Page 5394, line 10: Rather than bring in the concept of age of air (which is somewhat abstract and not otherwise important for this paper), it would be better to simply say something that conveys that it takes several years for changes in surface emissions to propagate to the stratosphere.*

Changed.



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*Page 5394–5395: In the discussion of trends in stratospheric chlorine, can you give some indication of the degree of uncertainty implied by the results of the previous studies described?*

We included uncertainties to the results of previous studies.

*Page 5395, lines 18–20: It isn't clear how the neural networks are used, why they were needed, or whether those details are even important to this paper.*

We deleted the corresponding sentences.

*Page 5396, lines 1–2: As per general comment 1, this seems to be a lot to expect from analysis of measurements from one flight, unless it can be shown/argued that those measurements are representative of the broader Cl distribution.*

We modified this sentence and restricted the assessment to the late winter Arctic vortex.

*Page 5396, line 12: The vortex in the lower stratosphere in 2011 was intact, well-defined and represented a strong transport barrier until approximately mid-April (e.g., Manney et al., 2011; also see any readily available potential vorticity maps in the lower stratosphere.*

We modified this sentence accordingly.

*Page 5396, lines 19–20: Please provide citations/support for this statement about the timing of the chlorine deactivation. The primary instrument measuring active chorine throughout the vortex on a daily basis at that time was Aura MLS, which had an anomaly and was temporarily shut down between 27 March and 19 April 2011; chlorine was still substantially activated on the first date, and completely deactivated on the second date (Manney et al., 2011). Are there other observations that pin down the timing of deactivation more specifically to that described here?*

There are also MIPAS satellite ClO observations published (Sinnhuber et al., Geophys.



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Res. Lett., 38, 2011) which show the chlorine deactivation. We included the Manney et al. and Sinnhuber et al. references again in the text.

*Page 5397, line 14, and ensuing discussion: The material on the reliability of the MIPAS-B data relies heavily on the results of Friedl-Vallon et al. (2004). Kleinert (Appl. Optics, 2006) discusses a nonlinear effect in the MIPAS-B2 detectors that is not accounted for in the methods of Friedl-Vallon et al. If a correction for this effect is used here it should be noted and the Kleinert paper cited; if not, an explanation should be given as to why it was not necessary.*

Of course, the non-linearity correction has been applied here. The reference Kleinert (Appl. Opt., 45, 425-431, 2006) has been added to the text.

*Page 5397, line 23 and page 5399, line 21: Why was the updated HITRAN database (Rothman et al., 2013, JQSRT) not used? How can material in a "2003" paper be used to "update" a "2009" database?*

We did not use the present HITRAN database since we detected some spectroscopic mistakes which are not contained in the previous HITRAN release. Hence, we used HITRAN data in combination with a MIPAS dedicated spectroscopic database as described by Raspollini et al. (Atmos. Meas. Tech., 6, 2419–2439, 2013). We modified the corresponding sentence accordingly.

*Page 5400, lines 25–27: How has the PSC scheme in the model been validated?*

A validation of the used PSC scheme with the help of HNO3, ClO and O3 data from the Microwave Limb Sounder (MLS) onboard NASA's Aura satellite was published by Kirner et al. (Atmos. Chem. Phys., 15, 2019–2030, 2015). We included this reference (together with an additional sentence) in the text.

*Page 5401, lines 1–3: Can you give a reference for the implementation of the nudging to ERA-Interim, and/or describe how closely it "ties" the model to realistic meteorology?*

The evaluation of the nudging technique was, for example, done by van Aalst (Ph.D.



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thesis, Institute for Marine and Atmospheric Research Utrecht, The Netherlands, 2005). We cite this publication. The temperature bias (in comparison to ERA-Interim) within the nudging area from ground until 1 hPa is very small (below 1 K).

*Page 5402, lines 5–7: Can you give a reference or other supporting evidence that these species are indeed negligible?*

We refer to the AGAGE database (Prinn et al., J. Geophys. Res., 105, 17751-17792, 2000) and included this citation in the text.

*Page 5403, line 6 and line 20: I'm guessing that "noise error" means error due to spectral noise?*

Yes (we added "spectral" in the text).

*Page 5403, lines 5–7: Although the time evolution of MIPAS-B ClO near 30 km does look problematic, the maximum values there look similar to what I'd expect – for instance, similar to those typically seen by MLS at high latitudes in the 30–40-km altitude region in late March – while the values from TELIS appear lower. Have these values (or values measured by these two instruments at other times) been compared with other measurements?*

ClO measurements of TELIS and MLS have been compared (de Lange et al., Atmos. Meas. Tech., 5, 487–500, 2012). Differences between both sensors are small and clearly within the combined error limits.

