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# Trends of HCl, $ClONO_2$ and HF column abundances from ground-based FTIR measurements in Kiruna (Sweden) in comparison with KASIMA model calculations

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## Abstract

Trends of hydrogen chloride (HCl), chlorine nitrate ($ClONO_2$) and hydrogen fluoride (HF) column abundances above Kiruna (Northern Sweden, 67.84° N, 20.41° E) derived from nearly 14 years (1996–2009) of measurement and model data are presented. The measurements have been performed with a Bruker 120 HR (later Bruker 125 HR) Fourier transform infrared (FTIR) spectrometer and the model used was KASIMA (KArlsruhe SImulation model of the Middle Atmosphere). To calculate the long-term trends, a linear function combined with an annual cycle was fitted to the data using a least squares method. The precision of the resulting trends was estimated with the so-called bootstrap resampling method. The relative trends were calculated on the basis of the linear fit result on 1 January 2000, 12:00 UTC.

For hydrogen fluoride, both model and measurements show a positive trend that seems to decrease in the last few years. This suggests a stabilisation of the HF total column abundance. For the summer data (August to November), the FTIR trend of $(+1.25 \pm 0.28)$%/yr agrees within errors with the KASIMA one of $(+1.55 \pm 0.11)$%/yr.

The trends determined for HCl and $ClONO_2$ are significantly negative over the time period considered here. This corresponds to the expectations because the emission of their precursors (chlorofluorocarbons and hydrochlorofluorocarbons) has been restricted in the Montreal Protocol in 1987 and its amendments and adjustments. The relative trend for $ClONO_2$ from the FTIR measurements amounts to $(-3.28 \pm 0.56)$%/yr and the one for HCl to $(-0.81 \pm 0.23)$%/yr. KASIMA simulates a weaker decrease: For $ClONO_2$, the result is $(-0.90 \pm 0.10)$%/yr and for HCl $(-0.17 \pm 0.06)$%/yr. Part of the difference between measurement and model data can be explained by sampling and the stronger annual cycle indicated by the measurements. There is a factor of about four between the trends of HCl and $ClONO_2$ above Kiruna for both measurement and model data.

The absolute values of $ClONO_2$ and HF calculated by KASIMA agree quite well with the FTIR measurements while KASIMA tends to underestimate the HCl column abundances.





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## 1 Introduction

Since the 1970s, anthropogenic chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and halons have been suspected to be able to deplete the stratospheric ozone layer (Molina and Rowland, 1974). A few years afterwards, measurements showed a strong decrease of ozone column abundances above Antarctica in Southern Hemisphere spring which was then called the Antarctic ozone hole. As a result of this discovery, the emission of CFCs and HCFCs was restricted in the Montreal Protocol in 1987 and its amendments and adjustments.

Since then, stratospheric ozone has been monitored closely by many different measurement techniques. In addition, it is very important to know the concentration of the ozone-depleting substances to be able to check the effectiveness of the Montreal Protocol and to predict the development of the ozone layer.

From the atmospheric content of the chlorine reservoir gases hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$), it is possible to infer the amount of activated chlorine which is able to deplete ozone. Together, HCl and $ClONO_2$ represent about 90% of all inorganic chlorine in the stratosphere.

Hydrogen fluoride (HF) in the middle atmosphere results nearly exclusively from the photodissociation of anthropogenic CFCs and HCFCs and thus is a valuable indicator for man-made changes. Due to its high stability, HF is also a good dynamic tracer (Chipperfield et al., 1997). As fluorine does not play an important role in stratospheric ozone depletion, there are no direct restrictions concerning its emission like the Montreal Protocol for chlorine and bromine, for example. But it is also contained in CFCs and HCFCs, so it is expected to be influenced by the Montreal Protocol, too.

In this paper, measurements of vertical columns of hydrogen chloride, chlorine nitrate and hydrogen fluoride with a Fourier transform infrared (FTIR) spectrometer are presented and compared with results from the atmospheric chemistry transport model (CTM) KASIMA (KArlsruhe SImulation model of the Middle Atmosphere). The key question addressed is whether the expected decrease of chlorine species can already





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be seen significantly in the vertical column abundances of HCl and $ClONO_2$ above Kiruna (Northern Sweden, 67.84° N, 20.41° E) and how the HF abundances develop.

In Sects. 2 and 3, the FTIR data acquisition and the KASIMA model, respectively, are described. Section 4 explains the bootstrap method used to estimate the precision of the calculated trends. The results are presented in Sect. 5 and summarised in Sect. 6.

