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.

This file contains the response to the questions and comments of the referees together with the modified manuscript. All changes in the text of the manuscript are marked with red colour.

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 evaluation: 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.

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, e.g., those at http://mls.jpl.nasa.gov/plots/met/met_plot_locator.php).

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. 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. 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.

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 because 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).

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, 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 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.)

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 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.

Response to referee #4:

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

General comments:

I think you should clarify more often that your chlorine species profiles are valid for the special day and the special atmospheric situation only.

We now mention more clear the measurement situation of a late winter Arctic vortex.

Concerning the budget, you should mention and argue/prove that you are able to calculate the budget from the species measured by MIPAS-B and TELIS because none of the species that you cannot measure is very important under the conditions of the flight day.

Minor CFCs (e.g. CFC-114 and CFC-115) and HCFCs (e.g. HCFC-141b and HCFC142b) which are not measurable by MIPAS-B/TELIS contribute to Cl_{total} not more than 1% above 24 km (Brown et al., Atmos. Chem. Phys. Discuss., 13, 23491–23548, 2013). Further species (above 24 km) which are not measurable by the balloon instruments are very short lived chlorine species which altogether amount to about 0.1 ppbv (Mébarki et al., Atmos. Chem. Phys., 10, 397-409, 2010; WMO, Report No. 52, 516 pp., 2011). However, the chlorine amount of these missing species is implicitly contained in the HCl measurement (since the short lived chlorine species are converted to HCl after being photolyzed) and hence included in the observed chlorine budget. We made some changes in the last paragraph of section 3 to make this more clear.

In the conclusions, only the chlorine budget is discussed, but not the partitioning. I think you should include at least one or two sentences summarizing the findings of Sect. 3.

There is already some discussion on the chlorine partitioning at the beginning of the conclusions. We extended this discussion.

Specific comments:

1. *Page 5393, line 16: As you are not discussing changes in trends in the rest of the paper, you probably mean the decreasing chlorine amount here, not a decreasing chlorine trend?*

Yes, that’s true. We changed the text accordingly.

2. *Page 5393, line 25, to page 5394, line 6: I suggest to rewrite these sentences because they are slightly confusing and the second sentence is very long.*

We only slightly changed these introductory sentences since the main reason for the complexity is the large number of (necessary) citations.

3. *Page 5394, line 26: It is not clear which time range the trend you cite from Zander et al. (1996), 0.10 ppbv/year, is referring to. Please include this information.*

We included this information in the text.

4. *Page 5396, line 1: The word "current" used for the status of the chlorine partitioning suggests (to me) that the results obtained are valid for a longer time range than they actually are (see also my first general comment). (In contrary, for the chlorine budget, the expression seems more appropriate to me.)*

We modified this sentence to make things more clear.

5. *Page 5396, lines 11-17: These three sentences do not really fit under the heading "Instruments, data analysis and modelling", they are more a description of the meteorological situation of the preceding winter and on the launch day. Please consider moving them to the end of Sect. 1, more precisely for example onto page 5396, line 5, or changing the heading of Sect. 2 somehow ("Data description"?).*

We moved these sentences to the last paragraph of section 1.

6. *Page 5396, line 21: I suggest to mention the geographical coordinates of Kiruna/Esrange.*

We included the coordinates in the text.

7. *Page 5397, line 28: It is not clear how the vertical spacing of the retrieval grid increases with height between the balloon flight altitude and the top altitude at 100 km.*

It increases gradually. This is written in the text now.

8. *Page 5398, line 20: Do the a priori profiles of the target species vary with time of day? In this case, I think you should mention it here or when discussing the ClO results (e.g., page 5402, from line 21 on).*

No, the a priori profiles don't vary.

9. *Page 5399, line 28 and following: If you retrieve the two isotopologues separately, it seems to me that you shouldn't need to take into account the relative abundances, just add your results, and maybe add some 0.01%, as H35Cl and H37Cl combine to only 99.99% of total HCl. You could change the sentence that starts in line 28 to just mentioning their relative abundances (and maybe whether you also find this relation).*

The natural abundances for the isotopes have been accounted for during the retrieval process and the volume mixing ratio was scaled with the individual isotope abundance. Hence, the combined HCl was deduced by calculating the sum of the isotopes weighted with their abundances. We slightly modified the text.

10. *Page 5401, line 18 to page 5402, line 7: In the introduction (page 5394, line 4), it sounds as if Cl2 was the most important active chlorine species. So I think you should add an explanation why you may neglect it here in the budget calculations (please also see my second general comment in this context).*

The species Cl2 is not important in the case of our measurement since the chlorine activation was only small by the end of March. Cl2 values in EMAC are no larger than 0.03 ppbv during day and zero during night. Here we only define the chlorine families. In the following discussion of the results we also give explanations on the impact of missing chlorine gases to the budget.

11. *Page 5402, line 11: It is not clear what "This" refers to. Please specify explicitly which of the two conditions for measuring ClOOCl (activated chlorine and no PSC signatures) were not fulfilled during the analysed balloon flight. If there were also PSCs (which I assume was not the case), maybe you should mention that when describing the meteorological situation.*

ClOOCl concentrations were below the detection limit. We explain this in the text now.

12. *Page 5402: Please add a citation to Eq. 6.*

It was explained by Wetzel et al. (Atmos. Chem. Phys., 12, 6581-6592, 2012). We included this citation in the text.

13. *Page 5403, line 2: The word "reproduced" sounds somehow strange to me when used for measurements. Please consider replacing it, e.g., by "shown".*

Changed.

14. *Page 5403, lines 2-8, and Figure 2: Why are the time and magnitude of the maxima in MIPAS-B and TELIS ClO different? (Maybe because the instruments look into different directions? In this context, please see the comments on Figure1.) And it is not completely clear from the statement here whether you use TELIS ClO data only above 26 km or for the whole altitude range.*

The instruments look in the same direction (we explicitly mention this now in Fig. caption 1). MIPAS-B ClO is quite difficult to retrieve since spectral line intensities of ClO are comparatively weak in the mid-infrared. Above 30 km, the signal to noise ratio is low and hence the maxima shown by MIPAS-B in this altitude regions are characterized by large error bars. However, at 19 km, the signal to noise ratio is higher such that ClO can be retrieved here with better accuracy. Anyhow, the overall accuracy of TELIS is better than the one of MIPAS-B and therefore we used the TELIS ClO data in the whole altitude range for calculating the chlorine budget (now written in the text).

15. *Page 5403, line 25 to page 5404, line 4: It is not clear how the "adapted" N2O-Cly correlation was determined and which measurements of MIPAS-B were used for this, or whether maybe only the total (tropospheric) chlorine in the calculation was adapted to the time of the balloon flight? Please go a little more into detail here.*

The word "adapted" is a mistake in the text since the correlation was directly applied to the MIPAS-B N2O measurement. The text has been changed accordingly together with a further explanation.

16. *Page 5404, lines 6-9: Please try to rephrase the end of this sentence. The "bias in the observations" confused me. As far as I understood, both the Cly and Cly* values discussed here are observations respectively deduced from them.*

We rephrased the text to make this issue more clear.

17. *Page 5404, lines 13-14: It is not clear whether "increasingly" means a temporal or spatial change. I suggest to rewrite the beginning of the sentence for example like "From about 17 km to the ground", or similar.*

Of course a spatial change (since no temporal change is shown here). We modified the text to make this distinct.

18. *Page 5404, line 18: Suggestion to add "above 24 km" or "in this altitude region" in this sentence.*

We followed the reviewer's suggestion.

19. *Page 5404, line 22: I would prefer you to replace the word "obvious" by "visible" because in my feeling, "obvious" is too strong in this context.*

Changed.

20. *Page 5404, lines 25-26: Please give a rough estimate of the ClONO2 deviation in % as well to make the large difference between model and measurement more obvious to the reader.*

We added this information to the text.

21. *Page 5405, lines 8-10: I suggest to rewrite the sentence, for example like this: "These higher N2O values are connected with lower Cly values according to the compact N2O-Cly relationship, resulting in an underestimation of the chlorine reservoir species (especially ClONO2)." Furthermore, I suggest to add a concluding sentence like (with or without the part in brackets): "So (at least part of) the ClONO2 deficit in EMAC can be explained by the underestimation of the subsidence in the model."*

We followed the reviewer's suggestion.

