Authors' response

The authors thank the reviewers for their helpful comments. In the following reply we have inserted the original comment in *italic face*. The replies are printed in normal face.

Anonymous Referee #1

Comment: *General Comments: This manuscript describes the retrieval of MIPAS HCFC-22 profiles from 2005-2012, validates them, and presents some figures showing its morphology. It concludes with a discussion of stratospheric trends from this short data set. It is long and poorly written, especially the retrieval section.*

Reply: The entire paper has been reworked with respect to language. Our reply to the criticism of the retrieval section is found under the respective specific comment.

Comment: *The validation section underused (maybe misused) the ACE data, which are a valuable tool for the validation.*

Reply: Misuse of data, we understand, is if we draw conclusions from the data which are not supported by the data. We could not identify any misuse in that sense. We comment on "underuse" in the context of the specific comments.

Comment: *Two balloon profile data sets are also used but are not appropriate for validating the MIPAS data.*

Reply: We disagree and comment on this in the context of the specific comments.

Comment: *There is little analysis of the MIPAS data. Figures are presented and described but not analyzed in any quantitative way. There is no HCFC-22 climatology in the Climatology section.*

Reply: There is quantitative analysis with respect to data quality assessment, growth rates, and time series. In the revised version we avoid the word climatology, because it causes misunderstandings and causes wrong expectations. Further, the dichotomy between qualitative and quantitative does not exist. Morphologies as discussed in Section 5.1, while not fully quantitative, are far more than only qualitative (R. Carnap, Introduction to the Philosophy of Science, Dover Publications, 1995).

Comment: *No meteorological data are used to support descriptions of HCFC-22 behavior or statements about processes affecting the distributions.*

Reply: We consider the use of meteorological data as questionable in the context of 2D distributions.

Comment: *Many statements about HCFC-22 stratospheric structures are known from previous studies (e.g., using ACE satellite data).*

Reply: While there exist trend studies for HCFC-22 (Rinsland et al, 2005; Brown et al., 2011) and budget studies for chlorine and fluorine from ACE-FTS (Nassar 2006a,b; Brown et al., 2013, 2014), no studies of global HCFC-22 distributions from ACE have been published, except those referenced in our paper. These publications do not contain the features discussed in our paper.

Comment: *The topic and the MIPAS data set used do have a place in the literature, so there is good 'raw material' here for a publication. However, this manuscript requires major revision. Some sections can be eliminated, others combined, and almost all need reorganization or rewriting. The comments below are organized by section; they note what I think the major problems are and how each section might be improved. Because of the significant revisions needed, it is premature to make many minor or technical suggestions.*

Reply: We comment on this in the context of the specific comments.

Comment: *The standard of English used is fair. I appreciate how challenging it is to write a scientific article in a second language! I strongly recommend having a native English speaker proofread the manuscript to improve readability. As an example 'The profiles obtained are' sounds better than 'Obtained profiles are'. A satellite measurement is a sounding but measurements aren't 'sounded. Also, the writing style uses many unnecessary words. E.g., 'has a more or less seasonal cycle. more or less adds nothing, try simply 'has a seasonal cycle'. 'So-called level 1B product': why 'so-called'?*

Reply: We have tried to improve the language of the manuscript and the paper has been proofread by native English speakers. However, language editing is now routinely done by professional language editors of ACP as part of the final publishing process. Thus, such issues should not affect the acceptance of the paper. In the manuscript we have never written that measurements are sounded. We have not written 'a more or less seasonal cycle' but 'for all altitude/latitude bins, a more or less pronounced seasonal cycle is...', which says that the seasonal cycle is more pronounced for some and less pronounced for som other bins. 'So-called' because 'level 1B product' is not a generic term but internal technical language of a specific community.

Comment: *Introduction*
p. 14786, Line 10. The most current determination of the atmospheric lifetime of HCFC-22 can be found in the 2013 SPARC report (a WMO publication). The SPARC lifetime is the same as reported here but it's a more current assessment of the lifetime.

Reply: The reference has been replaced.

Comment: *Section 2, MIPAS data*
No mention is made of the MIPAS sampling pattern. What is its latitude range? Is the range covered daily? Does is sample more at some latitudes than others? Does it measure all latitudes in all seasons?

Reply: The vertical sampling pattern is described in the original submission at the end of Section 2. The missing information on the horizontal sampling has been included in the revised version of the manuscript.

Comment: *Section 3, Retrievals*
This section is not well organized and it reads like a series of unconnected details regarding the retrievals.

Reply: We do not understand the comment. In the first sentence, we state in general terms what type of analysis method is used. Such an analysis method connects the retrieval space with the measurement space, using some constraint and prior information. This formalism is not repeated here because this would be redundant with many other publications, e.g. von Clarmann (2003) which is referenced at the end of the preceding section. In the following sentences we specify the retrieval space, the measurement space, and the constraint including the prior information. The second sentence specifies the measurement space in a sense that all tangent altitude are analyzed in one single step. The third sentence specifies the retrieval space (what are the variables; how are they discretized). In the fourth and sixth sentence we justify the use of the constraint and specify the constraint. The remaining part of this section discusses in more detail the spectral windows used and the problem of interference by other gases implied by the spectral analysis windows. It is not clear to us why this (admittedly but intentionally very short and compact) specification of the general method described elsewhere at length should be "a series of unconnected details".

Comment: *For example, the last paragraph of the section is on information displacement: how is this relevant to understanding the data?*

Reply: Information displacement is relevant in the same sense as the usual

averaging kernels except that the information displacement and information smearing is connected to effects in the horizontal, not in the vertical. Thus we think that this is essential part of the data characterization, as are the vertical averaging kernels.

Comment: *Stiller et al, ACP 2008, on SF6, provides a good example of a retrieval description. I suggest you consider this and other MIPAS publications to see how they explain their retrievals (e.g.,) – then rewrite accordingly.*

Reply: The related Section in Stiller et al. 2008 contains a discussion of specific retrieval problems of SF_6 which had not been discussed before. These problems needed a thorough discussion, thus their retrieval section is four times longer than that criticized here. In the case of HCFC-22 no such specific problems have been encountered, and the retrieval strategy closely follows our standard approach which has been described in about 50 (!) preceding papers. Thus we consider it justified to mention only the specific choices of processing parameters relevant to the retrieval of HCFC-22. It seems to us to be adequate to best possibly avoid redundancies, to keep related sections short, and to focus on the essental information.

Comment: *p. 14789, Line 20. What is a 'zero-level profile'?*

Reply: We use a profile which is constantly zero for all altitudes. Due to the particular regularization scheme chosen the choice of the particular vmr does not affect the vmr, we could as well have chosen 42 without any change in the results. The only thing that matters is that the a priori profile is chosen altitude constant. This along with the regularization matrix has the effect that the retrieved profile is a smoothed version of the true profile. The related statement in the paper has been reworded for clarity.

Comment: *How sensitive are the results to the a priori?*

Reply: This information is provided by the averaging kernels, which are included in the paper. The integrals over the averaging kernels are, at good accuracy, unity, thus our choice of the constraint does not imply any bias. This information has been added to the paper.

Comment: *p. 14790, lines 3-15. The writing does not flow well.*

Reply: This paragraph has been rewritten.

Comment: *Where do the temperature analyses come from? (state it and reference it)*

Reply: It had been stated already in the original manuscript (p14790 l7) that MIPAS temperatures had been used. A reference to von Clarmann et al. (2003, 2009) has been added in the revised version.

Comment: *line 23. 'Its dominating components' maybe 'primary components'. 5 things cant all dominate.*

Reply: We do not understand why one group of errors cannot dominate over another group. And if we apply this level of linguistic rigorosity, then 5 things can't all be primary either. Nevertheless, we have changed to 'most important'.

Comment: *p. 14791, line 2. What is regularization? It hasn't been defined.*

Reply: Although 'regularization' is a standard expression in inverse theory, this term has been defined in the revised version. Regularization makes a singular or close-to-singular matrix regular by application of a constraint.

Comment: *Section 4, Validation*
p. 14792, line 11. What do you mean by 'unsolved problems cause by different altitude resolutions'? All the validation comparisons you make involve measurements with altitude resolutions different than MIPAS, so this statement is puzzling.

Reply: Aircraft measurements provide measurements at one altitude level but usually no vertical profiles. To apply the averaging kernel profiles of the better resolved measurements, profiles are needed. All the other instruments provide profile measurements, thus the related problem could be solved (Either by application of averaging profiles or by concluding that the actual profile is smooth enough that this step is not needed). This explanation has now been included in the revised version of the paper.

Comment: *Lines 20-22. How does MIPAS sampling (latitude and season) compare to ACE?*

Reply: Information on the MIPAS sampling has been added in the MIPAS section. Some further information on the ACE-FTS sampling has been included here. However, since we compare only collocated measurements, not mean profiles, sampling errors are not an issue in the comparison.

Comment: *Section 4.1, ACE comparison (figures 4-7).*
By examining a limited latitude region and sorting by season, Figure 5 provides the most useful comparison of this section. The two data sets agree within their uncertainties below 20 km all the time while seasonal differences are revealed above 20 km. Why, then, do you combine all latitudes and seasons in the other

figures? So much information is lost.

Reply: We do not agree that the profiles really agree. The error bars of the profiles represent the typical uncertainties of a single measurement, estimated as the mean error over the sample. This information has now been included in the figure caption. They are important information in their own right but to judge if a bias is significant, the standard error of the mean difference is needed, which is approximated by the standard deviation divided by the number of profiles. These are shown as error bars in the middle panel of Figure 4 and are hardly visible. This is, because due to the large number of profiles available, the standard errors are very small. Thus nearly all of the biases are significant. This does not mean that the measurements are bad but just that even very small biases can become statistically significant if the comparison ensemble is large enough. In the revised version, the missing information has been added in the figure caption in order to avoid such misunderstanding.

We usually do all analyses separately for different latitudes and seasons, but often the characteristics of the differences turn out to be homogeneous. In this case we present global figures to save space. We are reluctant to overload the paper with redundant figures but if the editor requires it, we could provide additional figures as a supplement.

Comment: *In fact, Figure 6 gives the opposite impression as Figure 5: it shows continuous, nearly 1:1 agreement below 25 km or so. (Thus I cannot understand the statement that the points fall into 2 clusters, p. 14794, line 2).*

Reply: We think that it is exactly correct what we write: The red points are on average above the line and the blue and green points are on average below. Thus, we do not quite understand the concern of the reviewer.

Comment: *In general I find that the words written in this section do not align with what is shown in the figures. For example on p. 14793, line 11, The bias is significant at all altitude levels. It clearly isnt!*

Reply: The bias is larger than the standard error of the mean difference, thus we conclude that the bias is significant. Unfortunately we have missed in the original submission to mention that the standard errors of the mean differences are the tiny, hardly visible, error bars of the middle panel of Fig. 4. Figure captions have been improved to avoid this kind of misunderstanding.

Comment: *In Figure 7, there is a bimodal shape in the lower right histogram, but as global data are combined in this figure,...*

Reply: We routinely do this sort of analysis (and most of the others) for each

latitude band and season separately. However, in cases where these additional figures do provide only redundant information, we prefer to publish only the global plots, in order to save space.

Comment: *... who knows why this shape occurs? (But a different comparison would probably reveal the answer.)*

Reply: We know why. In this particularly case the bimodal distribution simply represents polar (lower mode) and midlatitudinal (higher mode) measurements. The number of tropical collocations is small and has thus minor impact on the histogram. The ACE-FTS modes are clearer distinguished because the South-North component of the line of sight of MIPAS, which observes roughly in the orbit plane, is more pronounced than that of ACE-FTS, whose line of sight is directed towards the sun. Since the mixing ratio gradients in North-South direction are typically larger than those in East-West direction, the MIPAS modes are smeared more than those of ACE-FTS. This information has been added to the text.

Comment: *Overall, the ACE comparison is inadequate. It could be a more valuable and useful part of this paper with comparisons that examine specific seasons and latitude ranges.*

Reply: We think we have refuted the criticism of our MIPAS-ACE comparison above.

Comment: *Section 4.2, Cryosamplers*
p. 14795, lines 3-6. These sentences are poorly worded. They serve as the introduction to the topic of the next paragraph and should be combined with it.

Reply: These sentences have been reworded and this and the following paragraph have been combined.

Comment: *The coincidence criteria is so broad (1000 km and 24 h) that when the profiles do not agree you really can't know why. If you use some meteorological analyses to show the profiles are from similar environment, then you would know whether it made sense to compare them.*

Reply: We disagree. We have plotted all MIPAS profiles matching the coincidence criteria around the balloon geolocation, and from their spread we can estimate which part of the difference can be attributed to natural variability. Furthermore, we have made a similar comparison for CFC-11 and CFC-12, involving the same set of measurements (Eckert et al., 2015, AMTD), and there we see that the profiles agree mostly very well. Thus we cannot attribute the differences to the broad coincidence criterion. We have added this argument to

the paper.

Comment: *As it is, Figure 8 shows mostly a lot of disagreement with the balloon profiles but the reason is probably geophysical variation thus there is no point to these comparisons!*

Reply: This is a good point but as said before, we have made a similar comparisons for CFC-11 and CFC-12 (Eckert et al., AMT 2015) and methane (Laeng et al., AMT 2015). These comparisons are close to perfect. This refutes that the differences found can be attributed to geophysical variation. If they were, then the other gases should show similar (or even larger, due to larger vertical and/or horizontal gradients) discrepancies. This issue is now discussed in the revised version of the manuscript.

Comment: *And why calculate a 2005-2011 mean profile at all? This gas is increasing rapidly – at least 25% over this time period. The multi-year mean is meaningless, and should a balloon profile match it, that is meaningless too. Unless you can demonstrate that in spite of the broad coincidence criteria that it makes geophysical sense to compare with MIPAS, these comparisons could be eliminated.*

Reply: We agree that comparison to multi-annual means is not useful in this case and have eliminated them.

Comment: *Section 4.3, MkIV comparisons*
p. 14796, lines 15-28. Too much detail on the MkIV instrument use the Toon reference and eliminate most of this.

Reply: We consider some of the information as important. E.g. the fact that the same spectral band is used which is used for MIPAS may be important to interpret the comparison. However, we agree that there were too many details and we have shortened the paragraph.

Comment: *p. 14797. Since there are no MIPAS data for the dates of the balloon flights, these flights are not useful for validation! Again, comparing to a multi-year mean is not satisfying or meaningful in a quantitative way. This section can be eliminated.*

Reply: We have removed all lines and panels which are related to multi- annual mean data and restrict the discussion to the comparison of collocated measurements and measurements of the same month, latitude and year. For MkIV, there is still a meaningful pair of measurements available (23 Sep 2007). Further, the MkIV balloon observations were made in September after a summer of Easterly stratospheric winds. Since the flow is zonal during the summer (no

wave activity) little zonal variation in composition is to be expected, which justifies comparison with a zonal monthly mean of the same year. We have used this approach for the 22 Sep 2007 data.

Comment: *Section 4.4 Summary of intercomparisons*
The summary states that, compared to the different data sets, the MIPAS bias is either low, high, or zero. This is not a result. It is exactly what was known before any comparisons were made.

Reply: We disagree. Now we know that there is no clear indication of a bias and that MIPAS does NOT stand out as particularly high or low. We did not know this before. We have reworded this statement for clarification in the paper.

Comment: *The balloon profiles really aren't adequate for this validation – that's fine, so don't use them.*

Reply: We disagree. The geolocation problem with the cryosampler data has been refuted by comparison of CFC-11, CFC-12 and CH4 data which rule out geophysical variability as explanation of the differences. Further, cryosampler data are the only stratospheric data set which does not rely on spectroscopic data and thus are the most independent reference data. For MKIV there is at least one coincidence available, and the comparison between MKIV and the MIPAS September mean of the same year has been justified above. Inclusion of multiple validation instruments has scientific value.

Comment: *The validation section would be greatly improved by expanding the ACE data comparisons as noted above. After a more thorough validation using the ACE data, I think you will be able to state much more definitively where the data sets agree and where there is bias (and how much).*

Reply: We agree that the ACE-FTS data are an excellent data source for comparison. Since, however, the current version of ACE-data used here have not yet been validated themselves, we consider it adequate to use also other data for MIPAS validation.

Comment: *Section 5. Climatology*
The data are presented in various ways (e.g., latitude v. time, altitude v. latitude, etc) but there is actually no climatology here.

Reply: We agree that 'climatology' was a misnomer for what we have presented. We have changed the title of the paper and the section header accordingly. We think that the chosen representations best support our conclusions. A adequacy of a classical climatology seems inadequate to us for a gas with a pronounced trend.

Comment: *In general, the analyses in the subsections are only descriptive (i.e., descriptions of what is already known) or speculative, and do not present any quantitative analyses.*

Reply: The content of Section 5 is both descriptive and explanatory. We think that also the descriptive part has scientific value, because it characterizes important aspects of the state of the atmosphere during the measurement period. We are reluctant to understand the term 'descriptive' in any pejorative sense here. A second issue in our discussion is the test of plausibility of the observed features as a part of data quality control. It is a necessary condition for considering the MIPAS data useful that they show the known features. In this sense we consider the cross-validation between MIPAS and available prior knowledge as useful and necessary. Thus, we do not see what is bad about the fact that MIPAS shows the known features. Closer analysis, however, reveals features which are prima facie unexpected. For these features we offer explanations, both to show that these features are not artefacts and because they hint at interesting processes. These explanations are morphological (Section 5.1) and quantitative (Section 5.2). Below, where the criticism is specified, we defend our explanations against the criticism of being speculative.

The fact that the mixing of monsoon air into the tropics is instantaneous and not restricted to the time when the monsoon breaks down is to our best knowledge a new finding.

The fact that the temporal development of HCFC-22 in the stratosphere cannot be explained by the trends measured at the surface and the known age of air induced time lag is also a new finding.

The fact that Asian HCFC-22 emission have become the major source of global upper tropospheric HCFC-22 has been plausible but our data are to our best knowledge the first empirical evidence in support of this hypothesis.

Comment: *No meteorological data are used in support of speculative statements about processes that might be indicated in the data. This section would be improved by including a climatology (i.e., mean distributions as a function of month/season, mean cycles, etc.) and by adding meteorological analyses to give support to the processes you describe.*

Reply: Climatologies are usually understood to be multi-annual monthly mean distributions along with their variabilities. For a gas with a pronounced trend we think that the presentation of climatologies in that sense is of limited use because this would imply averaging over an inhomogeneous data set. The representation in the paper has been chosen because it represents best the features

we discuss.

Comment: *Figures 10 and 11 are introduced (p. 14798, line 3) but the next figure mentioned is Figure 15 (line 19). Figures must be mentioned in sequence.*

Reply: Instead of referring to Figure 15, we have now inserted an additional figure. This serves two purposes: First, we can leave (old) Fig 15 in the section on temporal development (where it belongs to). Second, the new figure dedicated to the monsoon issue better resolves what we want to show and makes our explanation more obvious.