*Page 5403, line 14: Please give a/some reference/s supporting the statement that these ClONO2 values are typical.*

Such high values at the end of the winter were measured by MIPAS instruments several times (see, e.g., Oelhaf et al., Geophys. Res. Lett., 21, 1263-1266, 1994; von Clarmann et al., J. Geophys. Res., 102, 16157-16168, 1997; Wetzel et al., J. Geophys. Res., 107, 4280, 2002; von Clarmann et al., Atmos Meas. Tech., 2, 159-175, 2009). We added these citations to the text of the manuscript.



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*Page 5403, lines 14–16: This sentence is not very clear. I think you are pointing to a reduction in the vertical ClONO2 gradients as evidence that ClONO2 is lower than it would be if chlorine was completely deactivated, but you don't explicitly make the connection between lower ClONO2 "gradients" and lower ClONO2 "values". Perhaps this could be reworded to clarify.*

Yes, we reworded this sentence for better clarity.

*Page 5403, line 25 (first reference), and following text: Since you are using N2O from MIPAS-B, the uncertainties and retrievals for N2O should be discussed in section 2 (and included in Table 1).*

Done as suggested by the referee.

*Page 5404, equation (7), and discussion of N2O-Cly correlation: What is this proxy relationship based on (i.e., how was it derived)? Is this the same method discussed by Strahan et al. (J. Geophys. Res., 119, 14098-14109, 2014)?*

Cly from the cryosampler measurements is calculated as the difference between total chlorine and observed organic chlorine from the source gases CFC-11, CFC-12, CFC-113, CH3CCl3, CCl4, HCFC-22, HCFC-141b, and HCFC-142b. In addition, an input of 50 pptv of chlorine from short lived source gases is taken into account which is assumed to be transformed immediately to inorganic chlorine. Total chlorine from the gases is propagated into the stratosphere in the same way as an inert tracer, as described in Engel et al. (J. Geophys. Res., 107, 4136, 2002), using global mean observation data from NOAA ESRL. We added the explanation of the method to the text (the method is different to one in the above mentioned Strahan et al. paper).

*Page 5404, line 6, "...supposed to be vertically constant...": What work/theory shows that it is "supposed to be" vertically constant? Can you give a/some reference/s.*

The age of stratospheric air may slightly vary and therefore also Cly and Cltotal. Hence, we changed this to "approximately constant" (a reference is not necessary here be-



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cause this is obvious from our own vertical profiles shown in this paper).

*Page 5404, lines 8–9: How do you know the bias is in the observations rather than in the calculations?*

We changed “bias” to “deviation” to make this statement more neutral.

*Page 5404, lines 10–11: What is "the reference"? Can’t you check the N2O values observed at this altitude on this flight to test whether this statement is the case?*

Due to the stronger subsided MIPAS-B N2O Profile compared to the N2O reference, we find higher Cly* values (using the correlation with N2O) compared to measured Cly at altitudes below 21 km. We changed the text accordingly.

*Page 5404, lines 23–24: To my eye, this is only the case between about 15 and 20 km, not everywhere "below 20 km".*

The simulation is clearly lower than the observation between 15 and 20 km, but also (to a lesser extent) below 15 km.

*Page 5405, line 2: Can you give reasons for the Cly deficit in EMAC and/or references to support that there is such a deficit?*

The Cly deficit is connected with the mentioned ClONO2 deficit. The EMAC model underestimates the subsidence of the air masses in the late winter Arctic vortex. Hence, higher N2O values (in the model compared to the measurement) are connected with lower Cly values according to the compact N2O-Cly relationship, resulting in an underestimation of the chlorine reservoir species (especially ClONO2). So, at least part of the ClONO2 deficit in EMAC can be explained by the underestimation of the subsidence in the model. This is explained now in more detail in the text.

*Page 5405, line 11: Please specify where the "quasi-altitude constant" region is.*

Above 24 km (as written in line 12).



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*Page 5405, lines 22–23: It is not entirely clear to me how the missing chlorine species are included in the observations via HCl, and what "(after being photolyzed)" refers to? After what is photolyzed?*

The very short lived species (VSLS) are photolyzed and converted to HCl (region above 24 km). Therefore this amount of chlorine is contained in measured HCl, but is missing in simulated HCl since the VSLS are not included in the model. We changed the text to make this more clear.

*Page 5406, lines 8–9: The "cold period", defined as having minimum temperatures below the NAT PSC threshold lingered into the first several days of April 2011 (e.g., Manney et al., 2011).*

We changed the text accordingly.