22. *Page 5405, lines 11-12: Maybe move "above 24 km" directly behind "region".*

Changed.

23. *Page 5405, line 13: Connected with my comment concerning page 5404, lines 6-9, I suggest to rewrite "simulated value of Cly*" because in my understanding, it is a combination of measurements and EMAC model results in this case. Maybe change it to "value of Cly* deduced from the (EMAC) simulation"?*

We changed the text for better understanding.

24. *Page 5405, line 15: I suggest to start a new paragraph before "The mean...".*

Okay.

25. *Page 5405, lines 16-23: I found the argumentation not very easy to follow. My final understanding is the following: Some minor CFCs and HCFCs (for example CFC-114, CFC-115, HCFC-141b, and HCFC-142b) are not included in the EMAC model and not measured directly with MIPAS-B/TELIS. However, in 24 km above ground, the largest part of the actually emitted amount has already been photolyzed and the contained chlorine has therefore already reacted to become HCl (mainly). As a result, these minor species are indirectly contained in the measurements of HCl (above 24 km), but of course not in the model calculations. So in case my understanding of your argumentation is right, I suggest to rewrite the "However" sentence so that the connection with the photolysis becomes clearer. And maybe it would be good to add some more clarifying explanations. However, I do not understand the connection to the very short-lived species which are mentioned in the middle of this paragraph. If there is no connection, please swap the sentences starting with "The remaining deficit" and "However, the chlorine amount". If there is one, please try to clarify this.*

We modified the text to describe this issue more clear.

26. *Page 5405, line 18: HCFC-141b is mentioned twice.*

The second one is HCFC-142b. We changed this in the text.

27. *Page 5405, lines 23-24: Why is the percentage of inorganic chlorine above 24 km in EMAC larger than in the measurements (page 5404, line 18 says 95 %)? (Is this difference significant?)*

Taking into account the error bars of the measurement, this difference is clearly not significant.

28. *Page 5406, line 10: Please mention the EMAC value of Cltotal explicitly again.*

Okay.

29. *Page 5406, line 16: Please add a citation to the trend value -0.4% p.a. For consistency and easier readability, I suggest you change "% p.a." to "% year-1" (as on page 5394, line 26, and page 5395, line 28, for example).*

The citation belonging to these observations occurs already before this sentence. We changed a "the" in "these" to make it clear that trend and observations belong together.

30. *Page 5406, lines 18-20: Please add again the information here that these species are not part of the MIPAS-B/TELIS chlorine budget.*

Okay.

31. *Page 5406, line 22: To be more precise, I suggest to change "decreasing trend" to "decreasing amount" or "decreasing vmr" or "decrease of the stratospheric chlorine*

content" because it is not actually the trend that decreases (see comment concerning page 5393, line 16).

Changed.

32. *Page 5407, lines 5-9: I suggest to add "lower" between "hemispheric" and "stratosphere" (line 7). Furthermore, please rewrite/clarify/extend the last sentence. Maybe you could move the sentence starting in line 3 ("We finally conclude...") to the very end of the text?*

Modified.

33. *Page 5406, Sect. 4: I think somewhere in this section you should include one or two sentences with a conclusion concerning the stratospheric chlorine partitioning as measured by MIPAS-B/TELIS in comparison with the results from the EMAC model, i.e., summarize Sect. 3.*

We added some more text at the beginning of section 4.

34. *Table 3: If you cannot give an error estimate for the MIPAS-B/TELIS Cly*, I would suggest to remove "±0.00".*

The estimate is given and it is ±0.002 ppbv.

35. *Figure 1: Please improve the figure according to the suggestions of referee #3.*

We did improve this figure.

Technical corrections:

1. *Page 5395, line 2: I suggest to replace "occurred" (e.g., by "was performed" or "took place").*

Changed.

2. *Page 5395, lines 16+17: You forgot the "Array" in the definition of CLAES: Cryogenic Limb Array Etalon Spectrometer.*

Okay.

3. *Page 5398, line 8: I would find it better readable and understandable if you start this line with a lower-case letter in the word "where".*

Changed.

4. *Page 5401, line 7: A hyphen is missing between "chlorine" and "containing".*

Okay.

5. *Page 5402, line 25: Missing comma after "activation".*

Okay.

6. *Page 5404, line 8: Suggest to change "to" to "towards".*

Changed.

7. *Page 5404, line 25: Please add "by" after "deviates".*

Okay.

8. *Page 5405, lines 19-20: A hyphen is missing between "short" and "lived" (at two other occasions as well). And please add "to" between "amount" and "about".*

Changed.

9. *Page 5405, line 25: Please add "of" between "profiles" and "ClOx".*

Okay.

10. *Page 5406, line 7: Please remove the comma after "reveals".*

Okay.

11. *Page 5406, line 15: Change "this" to "these".*

Changed.

12. *Page 5406, lines 22-26: Please add a comma after "WMO (2011)", add "of air" after "mean age", and another comma before "we".*

Changed.

13. *Figure 4, last sentence of the caption: I suggest to change "Notice" to "Note".*

Okay.

Partitioning and budget of inorganic and organic chlorine species observed by MIPAS-B and TELIS in the Arctic in March 2011

G. Wetzel[1], H. Oelhaf[1], M. Birk[2], A. de Lange[3], A. Engel[4], F. Friedl-Vallon[1], O. Kirner[5], A. Kleinert[1], G. Maucher[1], H. Nordmeyer[1], J. Orphal[1], R. Ruhnke[1], B.-M. Sinnhuber[1], and P. Vogt[2]

[1]Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Karlsruhe, Germany

[2]Deutsches Zentrum für Luft und Raumfahrt, Institut für Methodik der Fernerkundung, Wessling, Germany

[3]SRON-Netherlands Institute for Space Research, Utrecht, the Netherlands

[4]Institut für Atmosphäre und Umwelt, J. W. Goethe Universität Frankfurt, Frankfurt, Germany

[5]Karlsruhe Institute of Technology, Steinbuch Centre for Computing, Karlsruhe, Germany

Correspondence to: G. Wetzel (gerald.wetzel@kit.edu)

Abstract

The Arctic winter 2010/2011 was characterized by a persisting vortex with extremely low temperatures in the lower stratosphere above northern Scandinavia leading to a strong activation of chlorine compounds (ClO_x) like Cl, Cl_2, ClO, ClOOCl, OClO, and HOCl which rapidly destroyed ozone when sunlight returned after winter solstice. MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) and TELIS (Terahertz and submillimeter Limb Sounder) balloon measurements obtained in northern Sweden on 31 March 2011 inside the polar vortex have provided vertical profiles of inorganic and organic chlorine species as well as diurnal variations of ClO around sunrise over the whole altitude range in which chlorine has been undergoing activation and deactivation. This flight was performed at the end of the winter during the last phase of ClO_x deactivation. The complete inorganic and organic chlorine partitioning and budget in the late winter Arctic stratosphere has been derived by combining MIPAS-B and TELIS simultaneously observed molecules. A total chlorine amount of 3.41 ± 0.30 parts per billion by volume (ppbv) is inferred from the measurements (above 24 km). This

value is in line with previous stratospheric observations carried out outside the tropics confirming the slightly decreasing chlorine amount in the stratosphere. Observations are compared and discussed with the output of a multi-year simulation performed with the Chemistry Climate Model EMAC (ECHAM5/MESSy Atmospheric Chemistry). The simulated stratospheric total chlorine amount is in accordance with the MIPAS-B/TELIS observation taking into account the fact that some chlorine source gases and very short-lived species are not included in the model.