## 2 FTIR data

Within the "Network for the Detection of Atmospheric Composition Change (NDACC)", measurements with a Fourier transform infrared spectrometer are performed in Kiruna in a cooperation between the Swedish Institute of Space Physics (IRF) in Kiruna, Sweden, the University of Nagoya, Japan, and the Institute for Meteorology and Climate Research (IMK-ASF) at the Karlsruhe Institute of Technology (KIT), Germany. The measurements at this site were started in March 1996. For the analysis here, results until November 2009 were included so that the time series are about 14 years long.

The instrument used first was a Bruker 120 HR Fourier transform spectrometer (FTS) which was upgraded to a 125 HR in July 2007. This upgrade only consisted in a change of the electronics and the scanner motor. Since the beginning of the measurements, the spectrometer is regularly quality-controlled by cell measurements as described by Hase et al. (1999). Within the error bar of the cell measurement (a few percent), the instrumental line shape (ILS) is equivalent to the theoretical one.

In winter, Kiruna is usually influenced by the stratospheric polar vortex so that atmospheric polar processes can be investigated with the spectrometer. As Kiruna is close to the polar circle, the polar night is quite short (about 1.5 months). This is a very important aspect because for the kind of measurements analysed here, the FTIR instrument needs the sun as source of radiation.

From the obtained spectra, column abundances (and vertical profiles) of various atmospheric trace gases absorbing in the infrared spectral region are determined with the inversion code PROFFIT (Hase, 2000; Hase et al., 2004). To calculate the a priori spectra needed for the inversion process, PROFFIT uses daily temperature and pressure





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profiles for Kiruna from NCEP (National Centers for Environmental Prediction) analyses provided by the automailer system of NASA's Goddard Space Flight Center. The required spectroscopic line data was taken from the HITRAN (HIgh-resolution TRANsmission molecular absorption) 2004 database (Rothman et al., 2005). The $ClONO_2$ cross sections in this dataset were provided by Wagner and Birk (2003). For HCl and HF, a Galatry lineshape function was used (Barret et al., 2005).

The time series analysed here consist of daily mean column abundances. The HCl series contains 978 data points for the whole time period (about 14 years), the $ClONO_2$ one 1004 and the HF series 915. The numbers differ slightly because not every spectral filter region can be measured every day, for example due to weather changes.

For each of the three investigated species, the height-dependent sensitivity of the retrieval was calculated for every measured spectrum on the 45 levels used, between 0 and 85 km. Example curves for the sensitivity are shown in Fig. 1. They are mean values, each one calculated from six arbitrary spectra with different solar elevation angles. The sensitivity in the stratosphere (about 15 to 50 km) is quite good as the values are nearly equal to 1. In the troposphere, it is much smaller, especially for chlorine nitrate. The HCl measurement has about 3.1 degrees of freedom (DOF) which means the vertical resolution amounts to roughly 10 km (up to about 35 km), and for HF, 2.5 DOF can be obtained, corresponding to about 10 km vertical resolution, too (up to about 30 km). From $ClONO_2$, only the vertical column can be determined as it has only about 1.1 DOF.

The mean relative statistical error amounts to around 29% for $ClONO_2$, 1.2% for HCl and 1.5% for HF (calculated after Rodgers, 2000).

## 3 KASIMA model data

The 3-D chemistry transport model KASIMA used in this study is a global circulation model including stratospheric chemistry for the simulation of the behaviour of physical and chemical processes in the middle atmosphere (Kouker et al., 1999; Red-





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dmann et al., 2001; Ruhnke et al., 1999). The meteorological component is based on a spectral architecture with the pressure altitude $z = -H\ln(p/p_0)$ as vertical coordinate where $H = 7$ km is a constant atmospheric scale height, $p$ is the pressure, and $p_0 = 1013.25$ hPa is a constant reference pressure.

For the present study, the version as described in Reddmann et al. (2001) which yields realistic stratospheric age of air values (Stiller et al., 2008) is applied, using ERA-40 and operational ECMWF (European Centre for Medium-Range Weather Forecast) analyses until 2002 respectively from 2003 on, up to 18 km, the relaxation terms of temperature, vorticity and divergence up to 1 hPa and the prognostic part of the model above. The model consists of 63 vertical layers between 7 and 120 km and has a horizontal resolution of approximately $5.6^\circ \times 5.6^\circ$ (T21). The photolysis rates are calculated online in KASIMA using the Fast-J2 model of Bian and Prather (2002).