Comment: *p. 14799, lines 7-9. While rapid uplift can explain why upper tropospheric values are nearly equal to surface values, they cannot explain mixing ratios that are higher than the surface. What would the source of the extra HCFC-22 be?*

Reply: Indeed we initially thought that there must something be wrong with our data. However, this is not true. The reason is roughly this. We look at 2D distributions. If there is a strong source of limited longitudinal extent somewhere, the excess vmr averages partly out when calculating the zonal mean. In a region, however, where the transport direction turns to zonal, the averaging goes along the transport direction, i.e. over a series of enhanced values, and the enhancement does no longer average out. Thus, in 2D we can see values which are larger than those in the source zonal band, although there is no other source further up in the atmosphere. In the 3D field we of course cannot have values larger than the source values at any place. Beyond this: We do not see East Asian surface values; surface values mentioned in this paragraph refer to clean air measurements where background concentrations are measured. So the apparent conflict is not even evident.

Comment: *Sections 5.1 and 5.2 have lots of qualitative discussion but there is no actual MIPAS data analysis that demonstrates any of the processes discussed; e.g., p. 14798, line 22: "The following scenario is suggested ...." Analyses, not suggestions, are required for publication. Why not bring in meteorological data to support your ideas?*

Reply: We admit that by using the term 'suggest' we undersell our analysis, thus we have reworded the related text. The fact that Asian countries' HCFC-22 emissions have increased is supported by a reference. The fact that there is uplift in the monsoon region, which would of course uplift also HCFC-22, is well established knowledge, and related references have been added. The literature referenced used a transport model driven by meteorological data, thus this request is now implicitly fulfilled. Indeed MIPAS HCFC-22 maps show a clear monsoon signal in the upper tropopause (newly included Figure, upper panel).

The flooding of the tropics and northern latitudes (the latter after the breakdown of the monsoon) with the excess HCFC-22 is clearly seen in the newly included Figure, lower panel. The fact that upper tropospheric transport and mixing in the tropics happens roughly in zonal direction is well established, and a reference has been added. Thus we see no gap in our chain of arguments and do not understand what is speculative about it. We admit that our chain of arguments in the original version of the paper appeared to have gaps without the references and the newly included figure.

Comment: *Also, Figure 15, which is used to show something about monsoon transport, crams 6 years of data on 5 surfaces into a very tiny space. The panels are illegible, the font impossible to read. It is impossible to see the details of a seasonal process such as monsoon transport with a tiny panel showing a 6-year time series.*

Reply: This is due to the landscape format of ACPD. In the final version, a full column will probably be available for these panels. The layout has not been chosen by us. Beside this, one can zoom into the figures in most PDF viewers.

Comment: *Other parts (e.g., first few paragraphs of 5.2) describe what is already very well understood about long-lived trace gas structures and seasonal cycles.*

Reply: We are not aware of any other published data set that actually contains information about the global altitude-resolved temporal development of HCFC-22 in the time period under investigation. The first part of Section 5.2. describes our data in the context of existing understanding of atmospheric processes. This strengthens the confidence both in our data and in the pre-existing assumptions. Given the novelty of our dataset in terms of global coverage along with temporal resolution, we consider it as appropriate to confront our a priori assumptions on atmospheric processes with the empirical data.

Comment: *Most air enters the stratosphere through the tropical tropopause, so interhemispheric (IH) differences in long-lived trace gases found in the troposphere are usually not found in the stratosphere. (CO2 has some but they disappear quickly with height.) If you speculate about IH differences in the stratosphere, you'll need a supporting analysis to demonstrate that tropospheric IH source differences are the cause.*

Reply: We do not agree. The interhemispheric differences of HCFC-22 are not explained by hemispherically different sources but by dynamical processes (e.g., polar seasonal cycle, semi-annual oscillation, QBO). For a source gas which has, contrary to CO_2, pronounced vertical and latitudinal mixing ratio gradients, any interhemispheric difference in stratospheric dynamics will cause differences

in the HCFC-22 distributions. Over the poles, the mixing ratio changes are mainly driven by subsidence of HCFC-22-poor air from above. Later, this air is mixed with HCFC-22-rich air from mid-latitudes. It is well known that inter-hemispheric differences with respect to these processes do exist.

Comment: *p. 14800, line 14. 'Interestingly, the breakup of the vortex seems to take place at all altitudes at almost the same time for the northern polar region.' The Arctic vortex final warming ('breakup') occurs in March or April and shows considerable interannual variability in how it breaks up (e.g., wave 1 or wave 2 warming). Its variability is much greater than the Antarctic vortex, so your statement doesn't make sense. The sharp discontinuities found each year in your figure appear too early in winter to be the breakup they are probably midwinter sudden warmings, not the final warming (breakup) that occurs in March or April. Please check your figures and interpretation.*

Reply: The 'same time' is not meant in an interannual sense but intends to say 'at the same time at all altitudes'. The wording in the manuscript has been changed for clarity. The discussion of the warming events has been revised. Indeed we have missed an important point: The sharp increase of HCFC-22 in the zonal means does not require a vortex breakup but can, in the 2D representation, also be caused by deformation or displacement of the polar vortex, i.e. by everything which leads to averaging over vortex and non-vortex air when the zonal mean is calculated. The early HCFC-22 increases in the northern polar winters just reflect this wave activity. Thanks a lot for attracting our attention to this issue.

Comment: *The lowermost stratosphere is generally below 16, not 20 km. It is below 380 K (below Hoskins' 'overworld').*

Reply: The wording has been changed.

Comment: *p. 14801, line 15. 'the seasonal cycle in the SH ... is not globally compensated but only weakened by the cycle of the NH': What does globally compensated mean?*

Reply: If NH and SH signals were exactly the same but out of phase by half a year, then they would cancel (compensate) on a global scale to zero annual cycle. The related text has been reworded for clarity.

Comment: *The results of the growth rate analysis in Section 5.3 (p. 14803) might be better displayed as a table. Too many different units are used to discuss growth rate, making it harder to compare results with previous studies cited. The Figures (16,17) use ppt/yr and%/decade. Studies cited on page 14803 use %/yr. Pick a unit and stick with it.*

Reply: A table has been added and the description has been shortened accordingly; we use pptv/yr and %/yr as units now; a caveat has been included that the reference values the percentage increases are based on vary from data source to data source and are mostly not even provided in the publications. For this reason we compare growth rates from MIPAS data to other growths rates in terms of absolute values (pptv/yr) only.
Further we have removed the comparison to growth rates published by Sherlock et al. (1997) because these data refered to 1985 and 1994 which is too old to be really comparable to MIPAS-derived growth rates, and we have added a comparison to growth rates published by Brown et al. (2011) that refer to the period 2004 – 2010.

Comment: *Section 5.4 Comparisons with surface measurements The NOAA/ GMD and AGAGE measurements are both precise and accurate: why compare in two separate sections? Please combine them into a single 'comparisons with surface'*

Reply In the original submission these data sets are already treated in one section (5.4). In the revised version we have combined the NOAA and AGAGE data sets in the figures, and have sorted the figures according to latitude bands, as suggested later in this review.

Comment: *section. p. 14804. 'the troposphere can be considered well-mixed'. Yes, sort of. As you can see in your own figures there are interhemispheric gradients of 20 ppt (10%) at the surface.*

Reply: The wording has been changed towards 'free troposphere' and 'within each hemisphere', and 'vertically' has been inserted, since this is what we intended to say.

Comment: *Why is the first paragraph of Section 5.4 talking about the dryness of stratospheric measurements when this section is about comparisons (of dry mole fraction) ground-based measurements with MIPAS tropospheric measurements? You haven't explained whether the MIPAS tropospheric measurements are wet and whether this will impact the comparisons with ground-based data. If there is an impact, what size is it? Big enough to cause a bias, or is it in the noise compared to other differences?*

Reply: Where MIPAS measures, the air is so dry that the difference between dry air mole fraction and actual mole fraction is not an issue. Any humidity which would cause any discernable difference between dry air and wet air mixing ratios requires so much water vapour that the water vapour signal would dominate the measurements and no HCFC-22 retrieval would be possible at all.

Thus, in the context of MIPAS measurements, the distinction between dry air and wet air mixing ratios is meaningless because the 'wet' air is still dry enough. Text w.r.t. this has been added.

Comment: *p. 14805. If MIPAS measurements and ground measurements are the same to within their overlapping uncertainties, then this means they AGREE. Say so.*

Reply: Isn't that what we say on top of page 14805?

Comment: *Figures 18 and 19 have too much data. It is hard to distinguish MIPAS behavior at different latitudes. I suggest organizing the comparisons into panels showing different latitude ranges (e.g., NH extratropics, tropics, and SH extratropics) and include the relevant GMD and AGAGE stations on each panel.*

Reply: Agreed and done.

Comment: *p. 14805, lines 21-24. Again, this is more speculative discussion that is not supported by meteorological analyses or other trace gas measurements. This section could be very interesting if you examined the HCFC-22 data as a function of altitude in the lower-most stratosphere (e.g., 12-16 km) in each hemisphere to identify seasonal transport processes in the lowermost stratosphere. Interhemispheric differences between the results may reveal process important to the cycles in each hemisphere.*

Reply: We do not see the gap in out chain of arguments. The fact that NH and SH air is mixed in the tropical convergence zone or at least close to the stratospheric entry point is established knowledge, and it is even used in the review to refute our explanation of stratospheric interhemispheric differences. Also the fact that the outflow of the Hadley cell takes place in the upper troposphere is well established knowledge. From this, we can deduce that the interhemispheric contrast must be smaller there than near surface. We cannot recognize the speculative component in the deductive-nomological explanation.

We admit, however, that there was an error in our text. Of course we do not mean the tropical pipe but the inter-tropical convergence zone.

We agree that there is room for a more thorough discussion of this issue, but this involves further species. We think think that a more thorough discussion of this issue shall not be made in a paper which focuses on a single species, because such an analysis is much better made using the complete suite of tracers provided by MIPAS.

Given the altitude resolution of MIPAS (3 km or worse), we consider it ques-

tionable if a lot can be learned from the examination of HCFC-22 as a function of altitude between 12 and 16 km.

Comment: *p. 14806. I see that you recognize that chemistry, emissions, and transport are all important to understanding HCFC-22 behavior. But this means that it cant be understood as simply as discussed here. An atmospheric model is required to adequately interpret the behavior.*

Reply: We would agree if we proposed new hypotheses here. What we do, however, is only to put our results in the context of existing explanations found in the literature. I think it is fair to state that our results support these findings, and for this we do not need dedicated model calculations of our own.

Comment: *Section 5.5. Stratospheric trends*
This paper examines a 7-year data set. Seven years is less than 3 QBO cycles. Each QBO cycle is different in length and its seasonal timing. It is not completely accounted for in the regression analysis by considering terms at 2 pressure levels.

Reply: By using an empirical QBO proxy we do not need to assume that the QBO is periodical. Beyond this, our regression analysis tool takes correlated residuals into account. Thus any systematic residual is accounted for in the respective error analysis.

Comment: *Because the regression analysis cannot adequately remove the QBO effect, the residuals (Figs. 17 and 20) have a QBO signature. To search for a trend (that indicates stratospheric circulation change) in a 7-year data set is by definition unreasonable.*

Reply: We disagree. If there was a significant residual QBO signal, this should be visible in Fig. 16. There, however, no systematic QBO signal is discernable, and the residuals are small (2% of the amplitude of the largest periodic). This is no wonder because the QBO is part of our regression model. Of course a short time series is no adequate data base for a climatological trend analysis. But that is not what we do. We analyze the linear component of the temporal development (which we call 'trend') within a time window and use it to analyze the atmosphere within the same time window. We do not extrapolate any trend nor do we use it in any climatological sense. Thus, it is not relevant how long the time series is. All uncertainties are included in the error estimation of the trends.

Comment: *There are end effects (2 years out of the 7 are endpoints!), the QBO cannot be adequately accounted for, and in the case of HCFC-22, there is an enormous annual growth (compared to a possible circulation change) in the species measured.*

Reply: This argument suggests that there are only seven data points. This is not true: We use monthly data, i.e. appr. 12 times 7 = 84 data points. That means that we have 82 data points that are not end points. QBO and seasonal cycle are included in the regression model. Thus, they cannot alias into the trend. Ambiguities between these coefficients due to non-orthogonality are considered in the error estimation and subsequent significance analysis.

With respect to the enormous annual growth we are not sure if we understand the argument of the reviewer correctly. Is the fact that differences of two large numbers are usually associated with a large error of the difference considered to be the weak point? If so, we defend our approach as follows: The uncertainties of our trends are calculated along with the trend estimation itself where autocorrelations are considered. The uncertainties are about 1-2% per decade. The growth rates from surface measurements are considered very accurate, and besides this, related errors are considered as irrelevant when differences between unexplained stratospheric MIPAS trends between different latitude/altitude bins are analyzed. The unexplained part of the MIPAS trends ranges between -40%/dec to +40%/dec, which is far beyond the uncertainty. From this we conclude, that our estimates are still significant.

Comment: *Section 5.5 should be eliminated.*

Reply: Since related criticism has been refuted, we have kept this section.

Anonymous Referee #2:

Comment: *The paper by Chirkov et al. provides important information about HCFC-22 ($CHClF_2$) data in the whole stratosphere and upper troposphere, as derived from MIPAS (Michelson Interferometer for Passive Atmospheric Soundings) global observations performed in the "reduced resolution mode" over a little more than 7 years, starting in January 2005. Several aspects are covered, from a brief description of the retrieval to the determination of the global distribution of HCFC-22 and the changes in its concentration with time and altitude over the available years.*

Potentially, this is an important contribution for a "Montreal Protocol species" which is poorly sampled in the upper atmosphere, with global measurements only available from ACE-FTS since the loss of the Envisat satellite three years ago. The paper fits well with the scope of Atmospheric Chemistry and Physics but includes several annoying imperfections which should have been corrected by the authors or spotted by the editor before submission or online publication. I would therefore recommend publication after some significant reorganization and re-

wording, also considering the suggested changes outlined or detailed below.

General comments
The current title includes the words "climatologies" and "trends". This clearly corresponds to two overstatements in a row for a data set covering 7 years or so. To avoid any misunderstanding, I recommend changing the title to something like "HCFC-22 measurements with MIPAS: retrieval, validation, global distribution and its evolution over 2005-2012".

Reply: This is an excellent idea. The title has been changed in order not to raise false expectations. Beyond this, the term 'climatology' is no more used in the paper but more specific terms are used. The term 'trend' makes more problems, because any attempt to avoid this term leads to cumbersome language. We have removed the term from the title and most section headers (except one). In the text a statement has been included that the term trend as used in this paper is not meant in any climatological sense but describes only the linear component of the temporal variation within the time window under analysis.

Comment: *This data set is very important for the scientific community. Beside the discussions, the current presentation is essentially restricted to a suite of (sometimes small!)...*

Reply: As said above, in the reply to reviewer #1, small figures occasionally are caused by the landscape format of the Discussion version of the paper. In the final publication a full column will be available for these figures.

Comment: *...color plots which will be of limited use to the interested reader. I would therefore strongly suggest to include the most important information in an electronic supplement, as done e.g. in Kellmann et al., ACP, 12, 2012. This supplement should at least include the underlying data used to build the color plots (starting Figure 10) and the time series of Fig. 16, allowing direct numerical comparison with model outputs, computation of "trends"*

Reply: Trend data is now made available as a supplement. The original HCFC-22 data are available via our data server. A link is now provided in the paper.

Comment: *Figure 12 presents interesting results showing similarities with material published recently for other stratospheric tracers, i.e. in Nedoluha et al. (doi:10.5194/acp-15- 6817-2015, see Fig. 10) and Mahieu et al. (doi:10.1038/nature13857, see Fig. 4). Wouldn't this be helpful when addressing the "HCFC-22 unexplained relative trend"? A brief discussion putting these findings into perspective is welcome in section 5.5.*

Reply: This has been included in the discussion

Comment: *Please, also consider the following suggestions and corrections: Page 14785-L7: the modeled spectrum is fitted to the observation, not the opposite! Change to "...fitting of the modelled spectra to measured limb spectral radiances".*

Reply: Agreed and corrected.

Comment: *Page 14786-L7: replace CHF_2Cl by $CHClF_2$ to conform to the IUPAC nomenclature of organic chemistry (i.e. here alphabetical ordering of the substituents).*

Reply: Agreed and done. But what about OH? :-)

Comment: *Page 14786-L15: I believe that the IPCC assessment (the so-called "AR-5") should also be cited here.*

Reply: Agreed and done.

Comment: *Page 14786-L18: the correct word for 2007 is "Adjustment", not "Amendment". So update to "The 2007 Adjustment to the Protocol..."*

Reply: Agreed and corrected.

Comment: *Page 14787-L20: ground-based might be misleading here, I suggest "from surface long-term data records"*

Reply: Agreed and done.

Comment: *Sections 3 and 3.1: even if the information is available from the references you are citing, you need to mention here the actual line or cross-section parameters adopted in the MIPAS retrieval scheme for the target and interfering species!*

Reply: Agreed and done.

Comment: *Page 14790-L2: suggest changing to "....the sole contribution of HCFC-22 is shown in red."*

Reply: Agreed and done

Comment: *Page 14790-L21: you are retrieving HCFC-22 from 7 years of observations, and the error budget provided in Table 1 corresponds to a single*

observation. How could this be? At the very least, we need to know if these numbers/figures are representative/typical, or correspond to a "best-case". E.g., do you see a significant scatter among the individual/per orbit error evaluations? This is also important in view of the comparisons with other instruments presented in section 4.

Reply: This error estimate is considered to be roughly representative for the entire data set but rather on the conservative side, due to the typically low lower stratospheric temperatures at tropical latitudes, which go along with a lower signal. A note on this has been included in the paper.

Comment: *Section 4.1: here also, you have to mention the origin of the line parameters used for the ACE retrievals. Different line parameters could lead to systematic biases. A proper validation exercise requires this kind of information.*

Reply: Good point! This information has been included for all spectrometers used in this study.

Comment: *Section 4.3: Same remark as for sections 3.1 and 4.1 (spectroscopy). Also, the MIPAS, ACE and MkIV retrievals use dissimilar windows. What about the possible impact of these choices on the (validation) results? This should be quoted.*

Reply: The windows are somewhat different, but this is basically to compensate the effects due to different spectral resolutions and different retrieval settings. Even with the same microwindows for all spectroscopic instruments the results are expected to vary, perhaps even more compared to the case when each instrument uses microwindows custom-tailored to the specific needs of the instrument and retrieval scheme.

Comment: *Page 14796-L25: change to "on a 1 km".*

Reply: Agreed and done

Comment: *Page 14796-L27: change to "Fort Sumner, NM".*

Reply: Agreed and done

Comment: *Section 4.4: The statistics of the comparisons (probably a word more appropriate than "validation" in the context of this paper) are extremely different. Only a handful MkIV or cryosampler flights are presented (btw involving MIPAS means...) when more than 8000 collocated measurements with ACE have been used! It is unclear to me whether this is properly accounted for in the concluding remarks of section 4.4.*

Reply: There are two aspects. With respect to noise, the ACE intercomparison is of course much more significant. However, there is not only noise but there are also systematic issues. These do not cancel out. This is why we also consider reference instruments which provide only a small number of correlated measurements. A note on this has been included in the manuscript.