1 Introduction

The discovery of the Antarctic stratospheric "ozone hole" in the 1970s (Farman et al., 1985) strongly intensified research to unravel the reason for this ozone depletion. Chemically active chlorine (ClO_x) species like Cl, Cl_2, ClO, ClOOCl, OClO, and HOCl are part of total inorganic chlorine Cl_y (ClO_x + HCl + $ClONO_2$). They play a dominant role in the catalytic destruction of stratospheric ozone during polar winter when low temperatures and heterogeneous chemical reactions on polar stratospheric cloud (PSC) particles have previously enabled active chlorine compounds (mainly Cl_2) to be produced from its reservoir species $ClONO_2$, HCl, and HOCl (e.g., Molina and Rowland, 1974; Solomon et al., 1986; Molina et al., 1987; Solomon, 1999; Crutzen and Oppenheimer, 2008). Due to the Montreal Protocol and successor agreements, emissions of dominant halocarbons were reduced such that total tropospheric (organic) chlorine is decreasing since 1994 after reaching a peak value of nearly 3.7 parts per billion by volume (ppbv) (O'Doherty et al., 2004; WMO, 2011). The stratospheric total chlorine peak occurred several years later, because it takes this time for emitted air masses to propagate into the stratosphere (Engel et al., 2002; WMO, 2011; Kohlhepp et al., 2012). The amount of equivalent effective stratospheric chlorine (chlorine and bromine halogens) is predicted to return to 1980 values around 2050 at mid-latitudes (Stolarski et al., 2010; WMO, 2011).

To assess and monitor the partitioning and budget of chlorine, a number of measurements of its individual compounds have been carried out to calculate the amount of inorganic (Cl_y), organic (CCl_y), and finally total chlorine (Cl_{total}). An early observation based on data from the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument was published by Zander et al. (1992). A mean stratospheric total chlorine volume mixing ratio (VMR) of 2.58 ± 0.10 ppbv was observed at 30 °N in 1985. Significantly enhanced values between 3.4 and 3.5 (± 0.4) ppbv in the 1992 Arctic lower stratosphere were estimated using retrieved data from the balloon-borne Michelson Interferometer for Passive Atmospheric Sounding (MIPAS-B) in combination with in-situ measurements (von Clarmann et al., 1995). A further slightly enhanced value of 3.53 ± 0.10 ppbv was detected during the ATMOS/ATLAS-3 November 1994 mission at northern mid-latitudes, also demonstrating the strong increase of stratospheric total chlorine before regulating measures could alter this linear trend of 0.10 ppbv per year in the time period from spring 1985 to fall 1994 (Zander et al., 1996). The same trend has been deduced between 1991 and 1995 by estimating total chlorine with the help of HCl observations from the Halogen Occultation Experiment (HALOE; Russell III et al., 1996). A further increased Cl_{total} value of 3.7 ± 0.2 ppbv was derived from MkIV balloon measurements carried out in the 1997 Arctic summer (Sen et al., 1999). This measurement took place close to the turn-over of the total stratospheric chlorine amount. Chlorine data obtained by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) in combination with in-situ measurements from the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE) campaign (Schauffler et al., 2003; Nassar et al., 2006) were used to estimate Cl_{total} between February 2004 and January 2005 in five latitude zones. A mean stratospheric Cl_{total} value of 3.65 ± 0.13 ppbv was determined for both the northern and southern mid-latitudes. This beginning temporal decrease of stratospheric chlorine was confirmed by observations from the Microwave Limb Sounder (MLS) from August 2004 until January 2006 (Froidevaux et al., 2006). A Cl_{total} value of 3.60 ± 0.13 ppbv at the end of this time period was inferred from HCl measurements and a decrease of about 43 pptv in the stratospheric chlorine loading within this 18 month period was detected.

The long term trend of stratospheric inorganic chlorine was investigated by using data of multiple space-borne sensors like ACE-FTS, ATMOS, MLS, CLAES (Cryogenic Limb Array Etalon Spectrometer), CRISTA (Cryogenic Infrared Spectrometer and Telescope for the Atmosphere) and HALOE (Lary et al., 2007). This time series confirms that stratospheric Cl_y peaked in the late 1990s and started to decrease as expected from the changing concentrations of tropospheric source gases and related transport times from the troposphere to the stratosphere. More recent published observations of Cl_{total} were performed by ACE-FTS covering the years 2004 until 2009. Nine chlorine containing species have been directly measured by the satellite instrument (Brown et al., 2011, 2013). These data were supplemented by a number of further trace gases which were calculated using the SLIMCAT 3-dimensional Chemical Transport Model (Chipperfield, 2006). Global mean stratospheric chlorine was found to decrease by 0.46 % per year in the time period under investigation.

The purpose of this paper is to assess the partitioning and budget of inorganic and organic stratospheric chlorine inside the late winter Arctic vortex. The winter 2010/2011 was characterized by a cold vortex defining a strong transport barrier until approximately mid-April (Manney et al., 2011; Sinnhuber et al., 2011). Temperatures were below the threshold associated for chlorine activation (~196 K) for more than 100 days between about 15 and 23 km. Consequently, an unprecedented Arctic ozone loss was observed which could be described for the first time as an Arctic ozone hole since ozone profiles in late March resembled typical Antarctic late-winter profiles (Manney et al., 2011; Sinnhuber et al., 2011). Trace gas profiles of individual chlorine compounds were retrieved from limb emission spectra recorded during a balloon flight of MIPAS-B and the Terahertz and submillimeter Limb Sounder (TELIS) on 31 March 2011 inside the polar vortex. A description of the instruments, data analysis and chemical modelling is given in Sect. 2. A discussion of the observed chlorine partitioning and budget follows in Sect. 3 together with a comparison of the combined measured data to simulations of the Chemistry Climate Model (CCM) EMAC (ECHAM5/MESSy Atmospheric Chemistry model).

2 Instruments, data analysis and modelling

The MIPAS-B/TELIS flight took place on 31 March 2011 over northern Scandinavia inside the Arctic vortex at the end of the chlorine deactivation period that started slowly in early March and accelerated towards the end of this month (Manney et al., 2011; Sinnhuber et al., 2011). The balloon gondola was launched from Esrange near Kiruna (Sweden, 67.9 °N, 21.1 °E) and reached its float level at about 35 km. Recorded limb sequences of MIPAS-B and TELIS are depicted in Fig. 1.

2.1 MIPAS-B instrument and data analysis

The balloon-borne limb-emission sounder MIPAS-B is a cryogenic Fourier Transform spectrometer which operates in the mid-infrared spectral range between about 4 and 14 µm. The maximum optical path difference of 14.5 cm of the beam in the interferometer allows a high unapodized spectral resolution of 0.0345 cm^{-1} (about 0.07 cm^{-1} after apodization with the Norton and Beer (1976) "strong" function) which allows the separation of individual spectral lines from continuum-like emissions in combination with a high radiometric accuracy of typically 1%. Values of the noise equivalent spectral radiance (NESR) are typically within $1x10^{-9}$ and $7x10^{-9}$ $W(cm^2\ sr\ cm^{-1})^{-1}$ for a single calibrated spectrum. Averaging over *n* spectra

($n \leq 5$) per single elevation scan reduces the spectral noise by a factor of $1/\sqrt{n}$. The instrument is characterized by a high performance and flexibility of the pointing system with a knowledge of the tangent altitude of better than 50 m at the 1-σ confidence limit. A comprehensive overview and description of the instrument together with processing of recorded interferograms to calibrated spectra including phase correction, Fourier Transformation to the spectral domain, and two-point calibration of the spectra from arbitrary to radiance units is given by Friedl-Vallon et al. (2004) and references therein. This includes instrument characterization in terms of the instrumental line shape, field of view, NESR, line of sight of the instrument, detector non-linearity (Kleinert, 2006) and the error budget of the calibrated spectra.