*Page 5406, lines 7–9: MLS measurements on 26 March 2011 (publicly available maps on MLS website) show ClO values up to about 0.9 ppbv in the core of the vortex, and a very non-uniform distribution with highest values in the core and near zero values near the edge of the vortex. The flight in question sampled air towards the outer part of the vortex (which would be apparent if you revise Figure 1 as I suggest below), where ClO would be expected to be lower than the maximum values. While significant deactivation undoubtedly occurred between 26 and 31 March, the non-uniformity of the ClO distribution in the vortex means that you cannot make a generalized statement about the overall degree of deactivation from these very localized measurements.*

We modified the text and restricted the statement to the outer part of the polar vortex above Finland.

*Page 5406, lines 16–18: What about ACE-FTS chlorine measurements in the Arctic in 2011? Can't you compare with these?*

As already mentioned above, there are some ACE-FTS measurements (version 3.5) from 31 March 2011 available to compare with MIPAS-B/TELIS observations. However,



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ACE-FTS geolocations are at least 1000 km south of the balloon tangent points during this time of the year such that a direct comparison is not possible. However, these Cltotal profiles derived from ACE-FTS are in agreement with the total chlorine inferred from the balloon instruments taking into account the combined error limits.

*Page 5406, line 22: Per general comment (1) above, and other comments on the localized (in space and time) nature of the measurements analyzed here, I think "confirms" is too strong. I would suggest something like "is consistent with".*

We followed the reviewer's suggestion and changed the text accordingly.

*Page 5407, lines 8–9: I don't understand what this final sentence is getting at, please clarify.*

The mentioned changes refer to the mean age of stratospheric air. We modified the text to make this issue more clear.

**Figures:**

*Figure 1: It is impossible to distinguish which dots are from which instrument on this figure. It is also difficult to get the context of where these measurements are within the vortex because too small a geographic area is shown. I would suggest a panel showing a larger latitude/longitude range, with just the boundaries of the area of the measurements shown, along with a panel showing a much smaller geographic region around the measurement locations with clearly distinguishable symbols for each instrument.*

We included a panel showing the whole polar vortex with a marker containing the approximate measurement region. We also changed the TELIS tangent point colour to yellow for better visibility.

*Figure 2: Needs to be larger (this may only be an issue in the ACPD format).*

These figure should indeed appear larger in the final ACP-format.

*Figures 4 and 5: The yellow used for Cly and Cly* is quite hard to see – I'd suggest*



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*choosing a different (more intense) colour.*

The colour used for Cly and Cly* is orange (maybe this is a problem of the printer used by the referee). Anyhow, we changed Figures 4 and 5 using a non-linear scale on the abscissa for better visibility of all plotted species (also some error bars have been omitted for better clarity).

**Wording suggestions:**

*Page 5393, line 10, "is" should be "has been".*

Changed.

*Page 5393, line 15: suggest changing "previously carried out" to "previous".*

Changed.

*Page 5393, lines 23–24, replace "the seventies of the last century" with "the 1970s".*

Done.

*Page 5394: using "cold" (or "warm") to modify "temperatures" is incorrect, since "cold" by itself means "low temperature". Rather, "low" (or "high") should be used.*

We modified the text accordingly.

*Page 5394: line 18, change "has been" to "was".*

Changed.

*Page 5395: line 10, change "of" to "from".*

Changed.

*Page 5396, line 15, "which" should be "that". (Note that "which" and "that" are often, though not consistently, misused throughout the paper, either one used when the other should be or "that" used and preceded by a comma, or "which" used and not preceded by a comma. A review of restrictive and non-restrictive clauses might help.)*



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Okay.

*Page 5396, line 21, I suggest adding "Locations of" before "Recorded".*

Recorded refers to the spectra and not to the locations.

*Page 5398, lines 5, 26; page 5403, line 14; page 5404, line 14; page 5405, line 26; page 5406, line 5; Figure 5 caption, 2nd to last line: "which" should be "that".*

Okay.

*Page 5398, line 26, add a comma after "error".*

Okay.

*Page 5399, line 3, add a comma after "retrieval".*

Okay.

Page 5400, line 3, I suggest changing "corresponding to" to "resulting in".

Okay.

*Page 5400, line 4, change "like" to "such as".*

Changed.

*Page 5400, line 11, change "on" to "of".*

Changed.

*Page 5400, line 24, add commas before and after "among others".*

Okay.

*Page 5401, line 14, "was" should be "were".*

Changed.

*Page 5402, lines 15-16, I think you mean "correspond to noon maximum and minimum*



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*values, respectively".*

Changed.

*Page 5403, line 4, "was" should be "were" page 5404, line 21, move "in detail" to after "some differences" and delete comma after "detail".*

Changed.

*Page 5405, line 20, add "to" between "amount" and "about".*

Okay.

*Page 5407, line 1, add a comma after "2011".*

Okay.

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