## 4 Trend analysis method

Largely due to Kiruna's high northern latitude, the column abundances of the investigated gases exhibit a non-negligible annual cycle. To account for this, a third order Fourier series is included in the fit function as follows:

$$f(t) = p_1(1 + p_2 t)A(t) \tag{1}$$

with

$$A(t) = \left(1 + \sum_{i=1}^{3} p_{i1}\cos(2i\pi t) + p_{i2}\sin(2i\pi t)\right) \tag{2}$$

and the time $t$ in years relative to 1 January 2000 (12:00 UTC) and the fitting parameters $p_j$. As it can be seen from the equation, the parameter $p_2$ corresponds to the relative trend, based on the value of the linear part of the fit on 1 January 2000, 12:00 UTC (i.e. the parameter $p_1$). A least squares method is used to fit function (1) to the data.





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In order to determine the confidence interval for a trend calculated like this, it is necessary to make an assumption on the distribution of the deviations of the data points from the fit. They might not be normally (Gaussian) distributed, for example due to inter-annual variations (resulting e.g. from the changing position and different development of the stratospheric polar vortex) which function (1) cannot account for. Therefore, the so-called bootstrap resampling method is applied to estimate the precision of the calculated trends (Efron, 1979; Efron and Tibshirani, 1993). This method has been used in trend studies from FTIR measurements before (Gardiner et al., 2008; Mikuteit, 2008; Vigouroux et al., 2008). It does not make any assumption on the distribution of the differences between data and least linear squares fit. It only assumes that there are enough data points for the deviations to sufficiently represent the underlying distribution themselves. The calculated deviations are added randomly (with replacement) to the best fit in order to create a new artificial data set with the same underlying distribution of the "random" effects. Now function (1) is fitted to the artificial data set which results in another value for the trend and the other fitting parameters. This resampling procedure is repeated 5000 times. From the 2.5 and 97.5 percentiles of the 5000 artificial trend values, a mean precision describing the 95% confidence interval is calculated. This would correspond to about two standard deviations if a normal distribution had been assumed instead.

## 5 Results and discussion

### 5.1 HF

As already mentioned, there are no explicit restrictions concerning the emission of fluorine like for chlorine and bromine, for example. FTIR measurements from Kitt Peak (Arizona, USA) show a strong increase of the hydrogen fluoride column abundance with $(10.9 \pm 1.1)$%/yr from 1977 to 1990 (Rinsland et al., 1991) that weakened during the 1990s: The trend from 1977 to 2001 amounts to $(4.30 \pm 0.15)$%/yr (Rinsland et al., 2002).





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For the time period investigated here (1996–2009), the trend of the HF column from the FTIR measurements in Kiruna is much weaker, but still positive: $(+0.65 \pm 0.25)$%/yr corresponding to $(+1.32 \pm 0.50) \times 10^{13}$ molec/(cm$^2$ yr) (Fig. 2).

If the time series is cut into two parts, the trend result is about the same from 1996 to 2002, but between 2003 and 2009, no change in the HF vertical column abundance is detectable (Table 1).

The trend modelled by KASIMA for HF above Kiruna over the complete time period amounts to $(+1.51 \pm 0.07)$%/yr corresponding to $(+2.49 \pm 0.12) \times 10^{13}$ molec/(cm$^2$ yr). So in this case, the model shows a stronger increase than the FTIR instrument observes. Part of the discrepancy can be explained by different sampling (Table 1): The trend from the KASIMA data on days with FTIR measurements only is weaker than that from all KASIMA data. When using only the measurements between August and November ("summer") and fitting just the linear part of function (1), the FTIR trend is nearly twice as strong as for all data and does agree with the modelled one within errors (Table 1). This suggests a strong influence of sampling and the annual cycle or rather of the polar vortex in winter and spring on the trend calculated from the HF measurements.

If the KASIMA HF series is cut into two like the FTIR one, the trend from 1996 to 2002 is stronger than the one for the whole series (Table 1). The trend between 2003 and 2009 is still positive, but relatively weak. So qualitatively, the FTIR measurements and KASIMA model calculations seem to agree on a stabilisation of the atmospheric hydrogen fluoride content. Still, one should keep in mind that when the time series are cut, the remaining ones are only 7 years long and thus too short to determine a reliable trend (see also Weatherhead et al., 1998).