Comment: *Section 5.1: This section starts with a brief description of Figures 10 and 11. Then suddenly, on line 19, you discuss about the results of Fig. 14 (compare Fig. 14, but with what?) and of Figure 15 on next line. These figures have not been described nor introduced in the text and they are mentioned before Fig. 12 and 13. This needs to be seriously revamped, eventually involving a new ordering of the figures and/or sections.*

Reply: We have included an additional figure. This serves two purposes. First, the figures are called in proper sequence. Second, the new figure better supports the discussion in Section 5.1

Comment: *Page 14799-L16: "compare Fig. 15, panel 2", what do you mean here? Do we need to compare panel 2 with the other ones? With another figure of the present paper, or of another paper? Please specify.*

Reply: It was meant to check panel 2 of Fig. 15. However, a new figure has been included and the wording has been changed.

Comment: *Section 5.4: an alternative title might be "Comparisons between tropospheric and surface growth rates".*

Reply: This sounds indeed much better, thanks. We have modified the title to "upper tropospheric"

Comment: *Page 14804-L6: change to "do not reach the ground".*

Reply: Agreed and changed.

Comment: *Page 14816-L11: change CHCLF2 to CHClF2.*

Reply: Agreed and corrected.

Comment: *Figure 8: the two different green curves are hard to distinguish once printed.*

Reply: The multi-annual mean has been removed. Thus, only one green curve remains.

Comment:*Figure 9: are the thin curves on the lower panel identified in the legend?*

Reply: The error bars have now been identified in the figure caption. Or is the problem with the grey curves? These are all MIPAS profiles within the collocation radius around the MkIV geolocation. The legend says "MIPAS collocated".

Comment: *Figure 15: the panels are really small, it would probably be preferable to arrange them as in Figure 13.*

Reply: In the ACP version the figures are printed in portrait instead of landscape format. Thus the figures will be larger.

Additional changes:
During revision we found a mistake in the date of one of the cryosampler flights: The flight did not happen, as assumed so far, on 3 October 2009 (20091003) but on 10 March 2009 (20090310). We have searched for the correct MIPAS colocations of this flight for the corrected date, and have revised the respective paragraph discussing the comparison of cryosampler and MIPAS data for this particular flight. The main conclusions from the MIPAS-cryosampler comparisons, however, have not changed.

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von Clarmann, T., et al., Retrieval of temperature, H2O, O3, HNO3, CH4, N2O, ClONO2 and ClO from MIPAS reduced resolution nominal mode limb emission measurements, Atmos. Meas. Tech., 2, 159-175, doi:10.5194/amt-2-159-2009, 2009.

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Global HCFC-22 measurements with MIPAS: retrieval, validation, global distribution and its evolution over 2005–2012~~climatologies and trends~~

M. Chirkov[1], G. P. Stiller[1], A. Laeng[1], S. Kellmann[1], T. von Clarmann[1], C. D. Boone[2], J. W. Elkins[3], A. Engel[4], N. Glatthor[1], U. Grabowski[1], C. M. Harth[5], M. Kiefer[1], F. Kolonjari[6], P. B. Krummel[7], A. Linden[1], C. R. Lunder[8], B. R. Miller[3], S. A. Montzka[3], J. Mühle[5], S. O'Doherty[9], J. Orphal[1], R. G. Prinn[10], G. Toon[11], M. K. Vollmer[12], K. A. Walker[2,6], R. F. Weiss[5], A. Wiegele[1], and D. Young[9]

[1]Karlsruhe Institute of Technology (KIT), Institute for Meteorology and Climate Research (IMK), Karlsruhe, Germany
[2]University of Waterloo, Department of Chemistry, Waterloo, Ontario, Canada
[3]NOAA/ESRL Climate Monitoring Division, Boulder, Colorado, USA
[4]Goethe-Universität Frankfurt, Experimental Atmospheric Research Institute for Atmospheric and Environmental Sciences, Frankfurt, Germany
[5]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA
[6]University of Toronto, Department of Physics, Toronto, Ontario, Canada
[7]CSIRO Oceans & Atmosphere Flagship, Aspendale, Victoria, Australia
[8]Norwegian Institute for Air Research, Kjeller, Norway
[9]Atmospheric Chemistry Research Group, School of Chemistry, University of Bristol, Bristol, UK
[10]Center for Global Change Science, MIT, Cambridge, MA, USA
[11]Jet Propulsion Laboratory and California Institute of Technology, Pasadena, California, USA
[12]Laboratory for Air Pollution and Environmental Technology, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Correspondence to: Gabriele Stiller
(Gabriele.Stiller@kit.edu)

Abstract. We report on HCFC-22 data acquired by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) in the reduced spectral resolution nominal observation mode. The data cover ~~in~~ the period from January 2005 to April 2012 ~~from version 5.02 level-1b spectral data~~ and the ~~covering an~~ altitude range from the upper troposphere (above cloud top altitude) to about 50 km. The profile retrieval was performed by constrained nonlinear least squares fitting of modelled spectra to the measured limb spectral radiances ~~to modelled spectra~~. The spectral ν_4-band at 816.5±13 cm^{-1} was used for the retrieval. A Tikhonov-type smoothing constraint was applied to stabilise the retrieval. In the lower stratosphere, we find a global volume mixing ratio of HCFC-22 of about 185 pptv in January 2005. The ~~linear growth~~ rate of linear growth in the lower latitudes lower stratosphere was about 6 to 7 pptv/yr in the period 2005 – 2012. The ~~obtained~~ profiles obtained were compared with ACE-FTS satellite data v3.5, as well as with MkIV balloon profiles and ~~in situ~~ cryosampler balloon measurements. Between 13 km and 22 km, average agreement within -3 to +5 pptv (MIPAS - ACE) with ACE-FTS v3.5 profiles is demonstrated. Agreement with MkIV solar occultation balloon-borne measurements is within 10 – 20 pptv below 30 km and worse above, while in situ cryosampler balloon measurements are systematically lower over their full altitude range by 15–50 pptv below 24 km and less than 10 pptv above 28 km. ~~Obtained~~ MIPAS HCFC-22 time series below 10 km altitude are shown to agree mostly well to corresponding time series of near-surface abundances from NOAA/ESRL and AGAGE networks, although a more pronounced seasonal cycle is obvious in the satellite data. This is attributed ~~,probably due~~ to tropopause altitude fluctuations and subsidence of polar winter stratospheric air into the troposphere. A parametric model consisting of constant, lin-

ear, quasi-biennial oscillation (QBO) and several sine and cosine terms with different periods has been fitted to the temporal variation of stratospheric HCFC-22 for all 10°-latitude/1-to-2-km-altitude bins. The relative linear variation was always positive, with relative increases of 40 – 70 %/decade in the tropics and global lower stratosphere, and up to 120 %/decade in the upper stratosphere of the northern polar region and the southern extratropical hemisphere. In the middle stratosphere, between 20 and 30 km, the observed trend is inconsistent with the trend at the surface (corrected for the age of stratospheric air). There exists a stronger positive trend in HCFC-22 in the southern hemisphere and a more muted positive trend in the northern hemisphere, implying a potential change in the stratospheric circulation over the observation period.In the middle stratosphere between 20 and 30 km, the observed trend is not consistent with the age of stratospheric air-corrected trend at ground, but stronger positive at the southern hemisphere and less strong increasing in the northern hemisphere, hinting towards changes in the stratospheric circulation over the observation period.

1 Introduction

HCFC-22 ($CHClF_2$) is a chlorine source gas and a greenhouse gas (IPCC, 2014). The sSources of HCFC-22 are anthropogenic emissions due to its use as a propellant and refrigerant. The gas is removed from the atmosphere by photolysis and by reactions with $O(^1D)$, Cl^-, and the OH radicalreaction with the OH radical. The chemical lifetime of HCFC-22 in the stratosphere is 165 161 years (12 years for its global total atmospheric lifetime), according to WMO, 2014 SPARC(2013), but has been estimated to a significantly longer span of 260±25 years by Moore and Remedios (2008). The radiative forcing potential of HCFC-22 is 0.208 $Wm^{-2}ppbv^{-1}$, and its ozone depletion potential is about 20 times lower than that of CFC-12 (0.04) (World Meteorological Organization (WMO), 2014). Production and import of HCFC-22 is limited by the Montreal Protocol on Substances that Deplete the Ozone Layer and will be banned by 2030 for dispersive uses in developed countries (United Nations Environment Programme, 2009). The 2007 Adjustment Amendment to the Protocol asks for a 100% reduction by 2030 for all countries, including developing nations also for developing countries – albeit with a 2.5% allowance for servicing of refrigeration and air conditioning equipment existing on 1 January 2030 for the period 2030-2040 and subject to review in 2015. ThereforeSo the overall reduction shall already be 97.5 - 100% by 2030.

Ambient HCFC-22 was first measured by Rasmussen et al. (1980) by air sampling in situ techniques. Atmospheric HCFC-22 abundances are typically measured on site by gas-chromatographic techniques or by collecting samples in flasks or by balloon-borne air-sampling measurements (Engel et al., 1997) followed by subsequent gas-chromatographic analysis in a central laboratory (Montzka et al., 2009; O'Doherty et al., 2004; Yokouchi et al., 2006) or by balloon-borne air-sampling measurements (Engel et al. 1997). Further, there exist remote measurements by infrared spectroscopy from ground-based (Rinsland et al., 2005b; Zander et al., 2005; Gardiner et al., 2008), balloon-borne (Murcray et al., 1975; Williams et al., 1976; Goldman et al., 1981), or space-borne (Zander et al., 1987; Rinsland et al., 2005a; Moore and Remedios, 2008) platforms in solar absorption geometry. Among recently flying space-borne instruments, only the Atmospheric Chemistry Experiment – Fourier Transform Spectrometer (ACE-FTS; solar occultation) and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS; limb emission) have been providing measurements of HCFC-22 (Kolonjari et al., 2012; Park et al., 2014; Moore and Remedios, 2008). The history of measurements is summarized in von Clarmann (2013).

In this paper we present and discuss HCFC-22 distributions and time series as retrieved with the MIPAS data processor developed and operated by the Institute for Meteorology and Climate Research at the Karlsruhe Institute of Technology (KIT-IMK) in Germany in cooperation with the Instituto de Astrofísica de Andalucía (IAA, CSIC) in Granada, Spain. In the next section we provide a description of the MIPAS instrument and measurements. The retrieval strategy and error estimation are summarized in Section 3. Section 4 reports on the validation of this data set, and Section 5 presents global distributions the climatology of HCFC-22 distributions and an assessment of temporal variations including a linear trend. The derived estimates of trends will be compared to those from ground-based long-term surface data records. Section 6 contains the discussion of the results and the summary.

2 MIPAS data

MIPAS measured the thermal emission of the atmosphere, and thus provided data during day and night. It was a cryogenic limb emission Fourier transform spectrometer (FTS) FTS designed for measurement of trace species from space (European Space Agency, 2000; Endemann and Fischer, 1993; Endemann et al., 1996; Fischer and Oelhaf, 1996). MIPAS was one of 10 instruments aboard the Environmental Satellite (Envisat). Envisat was launched into a sun-synchronous polar orbit on 1 March 2002 at approximately 800 km, with an orbital period of about 101 min (Fischer et al., 2008), resulting in more than 14 orbits per day. The end of the Envisat mission was declared on 9 May 2012 after loss of communication with the satellite on 8 April 2012.

MIPAS sounded the atmosphere tangentiallytangential to the Earth in the infrared spectral range (4.15–14.6 μm) covering tangent altitudes from about 7 to 72 km in its nominal ob-

servation mode. The instrument's field of view was approximately 3 km (vertically) × 30 km (horizontally). MIPAS operated from July 2002 to March 2004 with full spectral resolution as specified: 0.05 cm^{-1} in terms of full width at half maximum, after apodisation with the 'strong' function suggested by Norton and Beer (1976). The full resolution mode was stopped in March 2004. Starting from January 2005 and up to the end of the mission, the spectral resolution of MIPAS was degraded from 0.05 cm^{-1} to 0.12 cm^{-1} (apodised). These later measurements are referred to as 'reduced resolution mode'.

The data analysis reported in this paper relies on the ESA-provided so-called level-1b data product which includes calibrated phase-corrected and geolocated radiance spectra (Nett et al., 1999). The versions of ESA level-1b data used are IPF 5.02–5.06. All spectra under consideration here were recorded according to the nominal reduced resolution measurement mode, including per limb sequence 27 tangent altitudes between about 7 and 72 km, with the tangent altitude adjustment following roughly the tropopause altitude over latitudes. The vertical distance between adjacent tangent heights varies between 1.5 km in the upper troposphere/lower stratosphere up to 4.5 km in the mesosphere. One limb scan is recorded per each 410 km increment along the polar sun-synchroneous orbit, leading to a dense horizontal sampling which is independent of the season or latitude band. As a result, MIPAS covers all latitudes during one orbit.

3 Retrieval

The retrievalretrievals of HCFC-22 profiles presented here waswere performed with a MIPAS data processor dedicated for research applications, which has been developed at the Institut für Meteorologie und Klimaforschung (IMK) and complemented by components relevant to treatment of non-local thermodynamic equilibrium at the Instituto de Astrofísica de Andalucía (IAA). The non-LTE components are not used in this study because they are not relevant to the retrieval of HCFC-22.

The IMK retrieval processor consists of the radiative transfer algorithm KOPRA (Stiller, 2000) and the retrieval algorithm RCP (Retrieval Control Program). Local spherical homogeneity of the atmosphere is assumed here, i.e., atmospheric state parameters related to one limb sounding sequence are assumed not to vary with latitude or longitude but only with altitude. An exception is temperature for which horizontal gradients are considered in the retrieval (Kiefer et al., 2010). The general strategy of the IMK/IAA data processing has been documented in von Clarmann et al. (2003).

3.1 Retrieval of HCFC-22

HCFC-22 is retrieved by a constrained multi-parameter non-linear least-squares fitting of modelled to measured spectra.

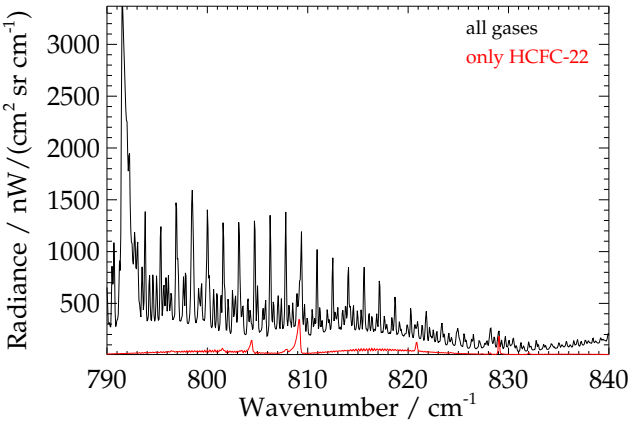

Figure 1. Typical spectrum of HCFC-22 (red curve) and combined spectrum of 24 gases (HCFC-22 included) (black curve) at 16 km tangent altitude.

Spectral data from all tangent altitudes are analysed within one inversion process, as suggested by Carlotti (1988). Volume mixing ratio (vmr) vertical profiles are retrieved on a fixed, i.e. tangent height independent altitude grid which is finer than the tangent height spacing (1-km steps from 4 to 35 km; then 5-km grid width from 35 to 50 km; 10 km grid width from 50 to 100 km; 120 km). In order to obtain stable profiles, the profiles have been constrained such that the first order finite difference quotient $\Delta\mathrm{vmr}/\Delta\mathrm{altitude}$ at adjacent altitude grid points was minimised, similar as proposed by Tikhonov (1963). An altitude-constant zero-level profile of zero mixing ratio throughout was taken as a priori, while the initial guess profile was from the MIPAS climatology (Kiefer et al., 2002). For the retrieval of HCFC-22 we have used 4 microwindows of the MIPAS spectrum (803.500 cm^{-1} to 804.750 cm^{-1}, 808.250 cm^{-1} to 809.750 cm^{-1}, 820.500 cm^{-1} to 821.125 cm^{-1} and 828.750 cm^{-1} to 829.500 cm^{-1}). For HCFC-22, the HITRAN2K spectroscopic database (Rothman et al., 2003) was used, with some updates for interfering species.

Fig. 1 shows the atmospheric limb emission radiance spectrum at 16 km tangent altitude including contributions from H_2O, CO_2, O_3, NO_2, NH_3, HNO_3, ClO, OCS, HCN, CH_3Cl, C_2H_2, C_2H_6, COF_2, C_2H_4, HNO_4, CFC-11, CCl_4, CFC-113, $ClONO_2$, CH_3CCl_3, CH_3OH, $C_2H_3NO_5$ (peroxyacetyl nitrate, PAN), C_3H_6O and HCFC-22 (black curve). In addition, the sole contribution of HCFC-22 is shown in red (red curve).

For some quantities, The following information from preceding retrieval steps was used for the retrieval of HCFC-22: a correction of the spectral shift caused by a less-than-perfect frequency calibration; the tangent altitudes height of the limb measurements;and temperature; and finally the mixing ratios of the species O_3, H_2O, HNO_3, ClO, $ClONO_2$,

CFC-11, HNO_4 as well as and C_2H_6. The vmr of CO_2 and all other remaining gases were are taken from a climatological database, and the temperature was retrieved from CO_2 lines (von Clarmann et al., 2003, 2009b).

Simultaneously with HCFC-22 and with adequate regularisation, we jointly fitted the following quantities: the mixing ratio of PAN;, a wavenumber-independent continuum absorption coefficient per microwindow and altitude accounting for aerosol emission; and an additive radiative offset for each microwindow. The data versions are V5r_F22_220 and V5r_F22_221. The only difference between these versions is the source of temperature analysis data used as a priori for the preceding temperature retrieval. Results are equivalent and different version numbers are used only to guarantee full traceability of the retrievals.

3.2 Diagnostics

Diagnostic quantities to characterise the HCFC-22 measurements include estimates of measurement noise, of retrieval errors caused by uncertainties in ancillary parameters used in the radiative transfer modelling, and the averaging kernel (AK) matrix (Rodgers, 2000).

Table 1 shows the estimated total retrieval error of a HCFC-22 profile measured at 18.6°S and 111.6°W on 9 January 2009. This error estimate is considered to be roughly representative for the entire data set but is rather conservative, due to the typically low lower stratospheric temperatures at tropical latitudes, which are associated with a lower signal. The total error is the square root of the quadratic sum of noise error and parameter errors. Its most importantdominating components are the uncertainty of the elevation pointing of the line of sight (LOS), the uncertainty of pre-retrieved O_3 mixing ratios, the gain calibration uncertainty, the residual spectral shift uncertainty, and the instrument line shape (ILS) uncertainty. The spectroscopic error (not reported in the table) is about 5%. In the given altitude range, errors resulting from uncertainties of interfering species contribute to the total error by less than 1%.