Forward radiance calculations were performed with the Karlsruhe Optimized and Precise Radiative transfer Algorithm (KOPRA; Stiller et al., 2002) which is a line-by-line and layer-by-layer model to simulate the infrared radiative transfer through the atmosphere. Molecular spectroscopic parameters for the calculation of limb emission spectra were taken from the high-resolution transmission molecular absorption database (HITRAN; Rothman et al., 2009) and a MIPAS dedicated spectroscopic data base (Raspollini et al., 2013). KOPRA also calculates derivatives of the radiance spectrum with respect to atmospheric state and instrument parameters and thus provides the Jacobians for the retrieval procedure KOPRAFIT (Höpfner et al., 2002). Since the vertical scan distance of adjacent tangent altitudes ranges between 1 and 1.5 km, the retrieval grid was set to 1 km up to the balloon float altitude. Above this level, the vertical spacing increases gradually to 10 km at the top altitude at 100 km. Considering the smoothing of the vertical part of the instrumental field of view, the retrieval grid is finer than the achievable vertical resolution of the measurement for a large part of the altitude region covered (especially above the observer altitude). To avoid retrieval instabilities due to this oversampling of the vertical retrieval grid, a Tikhonov-Phillips regularization approach (Phillips, 1962; Tikhonov, 1963) was applied that was constrained with respect to a first derivative a priori profile x_a of the target species:

$$\boldsymbol{x}_{i+1} = \boldsymbol{x}_i + [\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R}]^{-1} [\mathbf{K}_i^T \mathbf{S}_y^{-1} (\boldsymbol{y}_{meas} - \boldsymbol{y}(\boldsymbol{x}_i)) - \mathbf{R}(\boldsymbol{x}_i - \boldsymbol{x}_a)] \tag{1}$$

where $\boldsymbol{x}_{i+1}$ is the vector of the desired state parameters for iteration i+1; $\boldsymbol{y}_{meas}$ is the measured radiance vector and $\boldsymbol{y}(\boldsymbol{x}_i)$ the calculation of the radiative transfer model using state parameters of iteration number i; **K** is the Jacobian matrix containing partial derivatives $\partial \boldsymbol{y}(\boldsymbol{x}_i) / \partial \boldsymbol{x}_i$ while

$\mathbf{S}_y^{-1}$ is the inverse noise measurement covariance matrix and **R** a regularization matrix with the first derivative operator and a regularization strength parameter.

In a first step, a temperature retrieval was performed using appropriate CO_2 lines of two separate bands around 810 cm^{-1} and 950 cm^{-1} and a priori pressure-temperature information from European Centre for Medium-Range Weather Forecasts (ECMWF) analyses together with a CO_2 VMR profile updated with data from NOAA ESRL GMD (National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division; Montzka et al., 1999). The temperature retrieval 1-σ accuracy is estimated to be within about 0.7 K. Then, VMR profiles of the target species are individually retrieved in selected spectral regions (see Table 1). Profiles of species interfering with the target molecule were adjusted simultaneously during the retrieval procedure. An overview of the principal analysis of spectra with regard to chlorine- and nitrogen-containing molecules is given in von Clarmann et al. (1995) and Wetzel et al. (2002, 2010). The error estimation of the target parameter consists of random and systematic errors that were added in quadrature to yield the total error, which refers to the 1-σ confidence limit. Random errors include spectral noise as well as covariance effects of the simultaneously fitted parameters. Systematic errors mainly comprise spectroscopic data inaccuracies (band intensities), uncertainties in the line of sight, and gain calibration errors. The altitude resolution is calculated from the number of degrees of freedom of the retrieval, which corresponds to the trace of the averaging kernel matrix. Typical values for the retrieved parameters are given in Table 1.

Many trace gases measured by the MIPAS-B instrument were involved in a large number of validation activities and cross-comparisons on satellite sensors like MIPAS, ILAS/ILAS-II (Improved Limb Atmospheric Spectrometer) and SMILES (Superconducting Submillimeter-Wave Limb-Emission Sounder). For species used in this work we explicitly mention for evaluation: $ClONO_2$ (Höpfner et al., 2007; Wetzel et al., 2008, 2013), CFC-11 and CFC-12 (Wetzel et al., 2008, 2013), ClO (Sagawa et al., 2013), and N_2O (Wetzel et al., 2008; Payan et al., 2009).

2.2 TELIS instrument and data analysis

The cryogenic heterodyne balloon sounder TELIS was developed in a collaboration of three partners: the German Aerospace Centre (DLR), Rutherford Appleton Laboratory (RAL), United Kingdom, and the Netherlands Institute for Space Research (SRON). Each institute generated one channel: 1.8 THz (DLR), 500 GHz (RAL), and 480-650 GHz (SRON). A comprehensive description of the instrument is given by Birk et al. (2010) and de Lange et al. (2012). HCl and ClO results presented here were derived from spectra in the 480-650 GHz channel with a tunable superconducting integrated receiver (SIR) developed and characterized by de Lange et al. (2010) and de Lange et al. (2012). A local oscillator (LO) reference signal is mixed with the atmospheric signal in a non-linear mixer. The measured spectrum is the superposition of two spectra covering the frequency ranges $\nu_{LO} + \nu_{IF}$ and $\nu_{LO} - \nu_{IF}$, where ν_{IF} is the measured difference (intermediate) frequency (IF).

The analysis of the TELIS spectra is carried out in a similar way as for the MIPAS-B retrieval procedure. A forward line-by-line model is used to model the radiative transfer along the line-of-sight of the instrument. Spectroscopic parameters are also taken from the HITRAN database (Rothman et al., 2009). An instrument model to account for the specifics of the TELIS instrument is included in the forward algorithm. Further details on the forward model are described by de Lange et al. (2009) and references therein. The forward model is inverted with a Gauss-Newton iteration scheme in combination with a Tikhonov-Phillips regularization approach (Phillips, 1962; Tikhonov, 1963) as described in the previous section.

HCl retrievals are performed for both chlorine isotopes $H^{35}Cl$ and $H^{37}Cl$. The total amount of HCl can be determined by taking into account the isotope abundance of $H^{35}Cl$ (75.76 %) and $H^{37}Cl$ (24.23 %). While the precision error of HCl is very small (~ 0.01 ppbv) the systematic error estimate yields between 0.05 and 0.4 ppbv resulting in a total error of about 10 to 15 % in the region of the VMR maximum. Systematic error sources are instrumental uncertainties such as instrumental line shape and side band ratio inaccuracies, detector non-linearity, calibration and pointing errors. Furthermore, errors in the atmospheric pressure-temperature profile as well as spectroscopic data errors are taken into account. The largest uncertainty stems from the non-linear behaviour of the detector. This holds also for the ClO retrievals. The overall accuracy of ClO is almost entirely determined by systematic error sources. Similar to HCl, the total error for the species ClO typically remains within 10 and 15 % in the altitude region of its VMR maximum. An overview of the characteristics of the retrieved species is given in Table 2.

TELIS HCl and ClO observations have been evaluated using MLS measurements (de Lange et al., 2012). ClO was additionally compared to SMILES observations (Sagawa et al., 2013). This work also includes a cross-comparison to MIPAS-B ClO observations.

2.3 Model calculations

Measured data are compared to simulations performed with the Chemistry Climate Model EMAC which is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes (Jöckel et al., 2010). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al., 2006). For the present study we applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.50) in the T42L39MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approximately 2.8 by 2.8 degrees in latitude and longitude) with 39 vertical hybrid pressure levels from the ground up to 0.01 hPa. The applied model setup comprised, among others, the submodels MECCA (Sander et al., 2005) for the calculation of gas-phase chemistry and the submodel MSBM (Kirner et al., 2011) for the simulation of polar stratospheric clouds and the calculation of heterogeneous reaction rates. The PSC scheme was validated with the help of HNO_3, ClO, and O_3 data from the MLS instrument (Kirner et al., 2015).

A Newtonian relaxation technique of the prognostic variables temperature, vorticity, divergence and the surface pressure above the boundary layer and below 1 hPa towards the ECMWF reanalysis ERA-Interim (Dee et al., 2011) has been applied to simulate realistic synoptic conditions (van Aalst, 2005). Boundary conditions for greenhouse gases, chlorofluorocarbons (CFCs), and halons are adapted from observations (WMO, 2011; Meinshausen et al., 2011). Halogenated hydrocarbons are included according to the WMO-A1 scenario (WMO, 2011). Chlorine-containing tropospheric source gases considered in EMAC are CFC-11, CFC-12, HCFC-22, CFC-113, CCl_4, CH_3Cl, and CH_3CCl_3. Photolysis rates of HCFC-22 and CFC-113 are the same as for CFC-12. The simulation includes a comprehensive chemistry setup from the troposphere to the lower mesosphere with 104 gas phase species, 234 gas phase reactions, 67 photolysis reactions, and 11 heterogeneous reactions on liquid aerosols, nitric acid trihydrate (NAT) - and ice particles. Rate constants of gas-phase reactions are taken from Atkinson et al. (2007) and Sander et al. (2011). The model output data were saved every 10 minutes. The temporally closest output to the MIPAS-B measurements has been interpolated in space to the observed geolocations.