### 5.2 HCl and $ClONO_2$

According to previous measurements, the total combined abundances of anthropogenic ozone-depleting substances peaked around 1992–1994 in the troposphere and in the mid to late 1990s in the stratosphere (WMO, 2007). Therefore the trends





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for the total column abundances of HCl and $ClONO_2$ from the FTIR measurements in Kiruna are expected to be negative over the time period considered here (March 1996 to November 2009). This is indeed the case, but the relative trends differ considerably: The resulting value for hydrogen chloride is $(-0.81 \pm 0.23)$%/yr and for chlorine nitrate $(-3.28 \pm 0.56)$%/yr (Fig. 3 and Table 2). The absolute trends agree within their error bars: For HCl it amounts to $(-3.83 \pm 1.10) \times 10^{13}$ molec/(cm$^2$ yr) and for $ClONO_2$ to $(-3.75 \pm 0.70) \times 10^{13}$ molec/(cm$^2$ yr).

The result for HCl from the FTIR data is consistent with measurements by the MLS (Microwave Limb Sounder) instrument aboard the Aura satellite. The relative trend determined by Froidevaux et al. (2006) for the layer between 0.7 and 0.1 hPa between 60° N and 60° S for August 2004 through January 2006 amounts to $(-0.78 \pm 0.08)$%/yr.

Compared to the FTIR measurements, both the relative and the absolute trends calculated from the KASIMA model output for about the same time period are weaker (Table 2). The relative trend for HCl from January 1996 to December 2009 is $(-0.17 \pm 0.06)$%/yr and for $ClONO_2$ $(-0.90 \pm 0.10)$%/yr. It is interesting that KASIMA also shows a disparity of about a factor of four between the relative trends of hydrogen chloride and chlorine nitrate, quite similar to the FTIR data. And on the other hand, the absolute trends agree within their errors, like the ones from the measurements: For HCl, it amounts to $(-0.67 \pm 0.25) \times 10^{13}$ molec/(cm$^2$ yr) and for $ClONO_2$ to $(-0.84 \pm 0.10) \times 10^{13}$ molec/(cm$^2$ yr).

Part of the disparity between modelled and measured trends can be explained by the slightly different start and end dates combined with the annual cycle of the considered species: When the KASIMA time series of HCl and $ClONO_2$ are started and ended exactly on the same days as the FTIR series in March 1996 respectively November 2009, the trends become stronger and thus slightly closer to the FTIR results (Table 2, lines 5 and 11). To investigate the influence of sampling on the differences between model and measurements, KASIMA results were restricted to the days with FTIR measurements. Concerning the HCl time series, sampling does not seem to have a strong influence. For $ClONO_2$, the KASIMA trend on FTIR days only is stronger than the one





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with the FTIR start and end days and thus even closer to the trend from the FTIR measurements (Table 2).

When the linear part of function (1) is fitted to the data between August and November ("summer"), the HCl trend from KASIMA is larger and the one from FTIR smaller than for the respective whole time series so that the summer trends agree within errors. The $ClONO_2$ trends from model and measurements also become more alike (Table 2).

The difference between the trend from all data and the one from the summer data only is likely partly due to the fact that the linear least squares fit is not able to completely catch the large column abundances especially of chlorine nitrate in spring. This particularly concerns the measurements as the annual cycle is more pronounced there than in the model results.

Concerning the absolute values, it is already known (Hamann, 2007; Mikuteit, 2008) and can also be seen in Fig. 4 that KASIMA tends to underestimate the measured HCl column abundances by about 20%. One reason for this is that KASIMA does not include the part of the troposphere below 7 km. Instead, a lower boundary condition has to be prescribed. This of course influences the total column abundances. Furthermore, some tropospheric processes like for example wash-out have to be parameterised because the model does not simulate cloud or rain droplets. Depending on the data set used for nudging in KASIMA, the atmospheric dynamics varies. This can cause changes in the resulting total column abundances, too (Hamann, 2007). Increasing the horizontal resolution (to T42 instead of T21 which was used here) also leads to more realistic HCl column abundances because the processes at the polar vortex edge are represented more precisely (Hamann, 2007).

In case of chlorine nitrate, KASIMA agrees very well with the FTIR measurements (Fig. 5). Only the $ClONO_2$ maxima at the late vortex edge are underestimated by the model due to its limited horizontal resolution. One reason for the good agreement might be that the tropospheric $ClONO_2$ partial column is negligible and therefore the first arguments mentioned above do not apply strongly to $ClONO_2$.