The percentage of non-converged profiles is about 0.01 to 0.02%. The strength of the regularisation, i.e. the weight of the constraint, has been chosen to be altitude-dependent with a scheme proposed by Steck (2002) such that the retrieved profile represents approximately 5 degrees of freedom, corresponding to a typical altitude resolution of 3 km at 10 km height and 7 km at 30 km height, and further increasing with height (Fig. 2). Here the vertical resolution is provided in terms of full width at half maximum of a row of the averaging kernel matrix. The rows of the AK-matrix show how much information from other atmospheric altitudes contribute to the vmr on the given retrieval altitude. An example of the rows of the HCFC-22 averaging kernel matrix is shown in Fig. 3. The largest peaks of the averaging kernels are generally found in the upper troposphere. This is because the retrieval is more strongly regularised at higher altitudes. In general, the retrieval is well-behaved in a sense that the averaging kernels peak at their nominal altitudes (marked by diamonds in Fig. 3) between 12 and 50 km.The integral over the averaging kernels in this altitude range are, at good accuracy, unity, thus our choice of the constraint does not impose any bias.

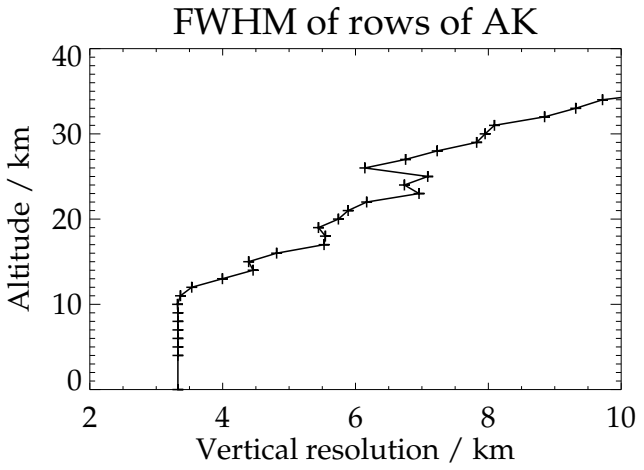

Figure 2. Altitude resolution in terms of full width at half maximum (FWHM) of a row of the averaging kernel matrix.

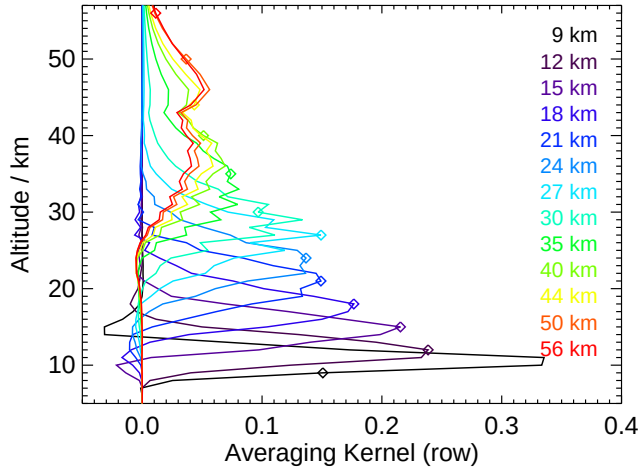

Figure 3. Rows of averaging kernel of HCFC-22 measurements for reduced spectral resolution nominal mode. The diamonds represent the nominal altitudes (e.g. the diagonal value of the averaging kernel matrix). For clarity, only every third kernel is shown.

The information evaluated by a limb retrieval is not located in one single point but spread horizontally along the line of sight direction. The horizontal information smearing of the HCFC-22 measurement is estimated by using the method of von Clarmann et al. (2009a). In terms of full width at half maximum of the rows of the horizontal averaging kernel matrix, the horizontal information smearing of a MI-

Table 1. Error budget of a V5r HCFC-22 (nominal mode, reduced resolution) retrieval on 9 January 2009, 18.6°S latitude and 111.6°W longitude degree, orbit 35874, for selected altitudes. The errors are given in units of mixing ratios (pptv), and additionally, in parentheses, in percentage units (%).

V5r HCFC-22 Height	Total Error	Noise	Parameter Error	O_3	LOS	Shift	Gain	ILS
40 km	14(17.3)	13(16.1)	5.7(7.0)	0.3(0.3)	1.7(2.1)	1.9(2.3)	0.3(0.3)	2.3(2.8)
35 km	12(11.2)	11(10.2)	6.1(5.7)	0.2(0.1)	1.4(1.3)	2.3(2.1)	0.5(0.5)	1.5(1.4)
30 km	12(9.0)	9.4(7.1)	7.3(5.5)	<0.1(<0.1)	1.1(0.8)	2.3(1.7)	1.0(0.7)	0.4(0.3)
25 km	13(8.0)	9.0(5.6)	9.1(5.6)	0.2(0.1)	3.2(2.0)	1.2(0.7)	0.6(0.3)	0.8(0.5)
20 km	14(7.0)	8.2(4.1)	12(6.0)	0.3(0.2)	5.2(2.6)	0.5(0.2)	0.5(0.2)	2.4(1.2)
15 km	13(5.6)	7.1(3.1)	11(4.7)	0.3(0.1)	1.2(0.5)	0.8(0.3)	1.6(0.7)	2.8(1.2)
10 km	13(6.8)	8.6(4.5)	9.6(5.0)	<0.1(<0.1)	1.8(0.9)	0.1(<0.1)	2.1(1.1)	2.0(1.0)

Table 2. Horizontal averaging kernels (full width at half maximum) calculated according to von Clarmann et al. (2009a) for retrieval altitudes between 40 km and 10 km for HCFC-22. Positive sign means displacement towards the satellite.

Height	FWHM	Displacement
40 km	554 km	-121 km
35 km	549 km	5 km
30 km	528 km	62 km
25 km	521 km	55 km
20 km	608 km	90 km
15 km	300 km	133 km
10 km	327 km	126 km

PAS retrieval typically varies between about 210 and 680 km for most species, altitudes and atmospheric conditions. For HCFC-22 the horizontal information smearing, calculated as the half width of the horizontal component of the 2D averaging kernel, is approximately 300 km at altitudes below 15 km, 608 km at altitude 20 km and approximately 550 km above (see Tab. 2).

The information displacement is defined as the horizontal distance between the point where the most information comes from and the nominal geolocation of the limb scan, which is defined as the geolocation of the tangent point of the middle line of sight in a MIPAS limb scan. The information displacement in case of HCFC-22 varies between -121 km at 40 km altitude (the negative sign refers to displacement beyond the tangent point with respect to the satellite) and 133 km at 15 km altitude, and is lowest and positive (i.e. displacement towards the satellite) in the middle stratosphere (see Tab. 2).

4 Validation

Validation of the HCFC-22 MIPAS IMK profiles is performed by comparison to coincident independent measurements. The availability of reference measurements for the validation of MIPAS HCFC-22 in the stratosphere is quite limited: the only space-borne instrument measuring the vertical profiles of HCFC-22 at the same time as MIPAS is ACE-FTS. We also perform the comparison with MkIV balloon profiles and with measurements at different heights performed with the balloon-borne cryosampler flown by the University of Frankfurt. Although there exist aircraft ~~air~~ measurements of HCFC-22 (e.g. Xiang et al., 2014), these have not been used, because of unsolved problems caused by the different altitude resolutions of MIPAS and the air sampling measurements. The application of averaging kernels to homogenise profiles of different altitude resolution as suggested by Connor et al. (1994) is only possible if the better resolving instrument provides vertical profiles but not if values at a single altitude level are available only.

4.1 Comparison with ACE-FTS

The Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) is a solar occultation instrument flying on the SCISAT satellite platform since August 2003 (Bernath et al., 2005). It takes measurements from the upper troposphere to about 150 km altitude. Temperature, pressure, atmospheric aerosol extinction, and the concentrations of a large number of atmospheric species are retrieved from these measurements with a vertical resolution in the order of 4 km. The SCISAT flies on a highly inclined circular orbit (650 km altitude), which implies that more than half of the ACE-FTS measurements occur at high (over 60°N and S) latitudes. It takes appoximately three months for all latitudes ($\sim$ 82°N–82°S) to be sampled by ACE-FTS.

HCFC-22 is retrieved by the algorithm described in Boone et al. (2005) and Boone et al. (2013) from a single window of width 25 cm^{-1} centered at 817.5 cm^{-1}. The ACE-FTS retrieved HCFC-22 profiles extend from the upper troposphere to about 30 km height, do not include any formal a priori information, and the reported errors are in the order of 3 to 5%, going up to 10% at the lowest and 8% at the highest alti-

tude limits of the retrieval. Spectroscopic data from HITRAN 2004 (Rothman et al., 2005) were used for HCFC-22 but for this species no updates have been made with respect to the HITRAN2K version used for MIPAS.

The analysis was performed on January 2005 – April 2012 data of ACE-FTS version 3.5, with collocation criteria of 500 km and 5 hours; this leads to a comparison subset of 8393 co-located measurements. In the case of multiple matches, only the closest MIPAS profile was used.

The comparison of global mean MIPAS and ACE-FTS HCFC-22 profiles (left panel of Fig. 4) ~~profiles~~ reveals a high MIPAS bias of 5 to 10 pptv at 17-29 km altitudes and a low MIPAS bias (between 0 and -3 pptv) at 10–13 km. Between 13 and 22 km altitude, the mean difference is -3 to +5 pptv. The bias is significant at all altitude levels. Analysis of the scatter of the differences versus the estimated combined precision of the instruments (Fig. 4, right panel) indicates an underestimation of the combined uncertainty, i.e. one or both instruments underestimate the random component of their errors (c.f. von Clarmann (2006)). It should, however, be kept in mind that the reported fitting error estimates of ACE-FTS include only measurement noise and do not include randomly varying parameter errors, which implies that perfect coincidence of the two curves on the right panel of Fig. 4 cannot be expected. Further, atmospheric variability within the radius defined by the coincidence criteria can contribute to these differences. This is particularly true because many of the ACE-FTS measurements occur at higher northern latitudes where atmospheric variability is quite pronounced.

The seasonality of the differences between ACE-FTS and MIPAS for southern polar latitudes is analysed in Fig. 5. Most pronounced differences occur at the top end of the ACE-FTS profiles, with ACE-FTS always lower than MIPAS, while the seasonality in the differences comes mainly from a very steep vertical gradient in the ACE-FTS profiles for polar summer between 16 and 20 km altitude (top left panel) which is not in the same way reproduced by MIPAS profiles. The very steep vertical gradient in this particular case leads to the highest bias of ACE-FTS vs. MIPAS of about 15 pptv around 16 km and a low bias around 20 km and above.

The correlation plots of ACE-FTS versus MIPAS (Fig. 6) corroborate the findings so far: the ACE-FTS and MIPAS data points fall into two clusters that match around 16 km altitude. Below this altitude (red and yellow colours) the regression line is slightly steeper than unity indicating a bias proportional to the absolute values, while above 16 km ACE-FTS has a small and almost constant low bias versus MIPAS.

The histogram plots (Fig. 7) represent the distribution of measured volume mixing ratios over latitude and time for a fixed altitude level. The histograms for ACE-FTS and MIPAS at 23 km are very similar in shape and position of the peak value, while at 16 km the ACE-FTS distribution of measured vmrs is somewhat wider. The latter is attributed to the fact that the ACE-FTS retrieval does not use any reg-

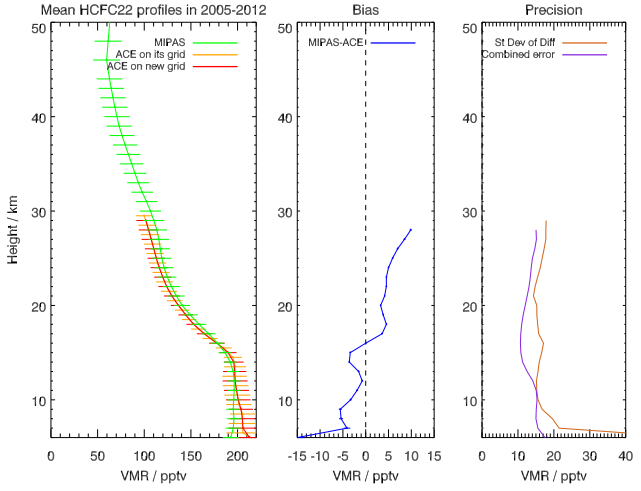

Figure 4. Mean profiles, bias, and standard deviation of the differences versus estimated combined retrieval error for ACE-FTS and MIPAS retrievals of HCFC-22. The original altitude grid on which the ACE-FTS data were provided uses the same grid spacing as MIPAS of 1-km, but is shifted by 0.5 km. Thus, the data were resampled on the MIPAS grid. The error bars in the left panel are the typical errors of a single profile, estimated as the mean error over the sample. The tiny error bars in the middle panel (hardly discernable) are the standard errors of the mean differences.

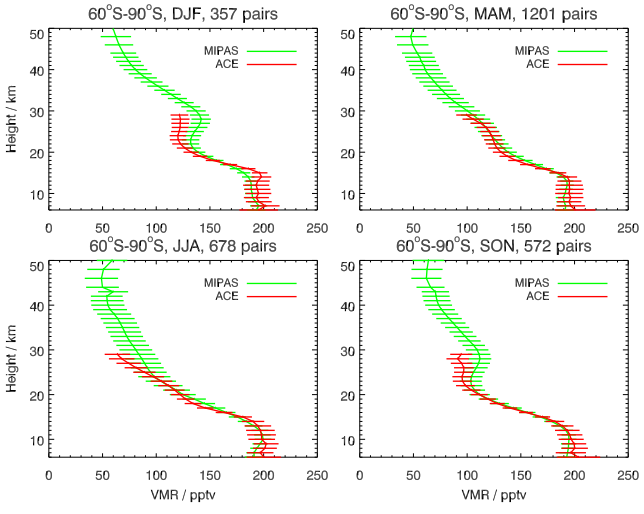

Figure 5. Seasonal mean vmr values (in pptv) of ACE-FTS (red) and MIPAS (green) in 2005-2012 at southern polar latitudes. Error bars represent the typical precision of a single profile, estimated as the mean error over the sample.

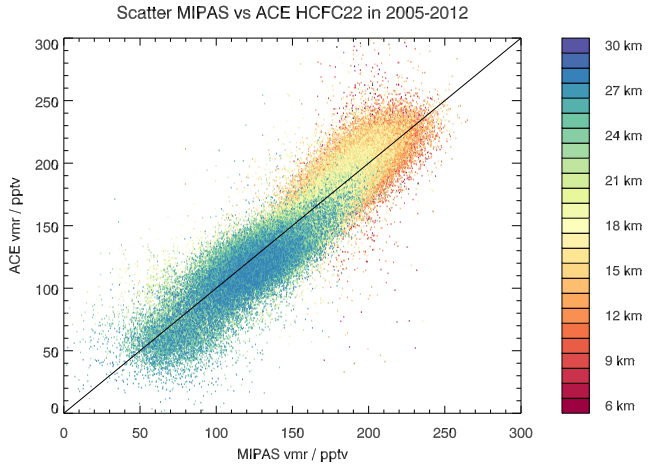

Figure 6. Scatter plot of ACE-FTS versus MIPAS HCFC-22 data points.

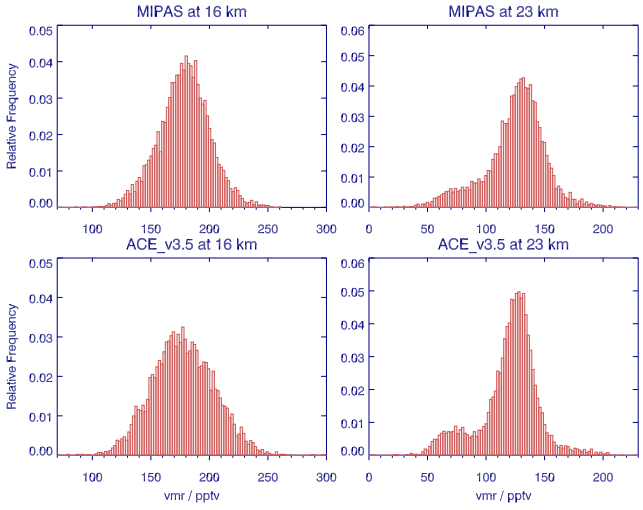

Figure 7. Histograms of MIPAS (upper panels) versus ACE-FTS (lower panels) HCFC-22 mixing ratios at 16 km (left panels) and 23 km (right panels) altitude.

ularisation, which leads to greater scatter. Nevertheless, both peak and extreme values match quite well and the histograms suggest a robust agreement between the two instruments, albeit with an altitude-dependent systematic offset as discussed above. The bimodal distribution at 23 km altitude is caused by differences in the air masses sounded by each instrument, where the polar air masses correspond to the lower mode and the mid-latitude air masses to the higher mode. The number of tropical collocations is small and has thus minor impact on the histogram. The ACE-FTS modes are more clearly separated than the MIPAS modes because of the differences in the North-South component of the lines of sight of each measurement technique. Since the mixing ratio gradients in North-South direction are typically larger than those in East-West direction, the modes of MIPAS that observes roughly in the orbit plane are more smeared than those of ACE-FTS whose line of sight is directed towards the sun.

In summary, although minor differences between MIPAS and ACE-FTS HCFC-22 measurements have been detected, the comparison justifies confidence in the data sets. Besides identified small biases in the order of <10 pptv the two data sets compare very well in absolute values, latitude distributions, and seasonalities.

4.2 Comparison with cryosampler profiles

The cryogenic whole air sampler, deployed on stratospheric balloons, is operated by the University of Frankfurt. The instrument collects high volume whole air samples which are frozen out by means of liquid neon. After the flight, the air is left to evaporate which provides high pressure whole air samples from different altitudes (Engel et al., 1997). A wide range of halocarbons are then analysed in these samples using a gas chromatograph ~~(GC)~~ coupled to a mass-spectrometer (Laube et al., 2008). The precision of the individual data points of the cryosampler measurements is typically in the order of 0.5%. The measurements were referenced~~data are reported relative~~ to a standard provided by the National Oceanic and Atmospheric Administration (NOAA) (e.g. Montzka et al., 2003) and the data were reported on the NOAA–2006 calibration scale, which shows excellent agreement (within 1%) to most other calibration scales (Hall et al., 2014; World Meteorological Organization (WMO), 2014).

Cryosampler measurements do not represent contiguous vertical profiles but rather individual independent point measurements. Hence, no regridding has been applied in this case: the cryosampler measurements were just reported as they were on the height where they had been taken.