3 Chlorine partitioning and budget

The unique combination of two different sensors, MIPAS-B and TELIS, working in different spectral regions (mid-infrared and microwave), enables the simultaneous measurement of virtually all relevant inorganic and organic chlorine molecules. The amount of inorganic chlorine $[Cl_y]$ is defined as:

$$[Cl_y] = [ClO_x] + [HCl] + [ClONO_2] \quad (2)$$

where active chlorine $[ClO_x]$ is calculated via:

$$[ClO_x] = [ClO] + [HOCl] + 2\,[ClOOCl] \quad (3)$$

The amount of organic chlorine $[CCl_y]$ is composed of:

$$[CCl_y] = 2\,[CFC\text{-}12] + 3\,[CFC\text{-}11] + [HCFC\text{-}22] + 3\,[CFC\text{-}113] + 4\,[CCl_4] + [CH_3Cl] \quad (4)$$

Total chlorine $[Cl_{total}]$ is given as the sum of both budgets:

$$[Cl_{total}] = [Cl_y] + [CCl_y] \quad (5)$$

Constituents, which are of minor importance for the Arctic stratospheric chlorine budget (like Cl_2, Cl, OClO, CH_3CCl_3, CFC-114, CFC-115, HCFC-141b, HCFC-142b, Halon-1211; see, e.g., Prinn et al., 2000) are neglected here. All the quantities defined in Eqs. (2) to (5) can be deduced from TELIS (measuring ClO and HCl) and MIPAS-B (measuring all gases except HCl) observations. However, the chlorine monoxide dimer ClOOCl is only measurable by MIPAS-B under activated chlorine conditions ($[ClOOCl] > 0.5$ ppbv) without any PSC emissions in the recorded spectra (Wetzel et al., 2010). On 31 March 2011, no PSC signatures are visible in the MIPAS-B spectra but ClOOCl concentrations are below the detection limit. However, [ClOOCl] can be estimated from [ClO] with the following relation (Wetzel et al., 2012):

$$[ClOOCl] = ([ClO_{noon}] + 2\,[ClOOCl_{noon}] - [ClO]) / 2 \quad (6)$$

while the amounts of $[ClO_{noon}]$ and $[ClOOCl_{noon}]$ which correspond to noon maximum and minimum values, respectively, can be both taken from EMAC simulations if the modelled ClO is constrained to the measured one.

MIPAS-B spectra have been recorded from night until day. The sunrise took place between 02:38 UTC at 36 km and 03:10 UTC at 9 km altitude. Fig. 2 shows the measured ClO cross section from 02:00 UTC to 04:38 UTC, corresponding to 64.0 °N, 30.1 °E and 63.5 °N, 28.9 °E. A temporal variation of ClO is clearly visible. The concentration of this species is a measure of whether the sounded air masses are still chlorine-activated or not. After sunrise the mixing ratio of ClO increases in a layer between 16 and 22 km from nighttime values below 0.05 ppbv to daytime mixing ratios up to 0.4 ppbv. During periods of strong chlorine activation, significantly higher values around 2 ppbv are observed (see, e.g., Santee et al., 2003; Wetzel et al., 2012). The ClO increase is shown similarly by both instruments, MIPAS-B and TELIS. The latter instrument measured not only with higher vertical resolution but also with higher temporal resolution compared to MIPAS-B, hence the TELIS data were transferred to the coarser temporal grid of MIPAS-B for better comparability. At higher altitudes above 26 km, MIPAS-B ClO temporal retrieval fluctuations are visible due to the large spectral noise error in this altitude region. As a consequence, the TELIS ClO data was used for calculating the chlorine partitioning and budget in the whole altitude range.

The decreasing ClO_x at the end of the Arctic winter in the lower stratosphere due to rising temperatures followed by shrinking ClO_x production from heterogeneous chemical reactions is in line with high amounts of $ClONO_2$ in this altitude region. The reaction of ClO with NO_2 produces the reservoir species $ClONO_2$. The measured time evolution of this molecule is displayed in Fig. 3. Measured $ClONO_2$ data exhibit high values that are typical for observations in the late Arctic winter (see, e.g., Oelhaf et al., 1994; von Clarmann et al., 1997; Wetzel et al., 2002; von Clarmann et al., 2009). Only in an atmospheric layer around 19 km the vertical mixing ratio gradient is small since $ClONO_2$ values are slightly lower than they would be if chlorine was completely deactivated. This observed signature is in line with the enhanced ClO amounts around 19 km as seen in Fig. 2. A significant diurnal temporal variation is not visible in the $ClONO_2$ data.

The mean measured chlorine partitioning and budget for early morning is displayed in Fig. 4. A spectral noise error weighted averaging was applied to calculate the mean profiles, although statistical errors of the individual species profiles are similar. The molecules ClO and ClOOCl exhibit a temporal variation over the measured time period. However, since their mixing ratios are very low at this time in the year, vertical profiles of these species have also been averaged over the observed time period, with almost no consequence. To obtain a proxy of total inorganic chlorine, a N_2O-Cl_y correlation was derived from air samples collected with the balloon-borne cryogenic whole air sampler BONBON in the Arctic between 2009 and 2011 according to the method described in Engel et al. (2002) and Wetzel et al. (2010). Cl_y 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, CH_3CCl_3, CCl_4, 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. (2002), using global mean observation data from NOAA ESRL. The proxy inorganic chlorine $[Cl_y^*]$ is calculated with the following dependence on the amount of $[N_2O]$, both given in ppbv:

$$[Cl_y^*] = 3.2008346 + 8.7786479 \times 10^{-6} [N_2O] - 2.9132361 \times 10^{-5} [N_2O]^2. \qquad (7)$$

This correlation has been applied to MIPAS-B measured N_2O and yields up to 3.20 ppbv Cl_y^* in the stratosphere. The amount of inorganic chlorine is dominated by the chlorine reservoir species $ClONO_2$ and HCl, the latter one especially above 24 km. Above this altitude, where the Cl_y VMR is (vertically) approximately constant, the mean observed Cl_y amounts to 3.25 ± 0.30 ppbv which is in agreement with the deduced Cl_y^* within the error bars although there is a tendency towards a small positive deviation in the observations compared to the Cl_y^* reference. The deviation between Cl_y and Cl_y^* below 21 km is caused by different degrees of subsidence of the air masses in the case of the discussed balloon flight and the reference which results in different N_2O mixing ratios in a specific altitude. Cl_y species play by far the largest part in the total chlorine budget from the lower to the upper Arctic winter stratosphere. From about 17 km downwards, the amount of organic chlorine gets increasingly dominant in the total chlorine budget. Source gases that contribute to CCl_y in dependence of their chlorine atoms contained in the molecule are visible in Fig. 4: CFC-12 (CCl_2F_2), CFC-11 (CCl_3F), HCFC-22 ($CHClF_2$), CFC-113 ($C_2Cl_3F_3$), CCl_4, and CH_3Cl. The mean amount of Cl_{total} is calculated as 3.41 ± 0.30 ppbv above 24 km. This means that about 95 % of total chlorine is inorganic in this altitude region.

The mean chlorine partitioning and budget as simulated by EMAC is shown in Fig. 5. The principal vertical profile shape of the measured chlorine species is well reproduced by the model. However, some differences in detail between simulated and observed data are visible. The modelled HCl VMR maximum appears slightly broader than the measured one. Below about 20 km, the simulation shows significantly lower values compared to the observation by TELIS. A striking difference is visible in the case of $ClONO_2$. The model clearly underestimates this reservoir species and deviates by 0.8 ppbv (42 %) from the MIPAS-B data in the region of the VMR maximum at 22 km although simulated and measured NO_y and NO_2 (a necessary reactant in the production of $ClONO_2$ via NO_2 plus ClO) agree in this altitude region. Since simulated HCl and ClO_x (near 22 km) are in agreement with the observed data, the simulated Cl_y deviation from the measurement can be attributed to the $ClONO_2$ deficit in EMAC. Around 19 km, the difference in simulated and measured Cl_y is largest due to very low HCl values in EMAC compared to the HCl seen by TELIS. The amount of available Cl_y below about 24 km is dependent on the degree of downwelling of the air masses inside the polar vortex. In EMAC, the subsidence of the air masses in the course of the winter was underestimated such that we find higher values of tracers like N_2O and CFCs at a given altitude of the lower stratosphere compared to the measurements. These higher N_2O values are connected with lower Cl_y values according to the compact N_2O-Cl_y relationship, resulting in an underestimation of the chlorine reservoir species (especially $ClONO_2$). So, at least part of the $ClONO_2$ deficit in EMAC can be explained by the underestimation of the subsidence in the model.

