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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Trends of HCl, $ClONO_2$ and HF column abundances from ground-based FTIR measurements in Kiruna (Sweden) in comparison with KASIMA model calculations" *by* R. Kohlhepp et al.

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Answer to the report of anonymous referee # 1

We thank referee # 1 for his/her constructive comments regarding our manuscript. In the following, citations from the referee report are written in italics.

- *Page 1490, line 11: This sentence "The relative trends were calculated on the basis of the linear fit result on 1 January 2000" is unclear. Clarify what is meant by calculating the trend based on the value of the linear part of the fit on 1 January 2000. Also Page 1494, lines 22-23.*
  The sentence in the abstract was deleted.
  On page 1494, the lines 22-23 were rewritten to: "and the time t in years relative to 1 January 2000 (12:00 UTC) and the fitting parameters p_j. Herein, p_1 is the value of the linear part of the fit on 1 January 2000 (12:00 UTC) because, by definition, $t = 0$ on this date. The absolute trend or rather slope of the linear (in units molec/cm^2) is represented by $p_1 p_2$, so that p_2 can be interpreted as the relative trend because it results from the absolute trend when normalising by p_1."

- *Page 1493, line 11 and Figure 1: Define what is meant by the height-dependent sensitivity. Does Figure 1 show total column averaging kernels or sensitivity as defined by Vigouroux et al., ACP, 2008?*
  Yes, it shows the sensitivity as defined by Vigouroux et al., ACP, 2008. This information was added in the manuscript as follows: "The sensitivity shown here is defined as the sum of the columns of the averaging kernel matrix. That means the elements of the averaging kernels were summed up for every height level as described by Vigouroux et al.(2008). This sensitivity is quite good in the stratosphere (about 15 to 50 km) as the values are nearly equal to 1, while in the troposphere, it is much smaller, especially for $ClONO_2$."

- *Page 1493, line 22: State which errors term(s) constitute the statistical error. Does statistical error = random error? What are the total errors? Is there a reference for how the errors are calculated? Explain why the $ClONO_2$ error is so much larger than those for HCl and HF.*
  In the statistical (=random) error, noise is included, as well as errors induced by the temperature profile used, the solar lines, the varying line of sight (LOS), the instrumental line shape (ILS) uncertainty and the baseline uncertainty in the spectra. This statistical error is assumed to decrease with an increasing num-

ber of measurements. The systematic errors in the measurements resulting for example from possibly wrong line parameters are not expected to considerably influence the trend results.
To the manuscript, we added: "The $ClONO_2$ random error is much larger than those of HF and HCl because $ClONO_2$ is more difficult to retrieve from the measurements due to its weak spectral signature and the relatively low total column abundances especially in summer."

- *Page 1493, Section 3: State whether the KASIMA model profiles were smoothed by the FTIR averaging kernels and a priori profiles, as described by Rodger and Connor, JGR, 2003.*
  No, they were not. The effect is considered to be small because in this study, we only investigate the total column abundances.

- *Page 1494, para 2: State here how the evolution of CFCs and HCFCs is treated in the model. Page 1499, para 1 indicates that they are prescribed. That information could be included here.*
  The time evolution of the global surface volume mixing ratios of the ozone-depleting substances is prescribed at the lower model boundary according to the so-called baseline scenario Ab which is a best-guess scenario following the Beijing Amendments in 1999 of the Montreal protocol (for more information on the scenario see chapter 1 of the UNEP/WMO Scientific Assessment of Ozone Depletion: 2002). These data which were recommended to be used as lower boundary conditions for the WMO Ozone assessment 2007 are provided in the framework of the SPARC CCMVAL initiative via http://www.pa.op.dlr.de/CCMVal/Forcings/Halogens/CCMVal_halocarbons_REF2.txt
  Concerning what was added to the manuscript, please have a look at the answer to the comment of Referee # 2 with respect to the same topic.

- *Page 1494, para 2: State what model data are extracted for the comparisons –*

at the nearest model gridpoint to Kiruna (if so, state latitude and longitude), or an average of nearby gridpoints?
To compare the KASIMA model data with the FTIR measurements the model data are interpolated to the location of Kiruna from the circumjacent grid points. This information was also added to the manuscript. Please see the answer to the comment of Referee # 2.