Coincidences between MIPAS and cryosampler measurements were considered~~searched for~~ within a spatial distance of 1000 km and a time window around the cryosampler measurement time of $\pm$24 hours. These coincidence criteria may seem large. However, in their work on the validation of CFC-11/CFC-12 and CH_4 measurements from MIPAS, where data from the same MIPAS geolocations and balloon flights were used, Eckert et al. (2015) and Laeng et al. (2015) found remarkably good agreement between MIPAS and the cryosampler data, except for biases confirmed by other validation instruments. Thus, it is rather unlikely that any differences found in the HCFC-22 comparison can be attributed to the relatively large spatial or temporal distance. ~~Besides the coincident data, we compare also seasonal means from MIPAS to the cryosampler data in order to estimate how far typical situations were sounded.~~ For the first two flights (first two~~upper~~ panels of Fig. 8) that took place in June 2005 in the tropics the agreement between MIPAS profiles and cryosampler measurements above 30 km altitude is better than 10

pptv. As expected, the individual co-located profiles agree better than the corresponding multi-annual seasonal zonal means to the cryosampler data. Nevertheless, the MIPAS profile with the closest coincidence differs significantly from the other coincident profiles in both cases, hinting towards inhomogeneous situations in the atmosphere. Below 30 km, for the first flight neither the closest coincident profile, nor the mean of coincidences , nor the climatological profile agrees with the cryosampler measurements. MIPAS data are higher than the cryosampler measurements between 15 pptv (mean coincident profile) and 35 pptv (closest profile). For the second flight, the cryosampler data points fall mostly within the error bars of the closest MIPAS profile.

The third flight (thirdmiddle left panel of Fig. 8) of the cryosampler instrument provided only four measurements, none of which being situated between 18 and 32 km. For all four data points, MIPAS is higher by 15-30 pptv. The cryosampler data of the fourth flight (fourth panel) show a narrow layer with very low HCFC-22 abundances around 23 km; within this layer the abundances are mostly far lower than the closest MIPAS profile. Pronounced oscillations appear also in some but not all individual MIPAS profiles, but have, where present, a significant high bias (20 to 50 pptv) compared to the cryosampler data. Other individual MIPAS profiles, in particular the profile of the closest coincidence, are rather smooth. The oscillating cryosampler data are attributed to an unusual atmospheric situation on this particular flight with a narrow lamina of HCFC-22 poor polar vortex air, and this situation led to strong small-scale variability. This hypothesis is corroborated by the large spread of the co-located MIPAS profiles. The lamina itself is either not encountered by the MIPAS measurements, or it is not resolved; MIPAS measurements represent for each profile point an air parcel of about 400 km in length times 30 km in width times 4 km in height. Below 18 km, the MIPAS profiles have a high bias of 15 to 20 pptv. The cryosampler data of the fourth flight (bottom right panel) show some oscillations around the closest MIPAS profile between 20 and 30 km altitude, which are not resolved by MIPAS, whose measurements represent for each profile point an air parcel of about 400 km in length times 30 km in width times 4 km in height. The MIPAS profile lies just between the oscillating cryosampler data points. The oscillating cryosampler data are attributed to a strong variability of the atmosphere on this particular day. This hypothesis is corroborated by the large spread of the co-located MIPAS profiles. Above 24 km altitude, the cryosampler data points lie within the spread of the MIPAS coincidences, while below 24 km, MIPAS profiles have a pronounced high bias of 30 to 50 pptv.

The last flight (bottom left panel of Fig. 8) stands out by a pronounced HCFC-22 minimum (also present in the profiles of other tracers measured during this flight) in MIPAS data at approximately 28 km. Below this altitude, the cryosampler measurements coincide nicely with the MIPAS data but the altitude coverage of the cryosampler data set on this day does not allow to confirm the positive mixing ratio gradient above.

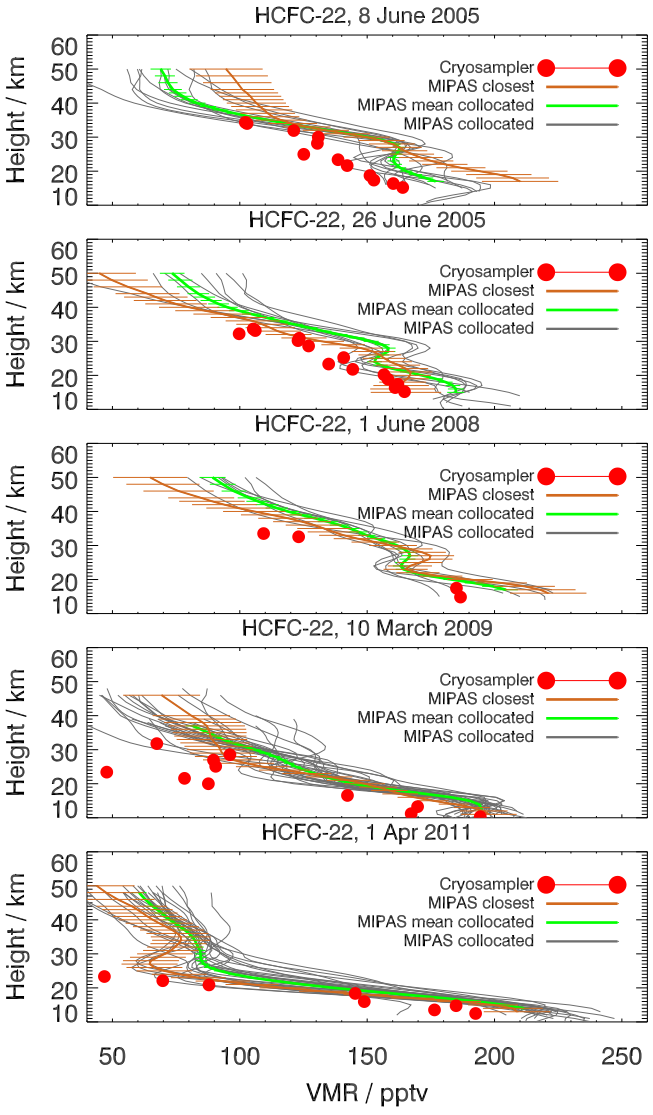

Figure 8. Five cryosampler profiles (red filled circles) and MIPAS HCFC-22 vmr profiles - all co-located (grey), closest collocations (orange), and the mean profiles from all collocations (green).monthly and seasonal means in corresponding latitude bands. Numbers in brackets are latitudes in degrees.

In summary, comparison to cryosampler data from five different profiles from tropical and northern polar winter atmosphere reveal a high bias of MIPAS HCFC-22 data of 15 to 50 pptv below 24 km;, while above 28 km, the high bias is reduced to less than 10 pptv. The analysis of the comparisons is partly complicated by very inhomogeneous atmospheric situations and the enormous difference between sampling volumes of cryosamplers versus satellite remote sensing instruments.

4.3 Comparison with MkIV balloon interferometer profiles

The MkIV interferometer from Jet Propulsion Laboratory (JPL) is a high-resolution solar absorption spectrometer for measurement of over 30 atmospheric constituents which is deployed on stratospheric balloon platforms with a typical float altitude of 37 km (Toon, 1991). MkIV measured HCFC-22 using two spectral windows, centered at the ν_4 Q-branch at 809.19 cm^{-1} and the $2\nu_6$ Q-branch at 829.14 cm^{-1}.The widths of the microwindows were 1.28 cm^{-1} and 0.72 cm^{-1}, respectively. Pseudolines derived from spectroscopic measurements (McDaniel et al., 1991; Varanasi, 1992; Varanasi et al., 1994) have been used as spectroscopic data (see http://mark4sun.jpl.nasa.gov/pseudo.html). ~~The instrument is designed so that the entire mid-infrared region can be observed simultaneously with good linearity and signal-to-noise ratio. In this region over 30 different gases have identifiable spectral signatures including HCFC-22.~~ The instrument obtains vmr vertical profiles of HCFC-22 between cloud top and balloon altitude. MkIV measured twothree HCFC-22 vmr vertical profiles co-located by MIPAS reduced resolution measurements~~during the MIPAS reduced resolution period.~~ The dataset is provided on a~~n~~ 1-km altitude grid between 10 and 40 km. The vertical resolution of the MkIV balloon profiles varies between 2-4 km. Data used here were measured during balloon flights from Fort Sumner, NM, with tangent altitude geolocations from 34.0°N–35.7°N and 108.8°W–114.1°W.

Figure 9 presents the two MkIV balloon profiles within the MIPAS reduced resolution period. The first MkIV profile, from September 22, 2007, was~~were~~ measured when MIPAS was temporarily inactive and no matches were found within 24 hours and 1000 km. The MkIV profile~~s~~ from 22 September 2007 was ~~in addition~~ compared to the MIPAS 30°N–40°N monthly mean of September 2007. These observations were made at the end of a summer of easterly stratospheric winds. Since the flow is zonal during the summer and wave activity is negligible, little zonal variation in composition is to be expected, which justifies comparison with a zonal monthly mean of the same year. For the profile from the sunrise of September 23, 2007, three co-located MIPAS profiles were found (grey lines).

Below 25 km the MIPAS profiles agree with the MkIV profiles within the error bars, with MIPAS HCFC-22 being in tendency lower for the co-located profiles, (right~~lower~~ panel) ~~, higher for the multi-annual September mean (top left panel) but~~and in good agreement for the September 2007 monthly mean. Above 25 km the vertical gradients of mixing ratios from MkIV and MIPAS diverge, with MkIV profiles decreasing stronger with altitude than those of MIPAS. Up to 32 km, the agreement is still well within the error bars. For the 22 September 2007 comparison the profiles agree even up to the highest MkIV altitude levels.

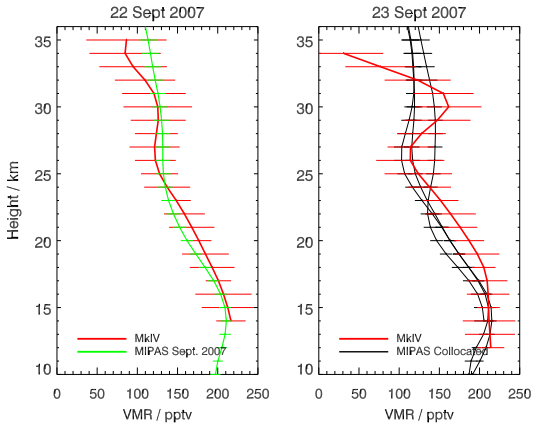

Figure 9. MkIV ~~profiles~~ and MIPAS ~~HCFC-22~~ co-located and~~,~~ monthly ~~and seasonal~~ mean vertical HCFC-22 profiles along with error bars. The mean profile is~~s are~~ taken in the 30°N-40°N latitude band where the two~~three~~ balloon flights took place.

4.4 Summary of the intercomparisons

The comparisons to the three available reference data sets, namely ACE-FTS, balloon-borne cryosampler data, and MkIV balloon measurements, do not provide a unique picture on MIPAS biases. Below about 20 km, MIPAS has either a low (ACE-FTS), a high (cryosampler) or no (MkIV) bias. Above 25 km the MIPAS bias is either clearly positive (ACE-FTS and MkIV) or small, i.e. less than +10 pptv (cryosampler). Between 20 and 25 km the bias can range from -30 pptv (MkIV) to +50 pptv (cryosampler). In summary we state that there is no clear indication of a bias, and MIPAS does not stand out as particularly high or low. MIPAS HCFC-22 data are found to be within $\pm$ 15 pptv (1σ) of reference data sets between 10 and 35 km altitude. The different size of the reference data sets needs to be taken into account. The large number of co-locations with ACE-FTS leads to a high statistical significance of deviations with respect to noise. Errors of systematic nature, however, do not cancel out by averaging, and with respect to these, the balloon measurements are considered equally useful despite the small number of co-locations. In addition, cryosampler data do not rely on spectroscopic measurements as the other three data sets and, thus, are the most independent reference data within the intercomparisons. Disagreement with cryosampler data hints towards a potential bias of all spectral measurements due to incorrect spectroscopic information.

5 Global distributions and temporal evolutionClimatology and Trends

5.1 Zonal means

Figures 10 and 11 show monthly zonal means of HCFC-22 vmr for December 2005 and 2010, and July 2006 and 2010, respectively, for all latitudes and altitudes up to 50 km. The months have been selected to be approximately in the same phase of the quasi-biennial oscillation (QBO). The typical distribution of a tropospheric source gas with photolytic sinks in the stratosphere is observed, with higher values in the tropics and lower altitudes, and lower values in the upper stratosphere and higher latitudes. Within the troposphere, MIPAS sees larger HCFC-22 abundances in the northern hemisphere (NH) than in the southern hemisphere (SH), owing to the global distribution of emissions, which is in agreement with previous results from Xiang et al. (2014), while in the stratosphere this kind of asymmetry is not observed. Furthermore, a substantial increase of HCFC-22 from the year 2005/2006 to the year 2010 can be derived from the MIPAS results.

The HCFC-22 distributions show a maximum in the tropical upper troposphere which is, at first glance, not expected for a source gas emitted at the ground. Closer inspection, however, reveals that in 2D distributions the situation is different, if we assume that there are extratropical localized sources and a localized uplift region and, after a certain altitude has been reached, injection into the zonal transport direction of the tropics. A source gas maximum as observed by MIPAS then can be explained by the following mechanism: Due to the local uplift of polluted air from localized sources the enhancement of the pollutant averages out to a certain degree when the zonal mean values for the lower altitudes are calculated. At higher altitudes the transport direction turns to zonal and averaging happens along the transport direction, involving summation over a series of enhanced values, and the reduction of the zonal mean by averaging over polluted and clean airmasses no longer takes place.

In the case of MIPAS HCFC-22, highest vmrs of up to 240 pptv are observed at the end of the observation period, and occur at altitudes between 10 and 15 km at 30 - 50°N during boreal summer and coincide with the position of the Asian monsoon anticyclone (Fig. 12, upper panel). After the break-down of the Asian monsoon anticyclone, during boreal fall, these HCFC-22 enhancements are spread over all longitudes and transported into the TTL, where they are subsequently distributed over the tropics, providing the isolated maximum layer of up to 225 pptv at low latitudes (Fig. 12, middle panel). This behaviour is nicely consistent with the general explanation scheme outlined above: HCFC-22 production was not restricted for developing countries during the relevant time, and some of these countries, e.g. China, have been large HCFC producers for years, while HCFC-22 production is controlled by the Montreal Protocol for industrialised countries. Indeed, Saikawa et al. (2012) found a surge in HCFC-22 emissions between 2005 and 2009 from developing countries in Asia with the largest emitting region including China and India. Also Montzka et al. (2009) suggested a shift from high to low latitude emissions during this period, consistent with these assertions. High HCFC-22 abundances from these industrial regions of Asian developing countries are transported upwards into the Asian monsoon anticyclone during summer. Transport calculations based on meteorological analyses confirm that emissions from these regions indeed feed the Asian monsoon system (Vogel et al., 2015). After having been lifted into close-to-tropopause levels inside the Asian monsoon anticyclone, the high HCFC-22 abundances are transported into the tropical tropopause region (Fig. 12, lower panel). Transport from the Asian monsoon anticyclone into the tropical tropopause layer as a dominant source of tropical seasonality was suggested by Ploeger et al. (2012) based on model experiments, and by

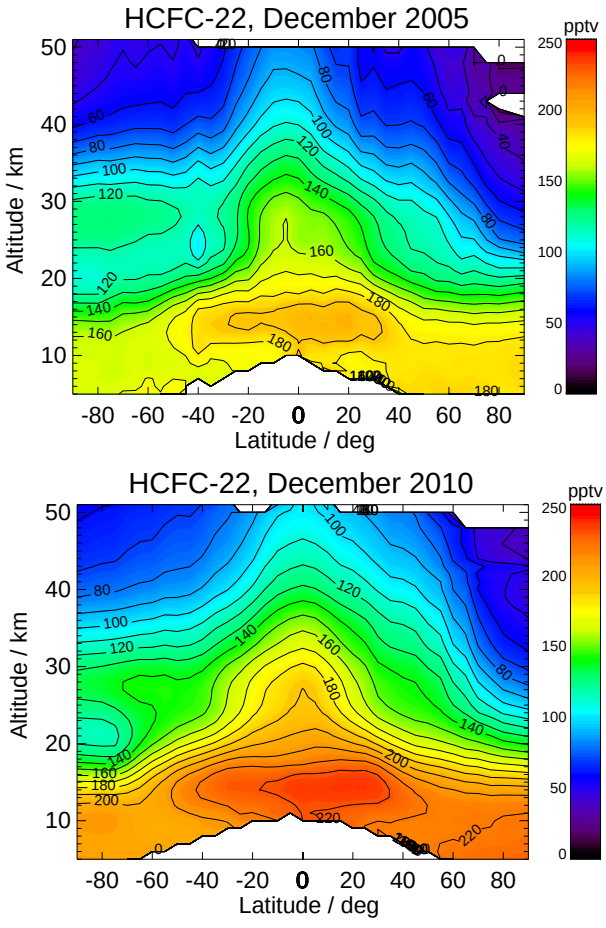

Figure 10. Monthly zonal means of HCFC-22 volume mixing ratios from 5 to 50 km for December 2005 (top) and December 2010 (bottom). The months have been selected to be approximately in the same QBO phase.

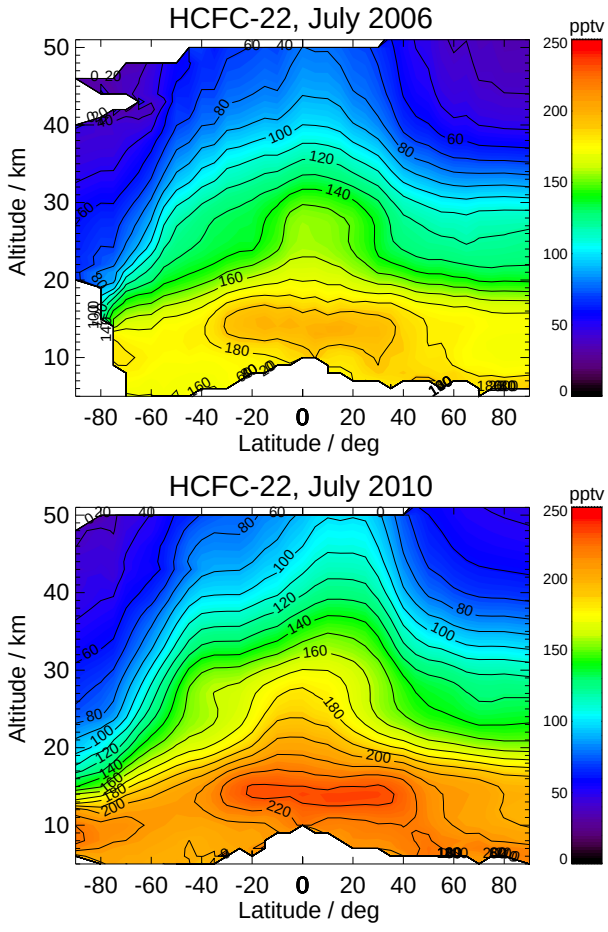

Figure 11. Same as Fig. 10, but for July 2006 (top) and 2010 (bottom)

Randel and Jensen (2013). Once intruded into the TTL, the enhanced HCFC-22 abundances are distributed over all the tropical longitudes and generate an isolated maximum layer between appr. 10 km and the tropopause. This process also may explain why the isolated HCFC-22 vmr maximum observed by MIPAS above about 10 km exceeds abundances measured at the surface at remote sites in mid-latitudes by both the Global Monitoring Division of NOAA's Earth System Research Laboratory (NOAA/GMD) and the Advanced Global Atmospheric Gases Experiment (AGAGE) (c.f. Section 5.4).