The simulated Cl_y reaches its maximum VMR in the quasi altitude-constant region above 24 km with a mean value of 3.16 ppbv which is slightly lower than the measured one and close to the simulated value of Cl_y^* (deduced from EMAC) which gives 3.19 ppbv. Below this altitude region, a similar bias between Cl_y and Cl_y^* as in the case of the observations is visible.

The mean amount of Cl_{total} in the model run is calculated as 3.21 ppbv above 24 km, which is 0.20 ppbv lower than the observed one. About half of this simulated chlorine deficit can be explained by the fact that some minor CFCs (e.g. CFC-114 and CFC-115) and HCFCs (e.g. HCFC-141b and HCFC-142b) as well as halons are not included in the EMAC model. Their contribution to Cl_{total} is not more than 1% above 24 km (Brown et al., 2013). The remaining deficit can be explained by very short-lived chlorine species which altogether amount to about 0.1 ppbv (Mébarki et al., 2010; WMO, 2011) and which are also not contained in the model simulation. However, the chlorine amount of these missing species is implicitly contained in the HCl measurement (since the short-lived chlorine species are converted to HCl after being photolyzed) and hence included in the observed chlorine budget. In the altitude region above 24 km, about 98 % of total chlorine in EMAC is inorganic. The shaded region of the budget profiles of ClO_x, Cl_y, CCl_y, and Cl_{total} shown in Fig. 5 takes into account all available chlorine species in EMAC that were not measured by MIPAS-B and TELIS. These molecules comprise Cl, Cl_2, OClO (belonging to ClO_x and Cl_y) and CH_3CCl_3 (belonging to CCl_y) and add up to 0.1 ppbv at 16 km to the total chlorine budget (mainly due to Cl_2 and OClO). However, at altitudes between 22 km and 36 km contributions of these gases to the chlorine budget are insignificant.

4 Conclusions

Observations from MIPAS-B/TELIS were performed at the end of the cold 2010/2011 stratospheric winter that was characterized by a persistent polar vortex enabling strong chlorine activation and ozone loss. The chlorine partitioning measured on 31 March 2011 reveals that in the outer part of the polar vortex (above Finland) the recovery of active chlorine (ClO_x) into the reservoir species (mainly $ClONO_2$) is almost completed by the end of March only a few days before the cold period had finished (Manney et al., 2011). This is verified by low amounts of daytime ClO of up to 0.4 ppbv around 19 km. The observed total stratospheric chlorine amounts to 3.41 ± 0.30 ppbv above 24 km (see Table 3). This is in accordance with the EMAC simulation (3.21 ppbv) taking into account the fact that some chlorine source gases and very short-lived species are not included in the model. The horizontal Cl_{total} distribution in EMAC (above 24 km) exhibits 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 Cl_{total} measurement accuracy of 0.3 ppbv such that the observations can be treated as representative at least for the geographical region of the Arctic vortex. Mean Cl_{total} values deduced from spectra recorded by the ACE-FTS instrument (Brown et al. 2013) give 3.44 ± 0.18 ppbv (morning occultations) and 3.50 ± 0.13 ppbv (evening occultations) for northern mid-latitudes and the Arctic in 2009. Extrapolating these data to 2011 with the chlorine trend (between 2004 and 2009) obtained from these ACE-FTS observations (about −0.4 % per year) yields Cl_{total} values of 3.41 ppbv (morning occultations) and 3.47 ppbv (evening occultations) comparable to the MIPAS-B/TELIS data. The accumulated amount of minor species (not measured by MIPAS-B/TELIS) like CFC-114, CFC-115, HCFC-141b, HCFC-142b, and Halon-1211 was estimated to about 0.7 % (~ 0.02 ppbv) of total chlorine at 30 km (Brown et al. 2013). Hence, the MIPAS-B/TELIS Cl_{total} value is in line with the data obtained from ACE-FTS solar occultations and is consistent with the decreasing amount of stratospheric chlorine. Considering the 2005 mean global tropospheric Cl_{total} from in-situ data of AGAGE (Advanced Global Atmospheric Gases Experiment) and NOAA ESRL databases, as compiled in WMO (2011), and transferring this value to 30 km taking into account a typical time lag of 6 years of stratospheric mean age of air (Engel et al., 2002, 2009; Stiller et al., 2008; WMO, 2011), we get an estimated Cl_{total} value of 3.40 ppbv for the year 2011, which is very close to the MIPAS-B/TELIS result.

We finally conclude that the stratospheric total chlorine as deduced from Arctic MIPAS-B/TELIS observations on 31 March 2011 confirms previously published total chlorine assessments and their related trends. A recently published study by Mahieu et al. (2014) shows a HCl concentration increase between 2005/2006 and 2010/2011 in large parts of the northern hemispheric lower stratosphere in combination with an increase in the mean age of stratospheric air of up to 0.4 years. However, in the Arctic above 24 km, ascertained changes of mean age of stratospheric air are small and do therefore not alter the findings above.

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Table 1. Set-up for MIPAS-B trace species retrievals and typical errors. Results are given for different state parameters in corresponding spectral windows together with the retrieval altitude resolution (Alt. reso.).

Species	Spectral range (cm^{-1})	Noise error[a] (%)	Total error[a] (%)	Alt. reso. (km)
$ClONO_2$	779.7 – 780.7	2 – 3	5 – 6	4 – 5
ClO	821.0 – 841.5	10 – 25[b]	20 – 30[b]	5 – 8
CFC-11	840.0 – 860.0	2 – 3	5 – 6	3 – 4
CFC-12	918.0 – 924.0	2 – 3	5 – 6	3 – 4
HCFC-22	828.0 – 830.0	3 – 10	8 – 15	3 – 6
CFC-113	813.0 – 830.0	3 – 10	20 – 25	3 – 6
CCl_4	792.0 – 806.0	1 – 5	10 – 20	4 – 6
CH_3Cl	742.5 – 755.0	1 – 5	8 – 15	9 – 13
HOCl	1215.0 – 1265.0	10 – 15	35 – 50	6 – 8
N_2O	1227.8 – 1303.1	2 – 3	5 – 6	2 – 4

[a] in the altitude region around the VMR maximum;

[b] daytime errors.

Table 2. Set-up for TELIS HCl and ClO retrievals with typical errors and retrieval altitude resolution (Alt. reso.).

Species	Spectral line (GHz)	Noise error* (%)	Total error* (%)	Alt. reso. (km)
$H^{35}Cl$	625.9	< 1	10 – 15	2 – 5
$H^{37}Cl$	624.8	< 1	10 – 15	2 – 5
ClO	501.3	< 1	10 – 15	2 – 4

* in the altitude region around the VMR maximum.

Table 3. Mean stratospheric chlorine budgets (ppbv) as measured by MIPAS-B/TELIS and simulated by EMAC in comparison to ACE-FTS observations (Brown et al., 2013) and in-situ data from AGAGE and NOAA ESRL databases (WMO, 2011).

Budget	MIPAS-B/TELIS	EMAC	ACE-FTS	In-situ
Cl_{total}	3.41 ± 0.30[a]	3.21[a]	3.41 / 3.47[b]	3.40[c]
Cl_y	3.25 ± 0.30[a]	3.16[a]	-	-
Cl_y^*	3.19 ± 0.002[a]	3.19[a]	-	-

[a] mean value between 25 and 36 km;

[b] mean value (for morning/evening occultations) between 30 and 70 °N for 2011, extrapolated from 2009 with trend between 2004 and 2009;

[c] mean global tropospheric value from 2005 corresponding to a stratospheric value of 2011 assuming a stratospheric mean age of 6 years.