- *Page 1494, line 15: Explain, or give a reference for, why a third order Fourier series is used to account for the annual cycle, rather than, for example, a simpler sinusoidal function.*
  The following sentence was added: "When calculating trends of stratospheric and tropospheric trace gases from measurements by FTIR instruments, Gardiner et al. (2008) found that a third order Fourier series was the best balance between representing the time series and avoiding to over-fit the data. "

- *Page 1494, lines 20-24: This section would benefit from revision to clearly define the absolute trend and the relative trend. Why is p2 the relative trend? Isn't it the linear trend? Is it divided by p1 to get the relative trend? But neither p1 nor p2 has an explicit dependence on time, so what is meant by "the linear part of the fit on 1 January 2000"?*
  We rewrote the paragraph, please also have a look at the answer to the first comment. The fit has a linear "part" ($p_1(1 + p_2 t)$) from which the trend can be determined, and a part considering the annual cycle (called $A(t)$ in equation (1)). Due to the definition of t here, it is zero for 1 January 2000 (12:00 UTC) so that the linear part of the fit on this date only consists of p_1. The term $A(t)$ also depends on time, but it is not necessarily zero for $t = 0$. As explained in the rewritten paragraph, the absolute trend $p_1 p_2$ can be normalised with p_1 (which is the value of the linear part of the fit on 1 January 2000, 12:00 UTC) so that a relative linear trend p_2 results.

- *Page 1496, para 2: Can you explain how it is possible for the HF trend from 1996-2002 can be the same as the trend from 1996-2009, when there is no trend from 2002-2009? This seems mathematically unlikely.*
  A time period of 7 years obviously is too short to determine a statistically significant trend in this case. The trend result depends on the start and end date or rather time of year, even with the third order Fourier series term being included. Moreover, a different sampling at the beginning of the time series in 1996 might influence the trend (see Fig. 2). It was only to document the tendency of the HF total column abundance to stabilise in the last few years why the trends were calculated for these two shorter time periods.
  Moreover, as visible in Fig. 2, the end of the fit to 1996-2002 does not correspond to the beginning of the fit to 2002-2009. If we had coupled these two trend calculations, i.e. fitted a function consisting of two linear ones with a break at the beginning of 2002, the described mathematically unlikely situation would probably not have occurred. Because we calculated the trends separately, we can see the influence of sampling and of the annual cycle on the trend determined for such a short time series.

- *Page 1496, lines 12-13: Why is August-November defined as summer? The vortex dissipates well before August and can start to reform in the fall.*
  The reason we defined summer like that was that the $ClONO_2$ total column abundances especially in June and July show larger scatter than before and afterwards. In general, its spectral signature is comparably weak. And in June and July, the total column abundances reach a minimum value, while H_2O, which is one of the interfering species in the micro-window used for the $ClONO_2$ retrieval, has comparably high column abundances so that it is even more difficult to determine the $ClONO_2$ abundance. For HCl and HF, the time of year chosen as "summer" was adapted to the $ClONO_2$ one.
  But finally, we recalculated the trends for the June to November period, called it

"summer/autumn" and replaced the old "summer" one. In this context, the following sentences were adapted and changed:
Page 1490, line 14 (in the abstract): The sentence was rewritten, also because it is more logical and consistent with HCl and $ClONO_2$ not to mention the summer/autumn results here. It now reads: "Between 1996 and 2009, KASIMA simulates an increase of $(+1.51 \pm 0.07)\%$/yr which exceeds the FTIR result of $(+0.65 \pm 0.25)\%$/yr."
Page 1496, line 12 was changed to: "When using only the measurements between June and November ("summer/autumn") and fitting just the linear part of function (1), the FTIR trend is stronger than for all data [...]."
Page 1498, line 3: The summer/autumn trends for HCl do not agree within errors anymore, so the first two sentences of the paragraph were rewritten to: "When the linear part of function (1) is fitted to the data between June and November ("summer/autumn"), the HCl and $ClONO_2$ trends from KASIMA are larger and those from FTIR smaller than for the respective whole time series so that the trends from model and measurements become more alike (Table 2)." Page 1499, line 8 was changed to: "When using the summer/autumn data only and fitting a linear trend, the KASIMA and FTIR results become more similar [...]."
Page 1499, line 13, the two sentences were changed to the following one: "The time series from the FTIR spectrometer shows a weaker increase of the HF total column abundances than the KASIMA one."
Page 1500, line 9, the following sentence was deleted: "As mentioned above, this is also the case for the HF trends."