~~Highest HCFC-22 vmrs, on an absolute scale, of up to 240 pptv at the end of the observation period, occur at altitudes between 10 and 15 km at 30 - 50°N during boreal summer (compare Fig. 14). Fig. 15 for 14 km altitude demonstrates that these high amounts, probably related to the Asian monsoon anticyclone, are transported into the TTL and subsequently distributed over the tropics, providing the isolated maximum layer of up to 225 pptv in the tropics. The following scenario is suggested: high HCFC-22 abundances from industrial regions of Asian developing countries are transported upwards into the Asian monsoon anticyclone during summer. This is plausible since HCFC-22 production was not restricted for developing countries during the relevant time, and some of these countries, e.g. China, have been large HCFC producers for years, while HCFC-22 production is controlled by the Montreal protocol for industrialised countries. Indeed, Saikawa et al. (2012) found a surge in HCFC-22 emissions between 2005 and 2009 from developing countries in Asia with the largest emitting region including China and India. Also Montzka et al. (2009) suggested a shift from high to low latitude emissions during this period, consistent with these assertions. Hoyle et al. (2011) demonstrated that atmospheric models produce vertical profiles of (however short-lived) chemical tracers with a local maximum just below the tropical tropopause. They explained their findings by rapid uplift of tracers due to deep convection, leaving less time for chemical conversion than outside the convective towers. This process would explain why the isolated HCFC-22 vmr maximum observed by MIPAS above about 10 km exceeds abundances measured at the surface by the Global Monitoring Division of NOAA's Earth System Research Laboratory at remote mid-latitude sites (c.f. Section 5.4). After having been lifted into close-to-tropopause levels inside the Asian monsoon anticyclone, the high HCFC-22 abundances are transported into the tropical tropopause region. Transport from the Asian monsoon anticyclone into the tropical tropopause layer as a dominant source of tropical seasonality was suggested by Plöger et al. (2012) based on model experiments, and by Randell et al. (2013) Once intruded into the TTL, the enhanced HCFC-22 abundances are distributed over all the tropics (compare Fig. 15, panel 2) and generate an isolated maximum layer between appr. 10 km and the tropopause.~~

5.2 Time series analysis of HCFC-22 for various altitudes and latitudes

The MIPAS HCFC-22 data presented here cover the so-called reduced resolution phase from January 2005 to April 2012. The instrument did not measure continuously in the nominal mode. This leads to frequent data gaps, but they are relatively short on average (1 to 2 days, occasionally longer). Some days were filtered out as well, since they contain too few measurements, and for certain phases there are data gaps in certain latitudes due to calibration measurements always performed at the same latitudes.

The averaged global time series of HCFC-22 volume mixing ratio from January 2005 to April 2012, including all latitudes from the South to the North Pole is shown in Figure 13. The global mean HCFC-22 volume mixing ratio increases at all altitudes with time. The global mean HCFC-22 volume mixing ratio at, for example, 16 km altitude was about 161 pptv in January 2005, and it increased up to about 210 pptv by April 2012. This provides us with a rough estimate of the

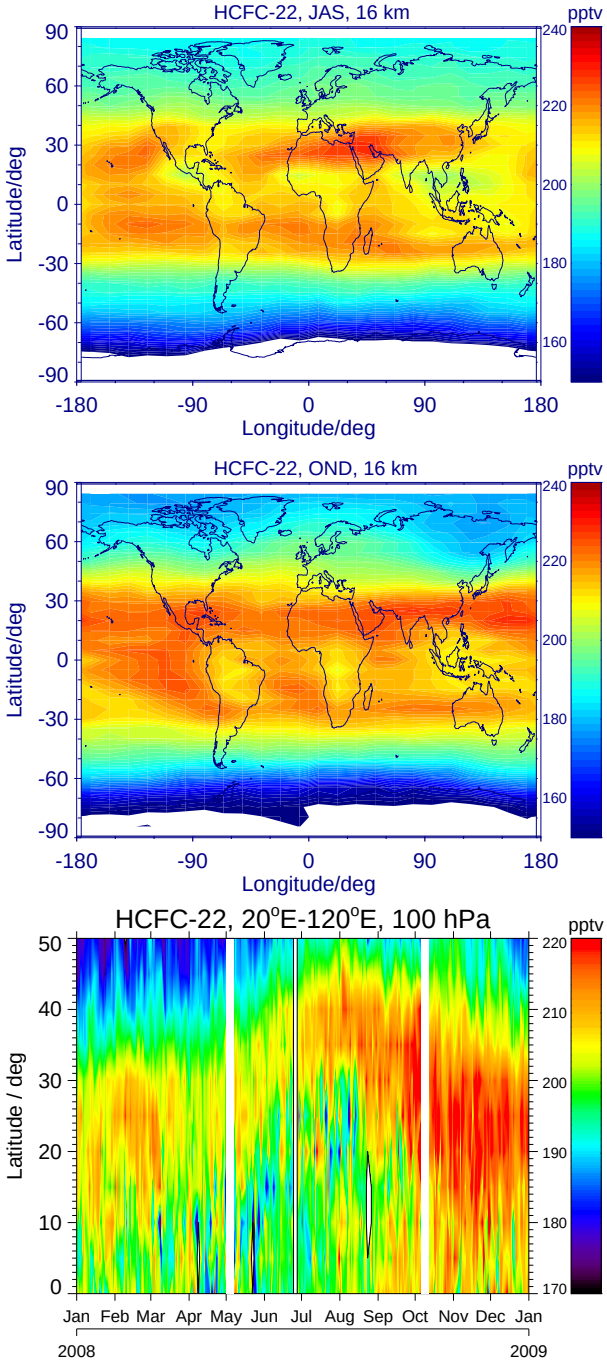

Figure 12. Top panel: Global HCFC-22 distribution in July/August/September for the years 2005 to 2011 at 16 km altitude. An enhancement over the Asian monsoon region is clearly visible. Middle panel: Global HCFC-22 distribution in October/November/December for the years 2005 to 2011 at 16 km altitude. The maximum previously located over the monsoon region has spread over all longitudes now. Bottom panel: The temporal development of HCFC-22 in the Asian monsoon region (i.e. daily averaged over 20°E to 120°E and shown for 0° to 50°N in 5° bins) at 100 hPa for the year 2008. Enhanced values are seen to propagate towards the tropics from August on.

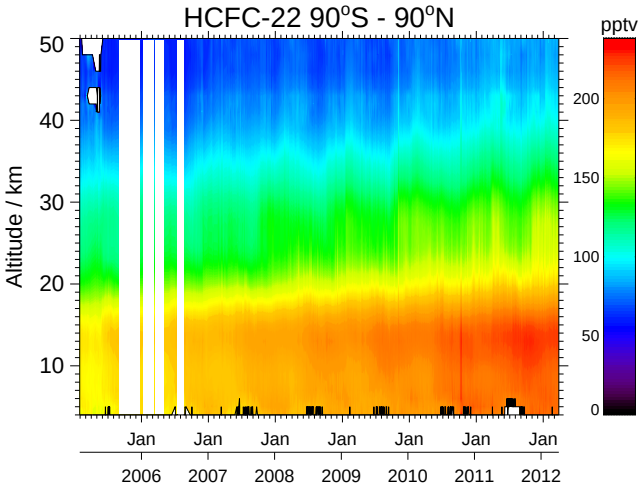

Figure 13. The globally averaged time series of HCFC-22 volume mixing ratio from January 2005 to April 2012.

increase of HCFC-22 content: it had increased by 49 pptv in 7 years, which is roughly 7 pptv per year.

For a more detailed analysis, we consider the mean mixing ratios in 20° latitude bands (Fig. 14 and 15). In these figures, it is again visible that the zonal mean abundance of HCFC-22 over the equator is much higher than over the poles at similar altitudes. In addition to the latitude dependence of the absolute volume mixing ratios, the oscillations due to the seasonal cycle are more pronounced at higher latitudes for the stratosphere, while a pronounced seasonal cycle in the upper troposphere can also be found at 30°N–50°N. In the stratosphere at the poles, any displacement of the polar vortex from the poles or its deformation will, in a 2D representation, cause numerical mixing, and by zonal averaging the sharp vortex boundaries are smeared out. In contrast, a breakup of the polar vortex would finally lead to physical mixing. In a 2D representation, physical and numerical mixing cannot be distinguished in any obvious way, but both processes would explain a rapid increase of stratospheric zonal mean polar HCFC-22 mixing ratios. Indeed, the onset of polar stratospheric wave activity has been verified to coincide in time with the observed increase of polar stratospheric HCFC-22 abundances.~~the break-up of the polar vortex, the latter being marked by low HCFC-22 abundances, results in a sharp increase of HCFC-22 in hemispheric spring.~~ Interestingly, the sudden increase of polar stratospheric HCFC-22~~the break-up of the vortex~~ seems to take place at all altitudes at almost the same time for the northern polar region, while for the southern polar region the increase of HCFC-22 is observed to start~~a break-up starting~~ at around 30 km and to slowly move~~moving~~ down. Thus~~visible as higher HCFC-22 abundances occurring first around 30 km and~~ low HCFC-22 abundances are observed to last~~lasting~~ longer at lower alti-

tudes, can be observed. This is explained by the fact that the increase at the northern latitudes is caused by wave activity along with numerical mixing as discussed above, while in the southern hemisphere it is caused by the breakdown of the polar vortex. The first kind of processes happens almost at the same time at all altitudes, while the vortex break-down is known to start at higher altitudes and to proceed downwards.

In this context it is also interesting to see that a local maximum of HCFC-22 appears just after austral vortex break-up around 30 km altitude (most pronounced in the years 2009 to 2011), which indicates that young HCFC-22-rich air from low latitudes is rapidly transported into the polar region at these altitudes. A similar observation has been made within the analysis of global distributions of mean age of stratospheric air (AoA) (Stiller et al., 2012).

In mid-latitudes in the middle and upper stratosphere, there is no clear seasonal cycle visible, while at lower altitudes, in the so-called lowermost stratosphere (below 20 km), the maxima are shifted towards hemispheric late summer/fall. This is consistent with the current picture of the phases of the Brewer-Dobson circulation, where the extratropical lowermost stratosphere is thought to be flooded by young tropical air during summer when the subtropical jet forms a weak mixing barrier only (Bönisch et al., 2011; Birner and Bönisch, 2011; Stiller et al., 2012).

Figure 16 provides the time series of HCFC-22 as latitude-time cross sections for certain altitude levels. At 10 and 14 km, high seasonality in the northern subtropical latitudes with maxima during summer and caused by the Asian monsoon uplift is obvious. Around 20 km a clear seasonal cycle at high latitudes can be seen. Around 30 km, a QBO variation in the tropics modulates the seasonal variation, while at 44 km the pattern is dominated by the semi-annual oscillation.

RevisitingComing back to Figure 13, it is obvious that the globally averaged distribution of HCFC-22 vmr in the stratosphere reveals also seasonal oscillations. While one might expect that NH and SH seasonal cycles average perfectly out on a global scale, this seems not to be the case. This is due to the fact that the SH seasonal cycle is not quite in the opposite phase to the cycle in the NH (see Fig. 16). In addition, the HCFC-22 seasonal cycle in the SH is more pronounced than in the NH, which is attributed to theprobably because of a more stable polar vortex which dominates the SH seasonal cycle. Hence, the seasonal cycle in the SH has a higher amplitude and thus causes a residual seasonal cycle on a global scale, and is not globally compensated but only weakened by the cycle of the NH. The hemispheric tropospheric means of HCFC-22 vmr (Figure 16, top panel) for the NH are generally higher than for the SH. This is due to higher industrial production of HCFC-22 in the NH.

5.3 Trend of HCFC-22

We have analysed time series of monthly means at specific altitudes for 10°-wide latitude bands by fitting the following

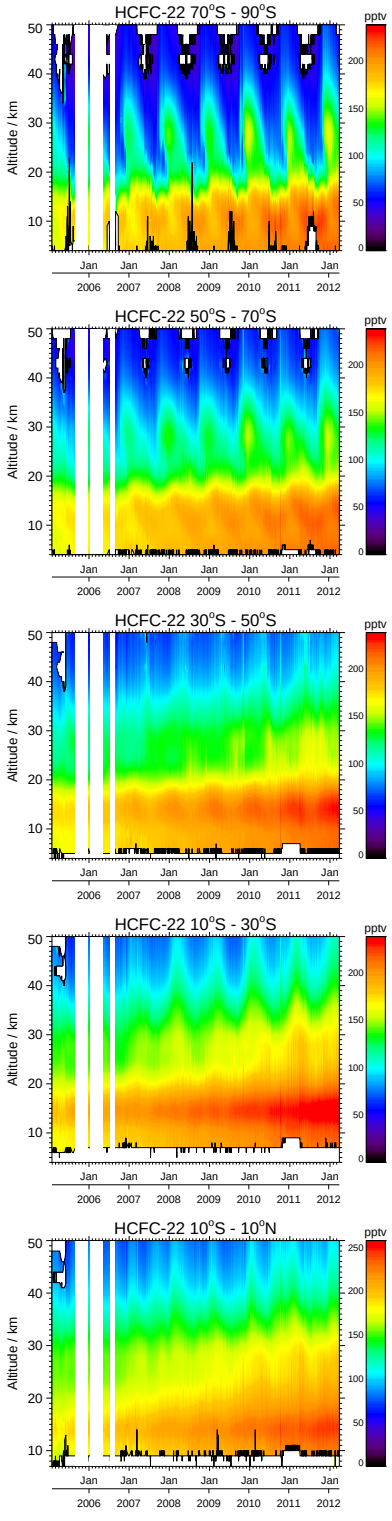

Figure 14. Time series of HCFC-22 vmrs from January 2005 to April 2012 for 70°S to 90°S, 50°S to 70°S, 30°S to 50°S, 10°S to 30°S and 10°S to 10°N (from top to bottom), generated from daily zonal means. White areas in the plots represent MIPAS data gaps. At low altitudes these are caused by clouds, while at high altitudes they are caused by a too low sensitivity of MIPAS. Data gaps covering all altitudes are associated with times when MIPAS did not measure.

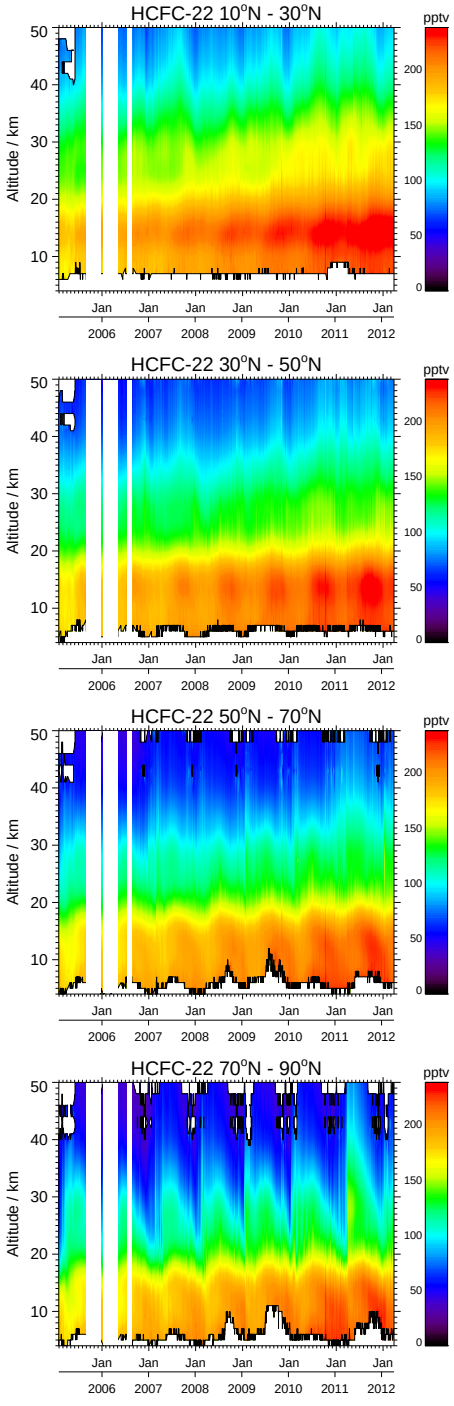

Figure 15. As Fig. 14, but for 10°N to 30°N, 30°N to 50°N, 50°N to 70°N and 70°N to 90°N (from top to bottom).

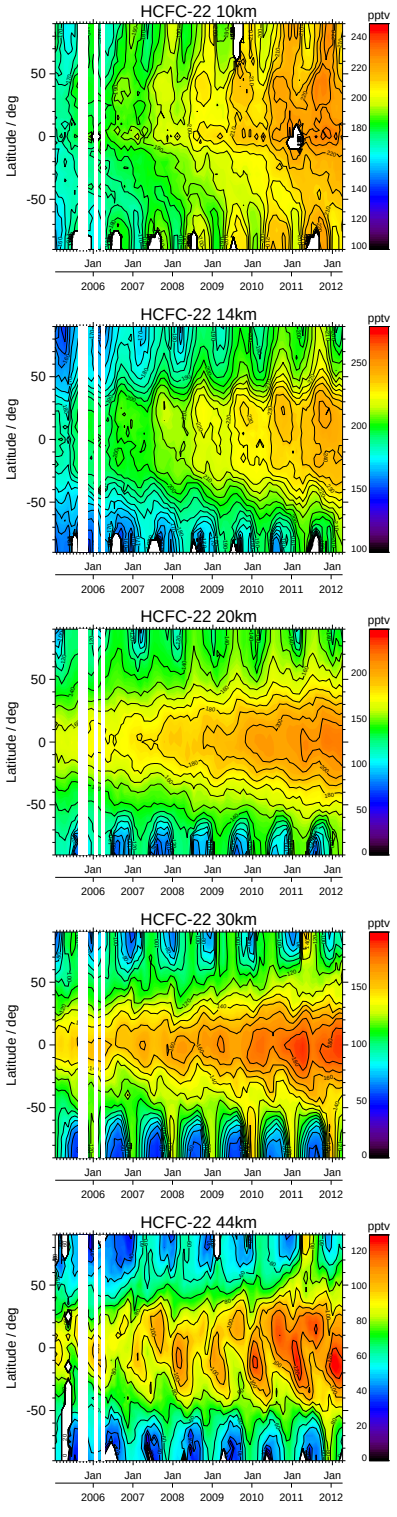

Figure 16. Latitude - time cross sections of HCFC-22 vmrs from January 2005 to April 2012 for altitudes of (from top to bottom) 10 km, 14 km, 20 km, 30 km, and 44 km, generated from monthly zonal mean data. Note different colour bars for different panels.

regression function to the data:

$$vmr(t) = a + bt + c_1 qbo_1(t) + d_1 qbo_2(t) + + \sum_{n=2}^{9} (c_n \sin \frac{2\pi t}{l_n} + d_n \cos \frac{2\pi t}{l_n}), \quad (1)$$

where t is time, a is the axis intercept, and b represents the linear component of the temporal variation, which for reasons of simplicity we call "trend", without claiming that it has any climatological meaning beyond the time window under investigation. qbo_1 and qbo_2 are QBO indices, and the terms under the sum are 8 sinusoidal functions of the period length l_n. The terms qbo_1 and qbo_2 are the normalized Singapore winds at 30 and 50 hPa as provided by the Free University of Berlin via http://www.geo.fu-berlin.de/met/ag/strat/produkte/qbo/index.html. qbo_1 and qbo_2 are approximately orthogonal such that their combination can emulate any QBO phase shift (Kyrölä et al., 2010). Coefficients a, b, c_1, ..., c_9, d_1, ..., d_9 are fitted to the data using the method by von Clarmann et al. (2010), where the full error covariance matrix of the HCFC-22 data is considered, with the squared standard errors of the mean (SEM) of the monthly zonal means as the diagonal terms. Further, a constant model uncertainty error term has been added to the data error covariance matrix, which represents the deficiencies of the regression model with respect to the true atmospheric variation and was, within an iterative procedure, scaled such that the resulting $\chi^2_{reduced}$ of the trend fit was close to unity, corresponding to combined data and model uncertainties consistent to the fit residuals. Since we cannot exclude that these perturbations to be accounted for by this additional error term have a typical duration of more than one month, covariance terms between adjacent data points were also considered in order to account for the resulting autocorrelation. Phase shifts of the variations are represented by common use of sine and cosine functions of the same period length. The first and the second sinusoidal functions represent the seasonal and the semi-annual cycles, and have the periods of 12 and 6 months, respectively. ToIn order to model the deviations of the temporal variation from pure sine or cosine shapes, i.e. to allow for irregular shapes like sawtooth shapes etc., the period lengths of the remaining 6 terms under the sum are chosen to be equal to 3, 4, 8, 9, 18 and 24 months. The general strategy of this particular fitting has been described in Stiller et al. (2012).