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The trend of the sum of the HCl and $ClONO_2$ column abundances amounts to $(-1.54 \pm 0.23)$%/yr corresponding to $(-9.10 \pm 1.42) \times 10^{13}$ molec/(cm$^2$ yr) for the FTIR measurements and $(-0.31 \pm 0.07)$%/yr corresponding to $(-1.51 \pm 0.32) \times 10^{13}$ molec/(cm$^2$ yr) for the KASIMA data. The model value reflects the CFC and HCFC content prescribed according to the WMO (2007) Ab scenario. As seen already in the separate trends for HCl and $ClONO_2$, there is a large difference between the modelled and measured trends which can partly be explained by the different start and end days respectively sampling. When using the summer data only and fitting a linear trend, the KASIMA and FTIR results agree within their errors (Table 2).

## 6 Conclusions

The trend of hydrogen fluoride is expected to be positive for the time range between 1996 and 2009. This is indeed the case for both the measurements and model calculations investigated here. When considering all data, the time series from the FTIR spectrometer shows a much weaker increase of HF total column abundances than the one from KASIMA. But the trends for the summer (August to November) data only from FTIR and KASIMA agree within their errors.

When the FTIR time series of HF is divided in halves, the calculated trends are not significant. One reason for this is that the two parts are simply too short to detect a reliable trend (see also Weatherhead et al., 1998). Still, the result when fitting function (1) is much smaller for the second half than for the first half both for the FTIR measurements and the KASIMA simulations. This suggests a decrease of the positive trend respectively a stabilisation of the HF column abundance in the last few years.

Both FTIR measurements and KASIMA model calculations show a significant decrease of the HCl and $ClONO_2$ vertical column abundances above Kiruna. The relative trends from KASIMA are weaker than those calculated from the measurements for all methods used here. There is a factor of about four between the relative trends of HCl and $ClONO_2$ in both measurement and model data. It can be seen in other northern





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polar FTIR station and model data as well (Kohlhepp et al., 2011). The reason for this difference is currently under investigation.

It has been shown that the start and end date respectively sampling influence the resulting trend. For the model time series sampled like the FTIR measurements, the trends are stronger than when using all KASIMA data and thus more similar to those from the measurements.

The trends of HCl, $ClONO_2$ and of their sum from model and measurements are also closer to each other when only the "summer" data between August and November are used. As mentioned above, this is also the case for the HF trends. One can conclude that the strong annual cycle respectively the processes in the polar vortex can influence the trend results.

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**Table 1.** Absolute and relative trends for HF column abundances from the FTIR measurements and KASIMA model calculations for Kiruna. The "summer" time series contain the data between August and November only.

| data source | period (mm/yyyy) | relative trend (%/yr) | absolute trend ($10^{13}$ molec/(cm$^2$ yr)) |
|---|---|---|---|
| FTIR | Mar 1996–Nov 2009 | +0.65 ± 0.25 | +1.32 ± 0.50 |
| FTIR summer | Aug 1996–Nov 2009 | +1.25 ± 0.28 | +2.26 ± 0.49 |
| FTIR | Mar 1996–Nov 2002 | +0.65 ± 0.69 | +1.31 ± 1.40 |
| FTIR | Jan 2003–Nov 2009 | −0.04 ± 0.66 | −0.09 ± 1.43 |
| KASIMA | Jan 1996–Dec 2009 | +1.51 ± 0.07 | +2.49 ± 0.12 |
| KASIMA summer | Aug 1996–Nov 2009 | +1.55 ± 0.11 | +2.14 ± 0.15 |
| KASIMA on FTIR days | Mar 1996–Nov 2009 | +1.21 ± 0.19 | +2.04 ± 0.31 |
| KASIMA | Jan 1996–Dec 2002 | +2.58 ± 0.18 | +4.30 ± 0.30 |
| KASIMA | Jan 2003–Dec 2009 | +0.80 ± 0.21 | +1.38 ± 0.35 |





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**Table 2.** Absolute and relative trends for HCl and $ClONO_2$ column abundances from the FTIR measurements and KASIMA model calculations for Kiruna. The "summer" time series contain the data between August and November only.