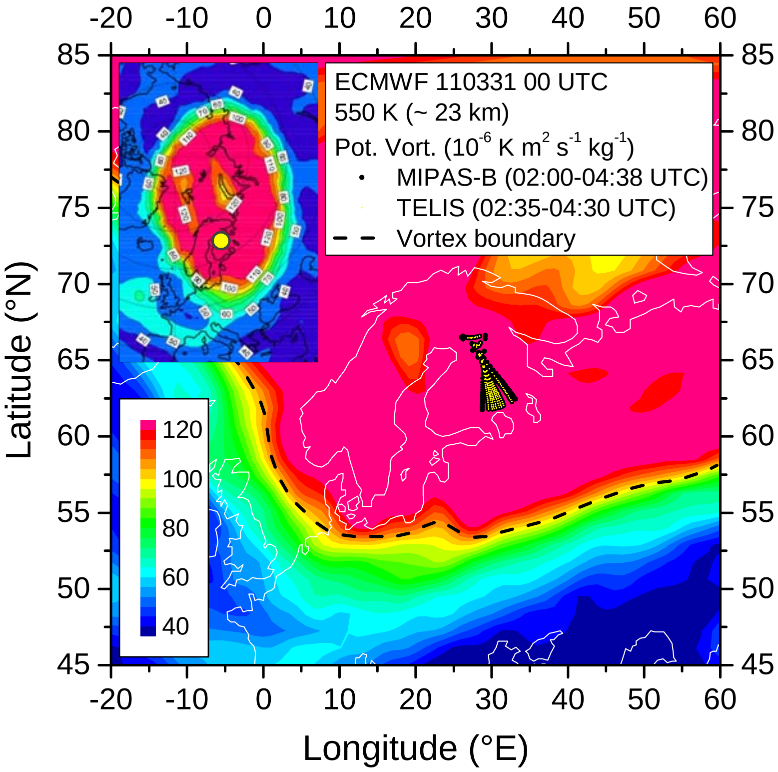

Figure 1. Potential vorticity (PV) field (in 10^{-6} K m^2 s^{-1} kg^{-1}) from European Centre for Medium-Range Weather Forecasts (ECMWF) analysis on 31 March 2011, 00 UTC. MIPAS-B tangent points are plotted as black solid circles and TELIS tangent points as yellow solid circles (altitude range: 9.1 to 35.4 km). Both instruments look in the same direction. The vortex boundary which represents the strongest PV gradient (Nash et al., 1996) is shown as black dashed line. The insert (top left) shows the approximate measurement region (yellow marker) in relation to the position of the whole polar vortex.

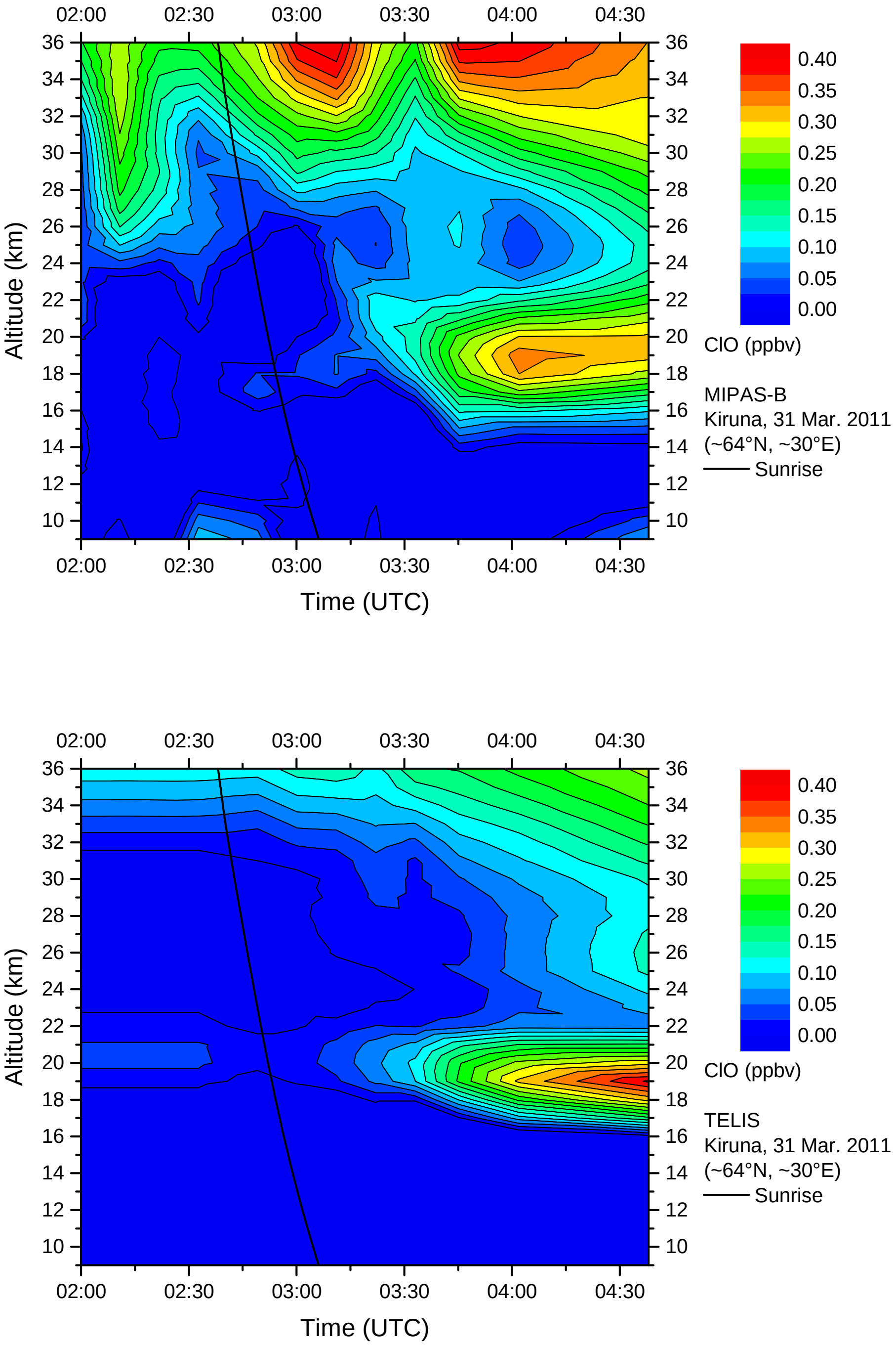

Figure 2. Temporal evolution of chlorine monoxide (ClO) mixing ratios (ppbv) as observed by MIPAS-B (top) and TELIS (bottom) on 31 March 2011 above northern Scandinavia between 02:00 UTC and 04:38 UTC inside the Arctic vortex within the latitude/longitude sector shown in Fig. 1. The black solid line marks the sunrise terminator. A residual activation of chlorine is visible between 16 and 22 km with slightly enhanced ClO values up to 0.4 ppbv.

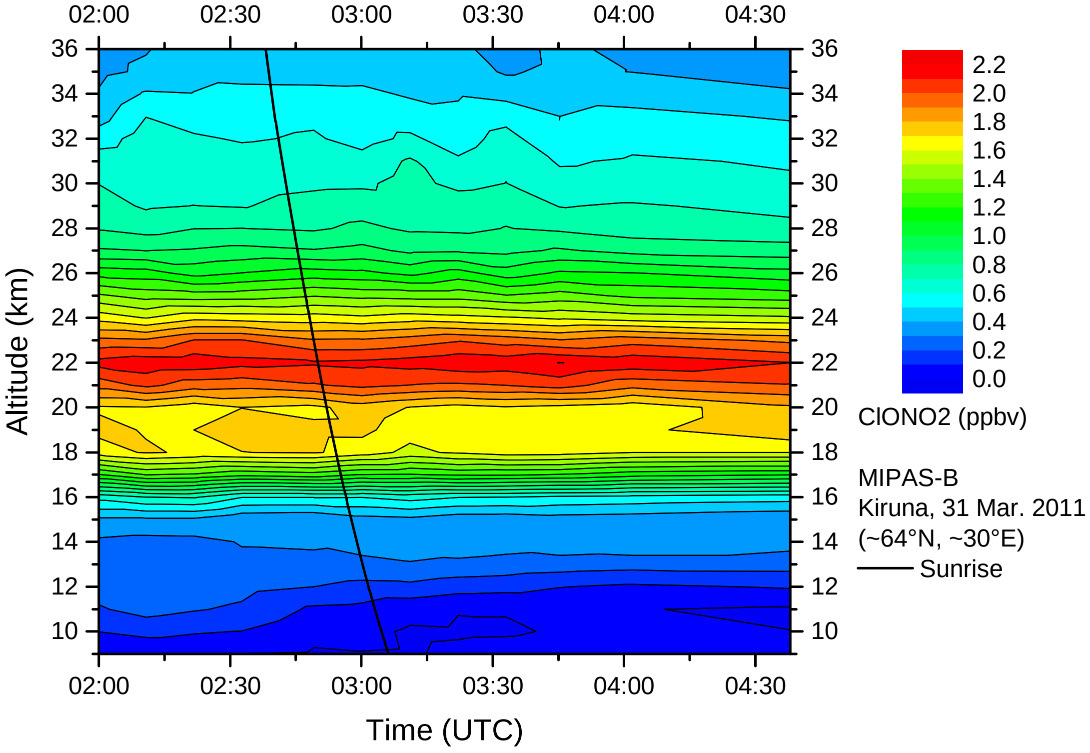

Figure 3. $ClONO_2$ mixing ratios (ppbv) as seen by MIPAS-B above northern Scandinavia on 31 March 2011 inside the late winter Arctic vortex. The black solid line marks the sunrise terminator.