Figure 17 provides some examples for time series and their fits for 3 different latitude bins and two altitudes. (40°S to 50°S, 0° to 10°S, and 50°N to 60°N, at 20 and 30 km, respectively). The lower panel of each figure provides the residuals between measured and fitted time series. The simple model is able to represent the observations very well in most cases. Besides the linear increase, for all altitude/latitude bins, a more or less pronounced seasonal cycle is the dominant feature of the time series. In the southern mid-latitudes, a clear QBO signal is also present. For the northern mid-latitudes at 30 km, we see also the impact of the semi-annual variation. The highest amplitudes in the temporal variation are reached in the 60° regions; in the inner tropics, the amplitudes are lower, particularly in the lowermost stratosphere. A strong linear increase is present in all altitude/latitude bins and varies considerably.

Fig. 18 summarizes the derived decadal trends for all latitude/altitude bins. The trend is positive for all latitude and altitude bins and highly significant (significance of 5σ or more). In the lowermost stratosphere below 20 km the trend is between 40 and 50 % per decade, while it varies between 30% per decade in the northern middle and high latitudes between 20 and 30 km, 50 to 60% per decade in the southern mid-latitudes from 20 to 50 km, and 70 to more than 100% per decade in the northern upper stratosphere at middle and high latitudes. The maximum of absolute trends is in the northern suptropics around 15 km, supporting our hypothesis that this region is fed by the strongly increasing East Asian emissions. In contrast, the relative trends are not highest in this region, due to the strongly enhanced volume mixing ratios measured there.

Recent HCFC-22 trends derived by earlier works for various time periods, altitudes and latitudes are summarized in Table 3 and compared to MIPAS-derived trends. It has to be noted that the relative trends are based on varying reference vmrs, most of which are not even reported. For this reason we discuss here the comparison of absolute trends only. In general, the trends derived from MIPAS observations are higher than the trends already published. The only exception are the trends at high southern latitudes by Moore and Remedios (2008) that were derived from a combination of ATMOS and MIPAS observations, and that are somewhat higher than our MIPAS-derived trends. One reason for the higher trends found by MIPAS is the inclusion of the Asian monsoon region in the zonally averaged trend data that are compared to the trends derived by other works, while those trends usually refer to single locations at remote sites. Moore and Remedios (2008) have published growth rates of HCFC-22 in the lower stratosphere (approximately 20 km) between 20°N and 50°N for the years 1994 to 2004 of 5.4±0.7 pptv/yr (3.5±0.4%/yr); between 60°S and 80°S they found 6.0±0.7 pptv/yr (4.3±0.5%/yr) for the years 1994 to 2003. These values compare well to the growth rates found for the period 2005 to 2012 from MIPAS (see Fig. 17, left column, and Fig. 18). Rinsland et al. (2005a) published the following growth rates for lower stratospheric HCFC-22 vmrs near 30°N latitude from ATMOS/ACE-FTS measurements: in 1985 the rate was 14.57±4.10%/yr, in 1994 it was 6.35±2.24%/yr, and in 2004 it was 3.92±2.08%/yr. Our growth rate of 4 to 5%/yr agrees reasonably well with the growth rate found for 2004.

The time series derived from Kitt Peak ground-based solar absorption measurements (Rinsland et al., 2005b) covers October 1987 to November 2002 with a best-fit increase rate of 5.66±0.15 pptv/yr for the 2.09 - 10 km trend. Compared

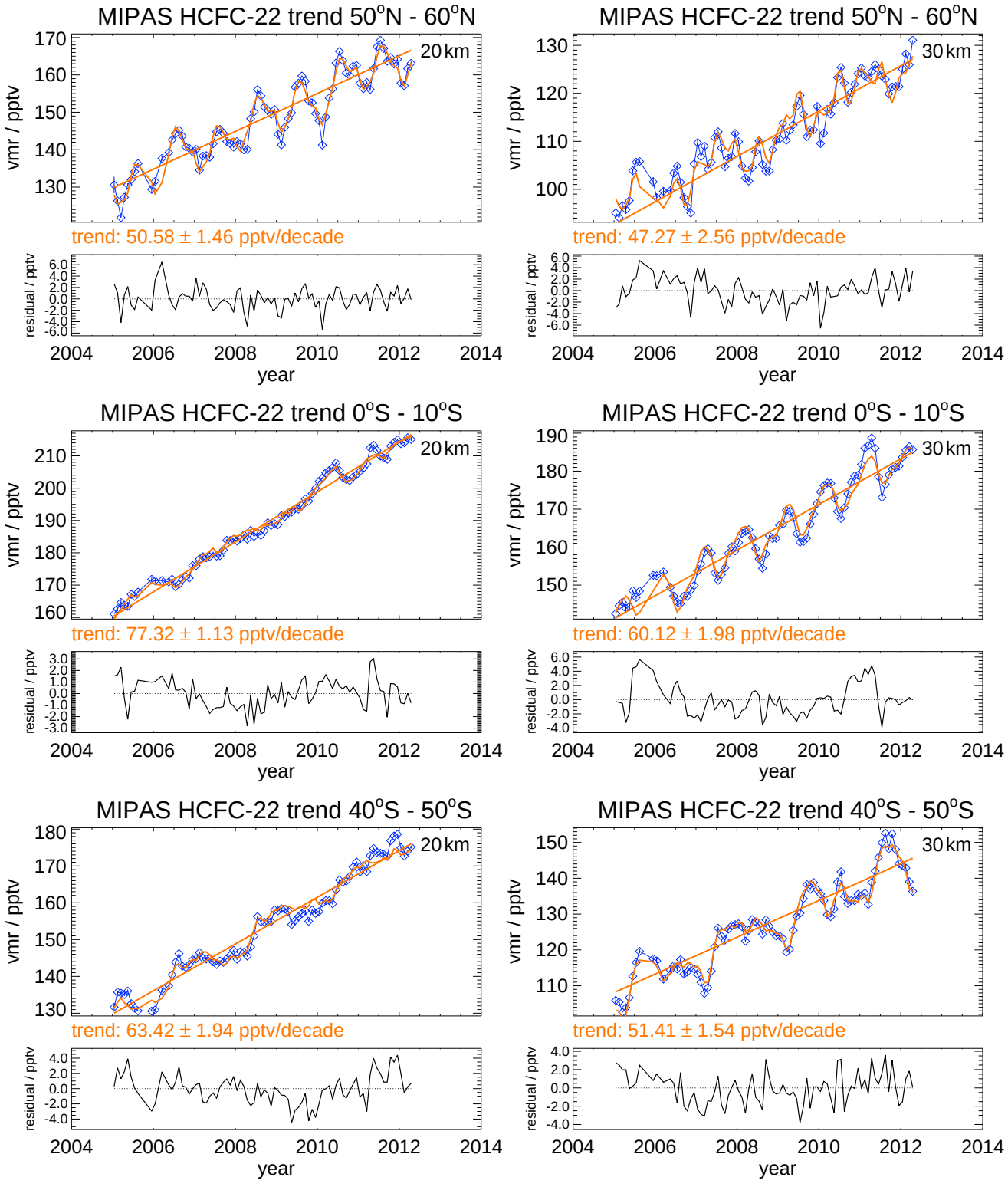

Figure 17. Time series of HCFC-22 volume mixing ratios (blue symbols) and their fits with the regression function described in the text (orange curves) at 20 km (left) and 30 km (right) altitude in three latitude bins. The linear trend component of the multi-parameter fit (straight orange line) is also shown.

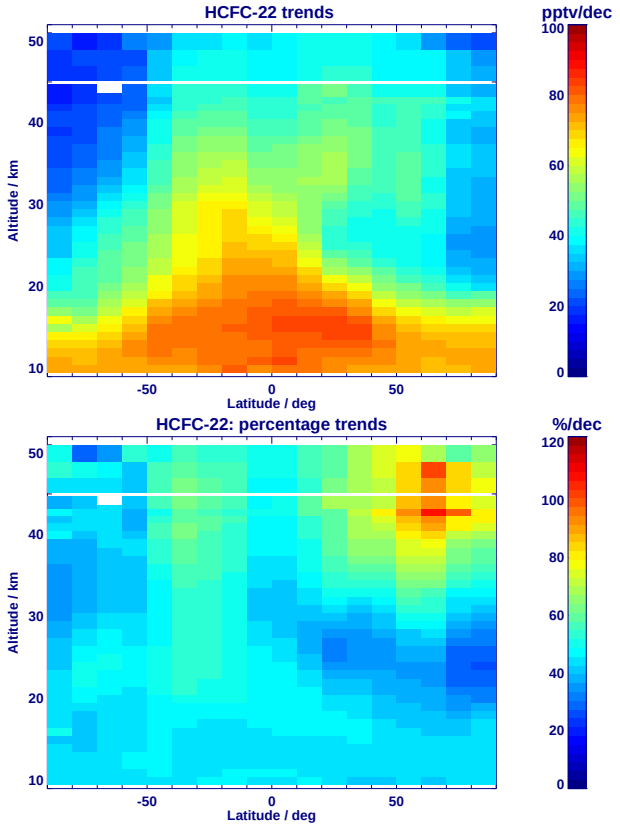

Figure 18. Trend of HCFC-22 volume mixing ratio for all latitude/altitude bins, in absolute units (pptv/decade) (top) and as percentage per decade relative to the background distribution in 2005 (i.e. the constant term of the regression analysis, see Eq. 1) (bottom). For the percentage trends, autocorrelations have been considered in the fit.

~~to this the tropospheric growth rate around 30°N derived from MIPAS for 2005 to 2012 is higher with a value around 7 pptv/year. Sherlock et al. (1997) derived exponential and linear increase rates of HCFC-22 between May 1985 and November 1994 at the station Lauder, New Zealand, of 7.5±0.3%/yr and 5.9±0.2%/yr. The growth rates derived from MIPAS for the lower stratosphere around 60°S are somewhat lower with 4 to 5%/yr.~~

5.4 Comparisons between upper tropospheric and surface growth rates ~~Comparisons with surface measurements of tropospheric growth rates~~

Two networks perform regular, long-term and highly precise near-surface measurements of various tracers, among them HCFC-22~~, close to the ground~~: these are the NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) and the Advanced Global Atmospheric Gases Experiment (AGAGE). Although not directly comparable, because MIPAS observations do not reach ~~to~~ the ground, we compare here mean tropospheric values (below 10 km altitude) retrieved from MIPAS data with the surface observations from NOAA/GMD and AGAGE, making use of the fact that within each hemisphere the free troposphere can be considered well-mixed in the altitude domain. This assumption is confirmed by aircraft measurements (Xiang et al., 2014). In this context it should be noted that surface measurements are reported as dry air mole fraction, while MIPAS~~stratospheric~~ measurements are reported in mixing ratios where the air with its actual water vapour content is the reference. Since the stratosphere is very dry where MIPAS measures, this makes no discernable difference. Near surface, however, this difference has to be taken into account but since air dries during uplift, the surface dry air mole fraction is exactly the quantity which is comparable to the MIPAS~~our stratospheric~~ values.

5.4.1 The Surface Networks

NOAA/GMD: NOAA/GMD runs flask measurements at remote site since 1992 (Montzka et al., 2009, 2015). These data are reported on the NOAA–2006 scale. These data are available via ftp://ftp.cmdl.noaa.gov/hats/hcfcs/hcfc22/flasks/. Global HCFC-22 data from NOAA/GMD in units of mole fraction in dry air at ground level are shown in Figure 19 for various measurement sites from the South Pole to the high Arctic. The data are not filtered for any pollution events, resulting in some enhanced values for the stations Trinidad Head and Mace Head that are occasionally influenced by nearby emissions. The MIPAS HCFC-22 monthly mean values for latitude bands selected to match the latitudes of the stations, averaged over all altitudes below 10 km, are shown for comparison with the same colour code as the respective station data.

~~Overall NOAA data and MIPAS upper tropospheric values show a good agreement and similar trends. While according to MIPAS the HCFC-22 global mean below 10 km altitude (not shown) increased from 161 pptv to 211 pptv between January 2005 and April 2012, the NOAA ground-based global mean for these months were 164 pptv and 216 pptv, providing an increase of 50 (MIPAS) and 52 (NOAA) ppt, respectively. The growth rate derived from NOAA/GMD data for the NH is only slightly higher than that inferred from MIPAS measurements below 10 km (52 vs. 49 ppt over 7 years).~~

~~In the SH, tropospheric MIPAS values are mostly significantly higher than the NOAA values and reach the NOAA values only during their seasonal minima (Fig.19). The reason is roughly this. MIPAS, whose measurements refer to the upper troposphere and above, sees more advected air from the tropical outflow, and the signal is modulated by a pronounced seasonal cycle, while the related ground-based measurements are clean-air measurements. This hypothesis is in tendency confirmed by SH aircraft measurements (e.g. Xiang et al., 2014), where an indication of higher mixing~~

Table 3. Recent trends of HCFC-22 depending on time period, altitude and latitude from earlier publications, compared to MIPAS-derived trends at the respective altitude/latitude.

Source	Time interval	Latitude/Altitude	Absolute trend / pptvyr^{-1}	Relative trend / %yr^{-1} [a]	MIPAS-derived trend / pptvyr^{-1}	MIPAS-derived trend / %yr^{-1}
Moore and Remedios (2008)	1994 – 2004	20°N–50°N / 20 km	5.4 ± 0.7	3.5 ± 0.4[b]	6.15 ± 0.24	4.24 ± 0.16
	1994 – 2003	60°S–80°S / 20 km	6.0 ± 0.7	4.3 ± 0.5[b]	4.88 ± 0.10	4.55 ± 0.09
Rinsland et al. (2005a)	1985	30°N / lower strat.		14.57 ± 4.1[c]		
	1994	30°N / lower strat.		6.35 ± 2.24[c]		
	2004	30°N / lower strat.		3.92 ± 2.08[c]	7.60 ± 0.21	4.56 ± 0.12
Rinsland et al. (2005b)	1987–2002	30°N / 2–10 km	5.66 ± 0.15	6.47 ± 0.17[b]	7.54 ± 1.53	4.32 ± 0.87
Brown et al. (2011)	2004–2010	30°S–30°N / 8–17 km	6.56 ± 0.20	3.7 ± 0.1[b]	8.02 ± 0.03	4.48 ± 0.02

[a] The reference vmrs on which the relative trends are based vary from data set to data set.
[b] Linear fit.
[c] Derivatives at the respective years from a parabolic fit.

ratios at higher altitudes is found, which is attributed to transport of NH air into the SH at higher altitudes in lower latitudes. It is interesting to see that among the SH time series, the seasonal cycle in MIPAS data is strongest for the southern polar latitude band, while the minima reached within this time series are the lowest among all latitude bands. This strong seasonal cycle is also visible in Fig. 16 and indicates flooding of the southern polar UTLS region with low-latitude air around the time of the polar vortex breakdown.

The MIPAS measurements show smaller differences between the hemispheres than the NOAA measurements. This is explained by the fact that MIPAS observes air at altitudes where the outflow of the tropical pipe contributes to the composition of air. Assuming that air uplifted within the tropical pipe is mixed between both hemispheres offers an explanation for the reduced hemispheric contrast in the MIPAS data. Also these findings are in agreement with those of Xiang et al. (2014).

Finally, the most obvious difference between NOAA/GMD surface time series and zonally averaged MIPAS upper troposphere time series is the pronounced seasonal cycle in the latter, with minimum values during NH spring and SH summer. Xiang et al. (2014) observed a seasonality in NOAA surface measurements of HCFC-22 with minima in northern summer and attributed this to increased scavenging through the OH radical reaction and seasonality in the transport. The best explanation of the observed seasonality, however, relies on an additional seasonality of the emissions of refrigerants with maxima in summer. This seasonality of emissions was derived by inverse modelling of aircraft measurements (Xiang et al., 2014). While OH scavenging and seasonal variations in transport could possibly explain the summer minimum observed by MIPAS in the SH, the springtime minimum in the NH is more probably related to intrusion of HCFC-22-poor stratospheric air at the end of the polar winter and during polar vortex breakdown. Similar springtime minima were also observed for other tropospheric source gases and have been attributed to stratospheric air intrusions (Nevison et al., 2004, 2011). The fact that the minima in the MIPAS time series at higher altitudes precede those at lower altitudes (c.f. Fig. 15, lowermost panel and Fig. 16) supports this. The amplitude of the seasonal cycle seems to be even more enhanced due to transport of high HCFC-22 abundances uplifted within the Asian monsoon anticyclone to higher latitudes during fall (compare Fig. 16, top panel).

AGAGE: AGAGE provides in situ measurements of a wide range of ozone depleting compounds and greenhouse gases, including HCFC-22, from several ground stations (Prinn et al., 2000, 2013; O'Doherty et al., 2004). AGAGE measurements used here are obtained using in situ gas chromatography with mass spectrometry (GC-MS) detection technique and are reported on the SIO-2005 calibration scale. NOAA flask results and AGAGE in situ data are compared every six months at common sites. Comparison of HCFC-22 from NOAA flasks, using the NOAA–2006 calibration scale to AGAGE in situ measurements based on the SIO-2005 calibration scale at Cape Grim, Samoa, Trinidad Head and Mace Head reveal the following differences: The average difference (NOAA minus AGAGE) across the 4 sites is -0.7 ± 0.5 ppt or 0.35 ± 0.25%. The differences are also relatively constant with time. These results are also very consistent to those found in the International Halocarbons in Air Comparison Experiment (Hall et al., 2014).