- *Page 1496, lines 14-15: How does the KASIMA summer trend compare with the KASIMA summer trend for FTIR days only?*
  In Tables 1 and 2, the results for the KASIMA summer/autumn trend on FTIR days were added for the three gases.
  For HF, one sentence was added and one (the second one here) was changed

slightly: “When the KASIMA results on FTIR days are reduced to the summer/autumn period, a slightly but not significantly larger trend than for all KASIMA data on FTIR days is found. These investigations suggest a strong influence of sampling and of the seasonal cycle on the trend calculated from the HF measurements.”
For HCl and $ClONO_2$, the following sentence was added: “The trend of $ClONO_2$ from the KASIMA data on FTIR days in summer/autumn is even closer to the FTIR summer/autumn results, while for HCl, the sampling influence is negligible again. Still, as the error bars are larger for the KASIMA data on FTIR days in summer/autumn, they overlap with the ones of nearly all other trend results.”

- *Page 1498, lines 14-16: Why not compare FTIR and KASIMA stratospheric partial columns? Does prescribing the lower boundary condition mean using a fixed 0-7 km partial column for KASIMA or a mixing ratio at 0 km or 7 km? Clarify. State approximately what percentage of the total HCl column is represented by the lowest 0-7 km. Is this also the case for HF and $ClONO_2$? If so, provide the same information.*
  The lower boundary of KASIMA is at 7 km pressure altitude. Mass fluxes of chemical constituents over this lower boundary are calculated by assuming no vertical gradient of the chemical constituent below the lower boundary. Assuming constant volume mixing ratios between 0 and 7 km of 50 pptv for HCl, 20 pptv for HF, and 1 pptv for $ClONO_2$ as an upper approximation, the partial column in this altitude range over Kiruna is in the order of about 6×10^{14} molec/cm^2 for HCl, 1×10^{13} molec/cm^2 for $ClONO_2$, and 2×10^{14} molec/cm^2 of HF representing about 10% in the maximum with respect to the total column of these substances.

- *Page 1499, line 5: Define the WMO 2007 Ab scenario.*
  The definition of the Ab scenario which is used for the WMO ozone assessment 2007 is given in our remark concerning the question of the treatment of the CFC and HCFC in the model (see above).

- *Page 1499, line 23: Are the HCl and $ClONO_2$ trends statistically significant?*
  The error bars of the trends calculated with the bootstrap method are smaller than the trends themselves, so the 95% confidence intervals don’t include zero. From this, we conclude that the trends of HCl and $ClONO_2$ are significantly negative. It is only the statistical (=random) error on the measurements which is important for the trend calculation because a systematic error leading to a constant offset would only very slightly influence the relative trend result. The statistical error from the measurements is automatically included in the bootstrap error bars because an increased random error increases the root mean square difference (RMSD) between data and fit, and the bigger this RMSD is, the larger will be the error bar determined by bootstrap resampling.

- *Page 1499, line 26: What is meant by “all methods used here”?*
  This expression was supposed to include the trends calculated from all KASIMA data between 1996 and 2009, from the KASIMA data on FTIR measurement days only, from the summer/autumn data only... But this part of the sentence was deleted so that it now reads: “The relative trends from KASIMA are weaker than those calculated from the measurements.”

Technical Corrections

- The use of “respectively” was corrected throughout the manuscript.

- *Page 1490, line 2: TOTAL columns*
  Was added.

- *Page 1490, line 6: state that KASIMA is a chemical transport model*
  Was done.

- *Page 1490, line 27: change “absolute values” to “total columns” throughout the paper, as this is a more meaningful description of the quantity being compared.*

Was changed in this sentence and removed on p. 1498, l. 12.