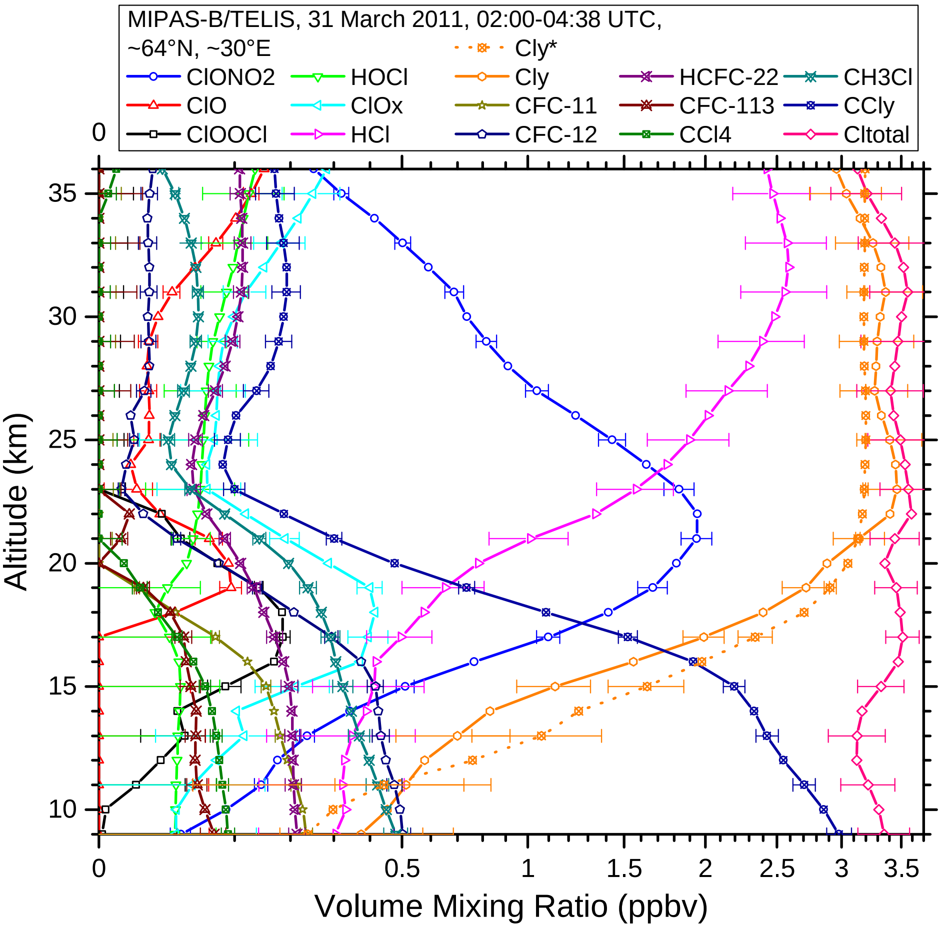

Figure 4. Partitioning and budget of inorganic, organic, and total chlorine as measured by TELIS (HCl and ClO) and MIPAS-B (all other species) in the Arctic stratosphere on 31 March 2011 (see legend for line style and note non-linear abscissa). The reservoir species HCl and $ClONO_2$ dominate the stratospheric inorganic chlorine budget. Cl_y^* deduced from observed N_2O data with the help of a N_2O-Cl_y correlation is shown for comparison. Note that for the calculation of the chlorine budgets the atomic content for each species has to be considered (some error bars have been omitted for better clarity).

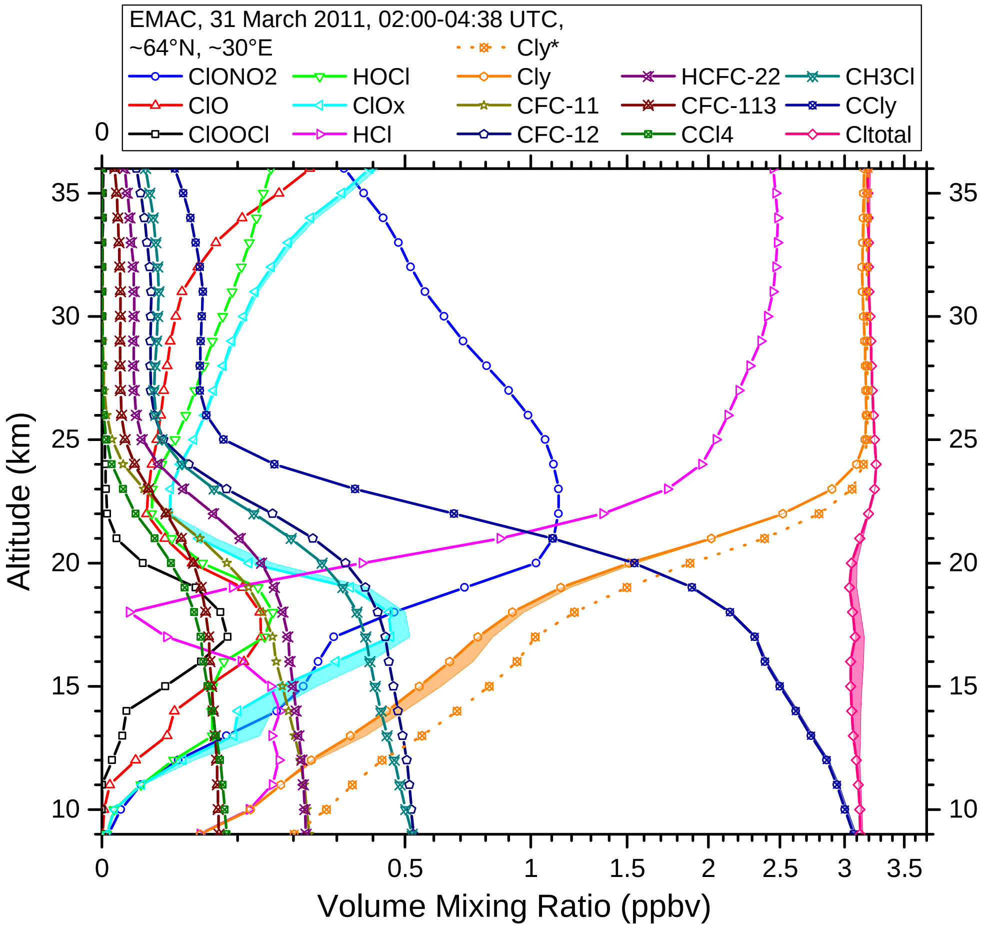

Figure 5. Partitioning and budget of inorganic, organic, and total chlorine as simulated with the chemistry climate model EMAC on 31 March 2011 (see legend for line style). Cl_y^* has been calculated from the simulated N_2O data according to Eq. (7). The budgets ClO_x, Cl_y, CCl_y, and Cl_{total} are calculated as listed in Eqs. (2) to (5). The shaded region of the budgets takes into account all minor chlorine species contained in EMAC (Cl_2, Cl, OClO, CH_3CCl_3) that were not measured by MIPAS-B and TELIS.