Figure 20 shows the HCFC-22 time series of these stations, which represent various latitude bands from northern to southern mid-latitudes. The variation among the values from different stations represent the inter-hemispheric differences of HCFC-22: NH values are about 10% higher than SH values, due to the main sources of HCFC-22 being located in the NH. Again, we have inserted for comparison MIPAS HCFC-22 global monthly mean values averaged for all altitudes below 10 km. The MIPAS data generally agree well with the tropical time series from the AGAGE

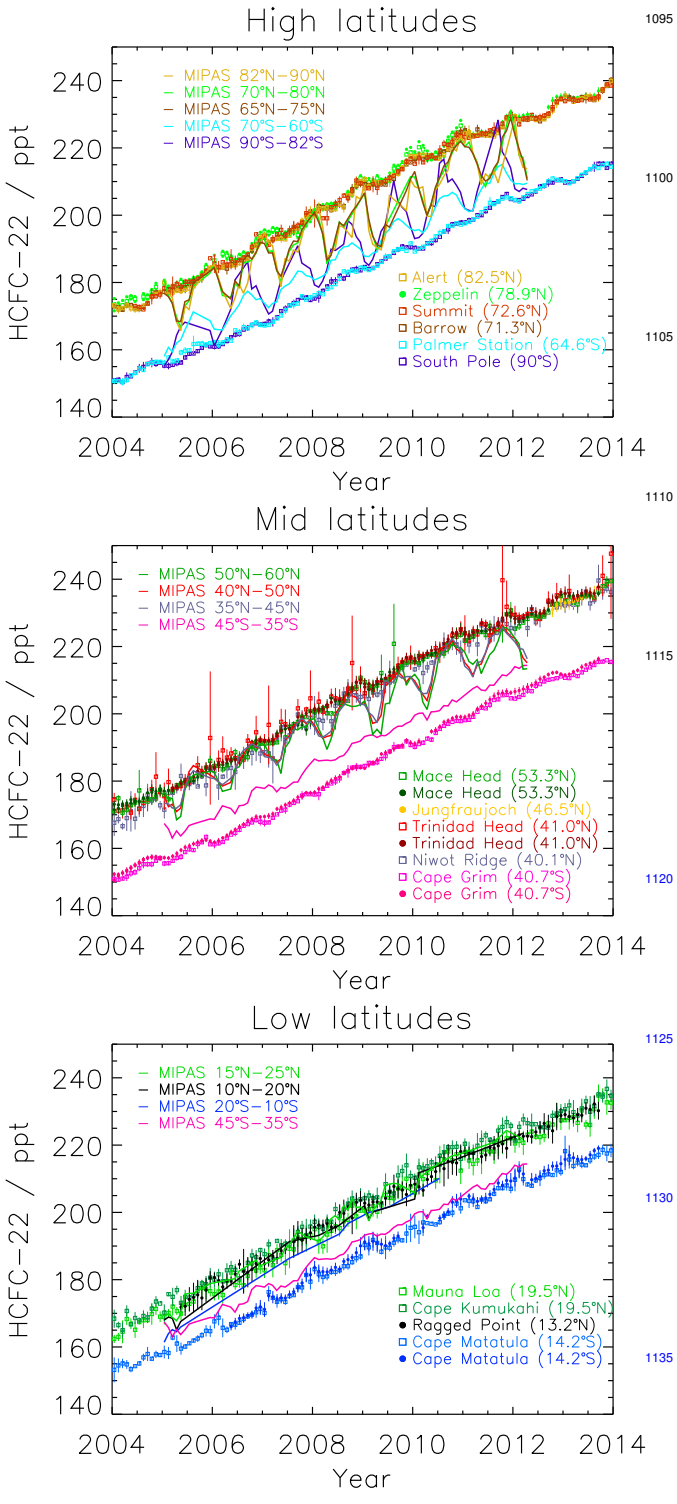

Figure 19. Comparison of HCFC-22 time series from several stations of the NOAA/GMD program and the AGAGE program with corresponding MIPAS values. Open squares: NOAA/GMD monthly mean data from several stations (see legend for colour code); filled circles: AGAGE monthly mean data from several stations (see legend for colour code); solid lines without symbols: MIPAS monthly mean data for 10° latitude bands around the respective station latitude; the colour coding matches that of the stations. The tick marks at the horizontal axis mark the beginning of the years. Top panel: high latitudes (between 60° and 90°N/S); middle panel: mid-latitudes (between 30° and 60°N/S); bottom panel: low latitudes (between 30°S and 30°N.)

~~network, both in absolute values and in the growth rate. As already seen in the NOAA comparison, the seasonal cycle in MIPAS data in the NH is far more pronounced and its amplitude increases towards high latitudes. Maximum values fit perfectly to AGAGE station data in the NH. The same explanation applies that was offered in the previous section: Arctic winter subsidence of HCFC-22-poor stratospheric air modulates the upper tropospheric NH time series with a northern winter/spring minimum.~~

~~The SH upper tropospheric annual cycle is not exactly in the opposite phase of its northern counterpart. The latitudes of the SH stations shown in this comparison are, however, generally lower than the latitudes of the NH stations. At these low latitudes the upper tropospheric air is not modulated that much by polar processes but by the change of the position of the intertropical convergence zone and the Hadley cell. In local summer these latitudes are affected by the outflow of the tropical pipe, providing young HCFC-22-rich air. This hypothesis is corroborated by the fact that the MIPAS time series at 45°S–35°S (pink full circles in Fig. 20) follows nicely the Cape Matatula (Samoa) (13°S, blue open squares) time series, while it appears to be uncorrelated with the Cape Grim (Tasmania) (42°S) data.~~

5.4.2 Comparison with MIPAS

Although NOAA/GMD and AGAGE provide independent data sets, no appreciable differences were found in any respect discussed here relative to MIPAS. Despite quite different approaches to making the measurements (in situ high frequency at relatively few sites compared to low frequency flask measurements at more sites), the surface data show the same broad features, distributions, seasonality, and trends. Thus, both data sets are discussed relative to MIPAS results together.

Overall, surface data from both networks and MIPAS upper tropospheric mixing ratios of HCFC-22 show a good agreement and similar trends (Figs. 19). The interhemispheric differences of the surface data are clearly visible, with mole fractions in the northern hemisphere being larger by about 10% than SH values, due to the main sources of HCFC-22 being located in the NH. MIPAS upper tropospheric mixing ratios agree best with tropical surface measurements, reflecting the fact that uplift of surface air is dominated by tropical processes.

In the SH, tropospheric MIPAS values are mostly significantly higher than the surface values at the same latitudes and reach these, if any, only during their seasonal minima (Fig. 19, top and middle panel). The reason is roughly this. MIPAS, whose measurements refer to the upper troposphere and above, sees more advected air from the tropical outflow, and the signal is modulated by a pronounced seasonal cycle, while the related ground-based measurements are clean-air measurements. This hypothesis is in tendency confirmed by SH aircraft measurements (e.g. Xiang et al., 2014), where

an indication of higher mixing ratios at higher altitudes is found, which is attributed to transport of NH air into the SH at higher altitudes in lower latitudes. It is interesting to see that among the SH time series, the seasonal cycle in MIPAS data is strongest for the southern polar latitude band (see Fig. 19, top panel), while the minima reached within this time series at the end of Antarctic summer are the lowest among all latitude bands. This strong seasonal cycle is also visible in Fig. 16 with maxima in polar southern spring and indicates flooding of the southern polar UTLS region with low-latitude air around the time of the polar vortex breakdown.

The MIPAS measurements show smaller differences between the hemispheres than the surface measurements. This is explained by the fact that MIPAS observes air at altitudes where the outflow of the intertropical convergence contributes to the composition of air. Assuming that air uplifted within the tropical pipe is mixed between both hemispheres offers an explanation for the reduced hemispheric contrast in the MIPAS data. Also these findings are in agreement with those of (Xiang et al., 2014).

Finally, the most obvious difference between surface time series and zonally averaged MIPAS upper troposphere time series is the pronounced seasonal cycle in the latter, with minimum values during NH spring and SH summer (see Fig. 19, top and middle panel). It is far more pronounced in the NH mid-latitudes than in the SH mid-latitudes and its amplitude increases towards high latitudes.

Xiang et al. (2014) observed a seasonality in the surface measurements of HCFC-22 with minima in northern summer and attributed this to increased scavenging through the OH radical reaction and seasonality in the transport. The best explanation of the observed seasonality, however, relies on an additional seasonality of the emissions of refrigerants with maxima in summer. This seasonality of emissions was derived by inverse modelling of (Xiang et al., 2014) aircraft measurements.

MIPAS maximum values fit perfectly to those of surface stations in the NH. While OH scavenging and seasonal variations in transport could possibly explain the summer minimum observed by MIPAS in the SH, the springtime minimum in the NH is more probably related to intrusion of HCFC-22-poor stratospheric air at the end of the polar winter and during polar vortex breakdown. Similar springtime minima were also observed for other tropospheric source gases and have been attributed to stratospheric air intrusions (Nevison et al., 2004, 2011). The fact that the minima in the UTLS in the MIPAS time series at higher altitudes precede those at lower altitudes (c.f. Fig 15 lowermost panel and Fig. 16, top two panels) supports this. The amplitude of the seasonal cycle seems to be even more enhanced due to transport of high HCFC-22 abundances uplifted within the Asian monsoon anticyclone to higher latitudes during fall (compare Fig. 16, top panel).

The SH upper tropospheric annual cycle is not exactly in the opposite phase of its northern counterpart. The latitudes of the SH stations shown in this comparison are, however, generally lower than the latitudes of the NH stations. At these low latitudes the upper tropospheric air is not modulated that much by polar processes but by the change of the position of the intertropical convergence zone and the Hadley cell. In local summer these latitudes are affected by the outflow of the tropical pipe, providing young HCFC-22-rich air. This hypothesis is corroborated by the fact that the MIPAS time series at 45°S–35°S (pink solid line in Fig. 19) follows nicely the Cape Matatula (Samoa) (14.2°S, blue open squares and filled circles) time series, while it appears to be uncorrelated with the Cape Grim (Tasmania) (40.7°S) data (pink open squares and filled circles).

While according to MIPAS the HCFC-22 global mean below 10 km altitude (not shown) increased from 161 pptv to 211 pptv between January 2005 and April 2012, the NOAA ground-based global mean for these months were 164 pptv and 216 pptv, providing an increase of 50 (MIPAS) and 52 (NOAA) ppt, respectively. The growth rate derived from NOAA/GMD data for the NH is only slightly higher than that inferred from MIPAS measurements below 10 km (52 vs. 49 ppt over 7 years).

5.5 Unexplained stratospheric trends

Differences between the MIPAS stratospheric percentage trends (relative to the HCFC-22 vmr in 2005) and the tropospheric trends corrected for AoA from NOAA/GMD are shown in Fig. 20. We used the NOAA/GMD global trends, extended linearly with a slope of 57 ppt/decade before 1992, and AoA from Stiller et al. (2012), according to the method described in Kellmann et al. (2012). We would like to stress that we do not necessarily expect the stratospheric trends to reproduce the tropospheric ones with a time lag depending on the AoA, because stratospheric circulation could change, affecting the time lag and possibly the level of HCFC-22 change in the air parcel observed. Furthermore the AoA spectrum could, in the case of a non-linearly increasing species, render the mean AoA non-representative. However, for an atmosphere without changes in stratospheric dynamics and δ-shaped age spectra, the differences shown in Fig. 20 are expected to be zero throughout. In contrast, we find positive and negative trend differences of up to 40 percent. The HCFC-22 trend in the northern mid-latitude lower stratosphere (15 - 30 km) is slightly smaller (up to -10%) than the trend at the ground at the time the air started its travel into the stratosphere, while in the southern mid-latitudes, the HCFC-22 trend is larger than the trend observed at surface level over all the stratosphere. In the polar regions, the trend is up to 40% lower at the South pole, and up to 40% higher at the North pole and the northern mid-latitudes. This pattern of trend differences is in agreement with the patterns found for CFC-11 and CFC-12 (Kellmann et al., 2012), and is in accordance with the AoA trends found by Stiller et al. (2012). Positive AoA trends in the northern mid-latitudes below 30

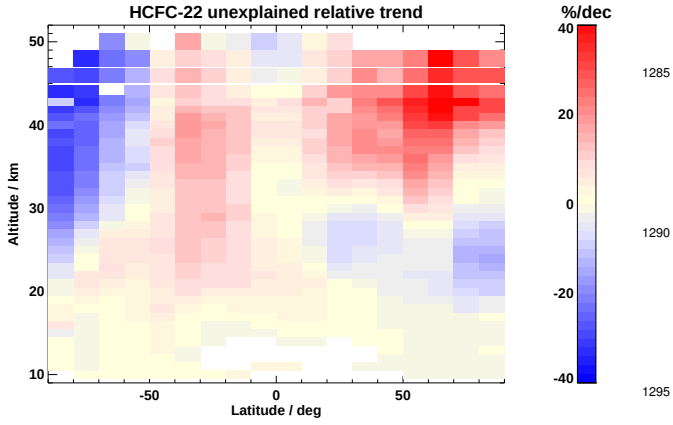

Figure 20. Differences between MIPAS stratospheric relative trends (referenced to the HCFC-22 background distribution in 2005, i.e. the constant term of the regression analysis (see Eq. 1) and relative trends at ground measured by the NOAA/GMD program (global means), the latter corrected for the time lag between the air parcels' start in the troposphere and its arrival in the stratosphere.

km and the southern polar region lead to increasingly longer exposure of HCFC-22 to loss processes in the stratosphere, and thus to a reduction of the positive HCFC-22 trend, while the general positive HCFC-22 trend is further increased in regions where the AoA becomes younger, leaving less time for stratospheric HCFC-22 loss processes. It should be noted that any incorrect assumption on AoA as such, used within the correction of surface trends, cannot explain both the positive and negative signs in the trend differences. The surface trend was slightly increasing all over the observation period covered by NOAA/GMD measurements, thus the correction by the AoA should always lead to smaller trends. Any incorrect assumption on the AoA would lead to incorrect differences, which, however, had always the same positive or negative sign. Thus, the occurrence of positive and negative trend differences is an unambiguous sign that the circulation must have changed over the MIPAS observation period. Our results further show that these circulation changes were different in the northern and southern mid-latitudes, as was concluded from the AoA data inferred from the MIPAS SF_6 data record (Stiller et al., 2012). These results confirm the hypothesis of Stiller et al. (2012) of interhemispheric asymmetries in circulation changes, for which further evidence has been found by Eckert et al. (2014) (interhemispheric asymmetries in decadal MIPAS ozone trends), Nedoluha et al. (2015) (interhemispheric asymmetries in decadal trends of N_2O from the Microwave Limb Sounder (MLS)), and Mahieu et al. (2014) (HCl trends and modelled age-of-air trends).

6 Summary and conclusions

HCFC-22 data from MIPAS for the period 2005 to 2012 were produced and analysed. Version 5 level-1b reduced resolution MIPAS measurements (nominal mode) of the period from 27 January 2005 to 8 April 2012 were inverted using the MIPAS IMK/IAA scientific data processor. The profile retrieval was performed by Tikhonov-constrained non-linear least squares fitting of measured limb spectral radiances. The total error of the retrieval is 7% on 20 km height and 9% on 30 km height, and the error budget is dominated by noise. A typical retrieved profile represents approximately 5 degrees of freedom, corresponding to an altitude resolution of typically between 3 km at 10 km height and 7 km at 30 km height, further increasing with height. The percentage of non-converged profiles is about 0.01 to 0.02 %.

The obtained profiles obtained were compared with ACE-FTS satellite data (v3.5), as well as with MkIV balloon profiles and in situ measurements performed by the University of Frankfurt. The comparisons are ambiguous with respect to a bias of MIPAS measurements; in general we can state that MIPAS agrees within ± 15 pptv (1σ) with ACE-FTS and MkIV the reference measurements. Between 13 km and 22 km, good agreement with MkIV and ACE-FTS profiles is demonstrated. A high bias of 30–50 pptv relative to cryosampler measurements was found below 24 km but no bias was found for higher altitudes.

The global distribution of HCFC-22 vmr reflects the mean circulation in the stratosphere and reveals also seasonal oscillations. The HCFC-22 annual cycle in the SH is more pronounced than in the NH. The HCFC-22 volume mixing ratio in the NH troposphere is generally higher than in the SH, due to main emission sources residing there. A volume mixing ratio maximum is situated at about 16 km height at low latitudes, which exceeds mixing ratios measured at all remote surface sites in the NH or SH. We attribute this to advection to low latitudes of HCFC-22-rich air uplifted in the Asian monsoon area. The source of this HCFC-22-rich air could be South-East Asia. United Nations Environment Programme, 2012 reports that China has been the largest global producer and consumer of HCFCs for a number of years.

A multi-variate regression analysis was performed for 10°-latitude/1-2 km altitude bins, with terms for linear variations, sinusoidal variations with various periods, and a proxy for the QBO variation. We find positive linear trends for all latitude/altitude bins, ranging from 83 pptv/decade in the northern subtropical lower stratosphere to 18 pptv/decade in the southern polar upper stratosphere. The absolutepercentage trends are in the range ofagree well with previous analyses. Percentage trends are highest in the southern mid-latitudinal stratosphere (50-70%/decade) and in the northern polar upper stratosphere (70 to 120 %/ decade) and lowest in the northern lowermost stratosphere (around 30%/decade). The highest seasonal amplitudes are observed in the 60° regions; in the tropical lower stratosphere the amplitudes are low.

Global NOAA/GMD, AGAGE and MIPAS tropospheric values show good absolute agreement and similar trends. Based on the absolute values of HCFC-22 from MIPAS and on the MIPAS derived HCFC-22-growth rate, one can conclude that the HCFC-22 global volume mixing ratio in the lower stratosphere has risen by 49 pptv in 7 years. A pronounced seasonality has been detected in the upper troposphere with minima in spring in the NH and in local summer in the SH. The latter is attributed to the seasonality of the main tropical uplift and outflow regions. The seasonality in the NH is attributed to the intrusion of HCFC-22-poor stratospheric air at the end of the Arctic winter. Inconsistencies in percentage trends between ground-based and age-corrected MIPAS stratospheric trends hint at recent changes in stratospheric circulation. Similar indication has been found by analysis of trends of the mean AoA (Stiller et al., 2012), ozone (Eckert et al., 2014) and CFC-11 as well as CFC-12 (Kellmann et al., 2012). A more detailed analysis of these circulation changes is currently under investigation.

MIPAS HCFC-22 data presented here can be downloaded after registration from http://www.imk-asf.kit.edu/english/308.php. The HCFC-22 trends shown in Figs. 18 and 20 are provided as numerical values in the Supplement.

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