- *Page 1490, last paragraph: It would be more logical to discuss the agreement between the modeled and measured columns before discussing the agreement in the trends. Make this the second paragraph in the Abstract?*
  We changed the order of the paragraphs as suggested.
- *Page 1491, line 2: "have been suspected to be able" is awkward – "have been known to", "have been predicted to"*
  It was changed to "have been predicted to deplete".
- *Page 1491, line 4: in THE Southern Hemisphere spring, which*
  Was added.
- *Page 1492, line 24: as A source of radiation*
  It was changed to "as the source of radiation".
- *Page 1493, line 17: usually DOFS (degrees of freedom for signal) rather than DOF*
  Was changed.
- *Page 1494, line 8: "using . . . analyses until 2002 respectively from 2003 on, . . ." is unclear - rewrite*
  The sentence or rather the whole paragraph was rewritten, please see the answer to the comment of Referee # 2.
- *Page 1494, line 21: "As can be seen from Equation (1), the parameter . . ."*
  This expression was removed when the paragraph was rewritten.
  On page 1495, line 23, the use of "function" was changed to "the function in Equation (1)".
- *Page 1495, lines 5 and 14: change function (1) to Equation (1)*
  It was changed to "the function defined by Equation (1)".

- *Page 1495, line 23: "fluorine, unlike the case for chlorine and bromine."*
  Was changed.
- *Page 1496, line 23: time series IS cut*
  It was not changed because "series" was intended to be plural here, corresponding to the HF time series from FTIR and KASIMA.
- *Page 1497, lines 4, 16, 17; Page 1498, line 24, Page 1499, line 11; etc.: stick with HF, HCl and $ClONO_2$ throughout, once the chemical symbols are defined*
  It was changed accordingly.
- *Page 1497, lines 18-19: It is not clear what is being compared here – clarify: "And on the other hand, the absolute trends agree within their errors, like the ones from the measurements:"*
  We changed the sentence to: "And like the ones from the measurements, the absolute trends of HCl and $ClONO_2$ from the KASIMA data agree within their errors" so that now hopefully it is clearer that the absolute trends of HCl and $ClONO_2$ agree within their errors, and that this is the case both for the KASIMA simulations and for the measurements.
- *Page 1498, line 9: change catch to capture*
  Was done.
- *Page 1498, line 10: "is more pronounced in the data than in the model results."*
  The sentence was changed to: "This particularly concerns the FTIR data as the annual cycle is more pronounced in the measurements than in the model results." (We did not use the suggested sentence because a few times in the manuscript, the expression "model data" has been used so that "data" not only refers to the measurements, but sometimes also to the model results.)
- *Page 1498, line 17: "processes, for example, wash-out, have . . ."*
  Was corrected.

- *Page 1498, line 28: delete first*
  We did not do this but changed the sentence in order to make it clearer: "One reason for the good agreement might be that the tropospheric $ClONO_2$ partial column is negligible and the argument concerning the prescribed tropospheric partial columns in KASIMA does not apply strongly to $ClONO_2$."

- *Page 1499, lines 8 and 22: correct the use of "respectively"*
  Was done.

- *Page 1499, line 27: change It to This*
  Was done.

- *Page 1500, line 1: change station to measurements*
  The word "station" was deleted and not replaced because "measurements" is already used in the sentence before.

- *Page 1500, lines 3 and 10: correct the use of "respectively"*
  Was corrected (removed).

- *Figure 1 caption: Define sensitivity. Give the solar zenith angles of the six spectra?*
  The caption was rewritten to: "Height dependency of the sensitivity of the retrieval as defined by Vigouroux et al.(2008) for HF (blue line), HCl (red line) and $ClONO_2$ (green line). The curves shown represent mean values each calculated from six arbitrary spectra with different solar elevation angles ranging from about 2 to 38 °."

- *Figure 2 caption: Correct the use of "respectively"*
  Was done.

Other changes

- In the acknowledgements, the following sentence was added: "We acknowledge support by Deutsche Forschungsgemeinschaft and Open Access Publishing Fund of Karlsruhe Institute of Technology."

- The tables 1 and 2 were changed slightly: In the captions, we added the sentence "The time range considered is 1996–2009 (unless otherwise identified)." and removed the column containing the time ranges because especially for summer/autumn (June–November), the notation was a little confusing.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 1489, 2011.