| species | data source | period (mm/yyyy) | relative trend (%/yr) | absolute trend ($10^{13}$ molec/(cm$^2$ yr)) |
|---|---|---|---|---|
| HCl | FTIR | Mar 1996–Nov 2009 | −0.81 ± 0.23 | −3.83 ± 1.10 |
| HCl | FTIR summer | Aug 1996–Nov 2009 | −0.42 ± 0.30 | −1.95 ± 1.38 |
| HCl | KASIMA | Jan 1996–Dec 2009 | −0.17 ± 0.06 | −0.67 ± 0.25 |
| HCl | KASIMA summer | Aug 1996–Nov 2009 | −0.26 ± 0.09 | −0.95 ± 0.34 |
| HCl | KASIMA | Mar 1996–Nov 2009 | −0.33 ± 0.06 | −1.28 ± 0.25 |
| HCl | KASIMA on FTIR days | Mar 1996–Nov 2009 | −0.33 ± 0.17 | −1.29 ± 0.65 |
| $ClONO_2$ | FTIR | Mar 1996–Nov 2009 | −3.28 ± 0.56 | −3.75 ± 0.70 |
| $ClONO_2$ | FTIR summer | Aug 1996–Nov 2009 | −3.04 ± 0.69 | −2.72 ± 0.59 |
| $ClONO_2$ | KASIMA | Jan 1996–Dec 2009 | −0.90 ± 0.10 | −0.84 ± 0.10 |
| $ClONO_2$ | KASIMA summer | Aug 1996–Nov 2009 | −0.98 ± 0.16 | −0.65 ± 0.11 |
| $ClONO_2$ | KASIMA | Mar 1996–Nov 2009 | −1.04 ± 0.11 | −0.98 ± 0.10 |
| $ClONO_2$ | KASIMA on FTIR days | Mar 1996–Nov 2009 | −1.43 ± 0.28 | −1.33 ± 0.28 |
| HCl + $ClONO_2$ | FTIR | Mar 1996–Nov 2009 | −1.54 ± 0.23 | −9.10 ± 1.42 |
| HCl + $ClONO_2$ | FTIR summer | Aug 1996–Nov 2009 | −0.66 ± 0.29 | −3.55 ± 1.57 |
| HCl + $ClONO_2$ | KASIMA | Jan 1996–Dec 2009 | −0.31 ± 0.07 | −1.51 ± 0.32 |
| HCl + $ClONO_2$ | KASIMA summer | Aug 1996–Dec 2009 | −0.38 ± 0.10 | −1.60 ± 0.41 |





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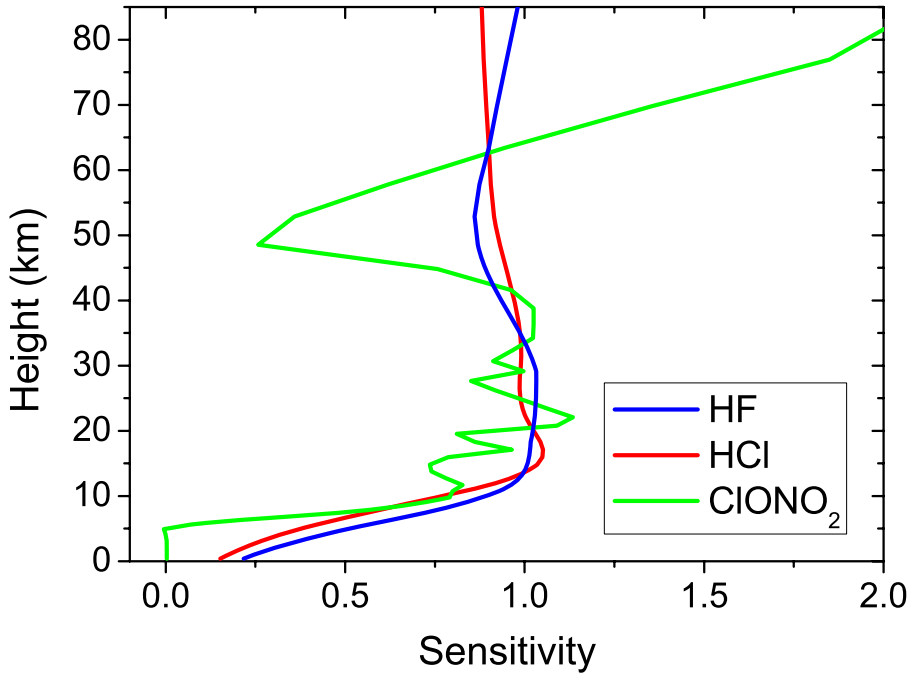


**Fig. 1.** Height dependency of the sensitivity of the retrieval for HF (blue line), HCl (red line) and $ClONO_2$ (green line). The curves shown represent mean values each calculated from six arbitrary spectra with different solar elevation angles.





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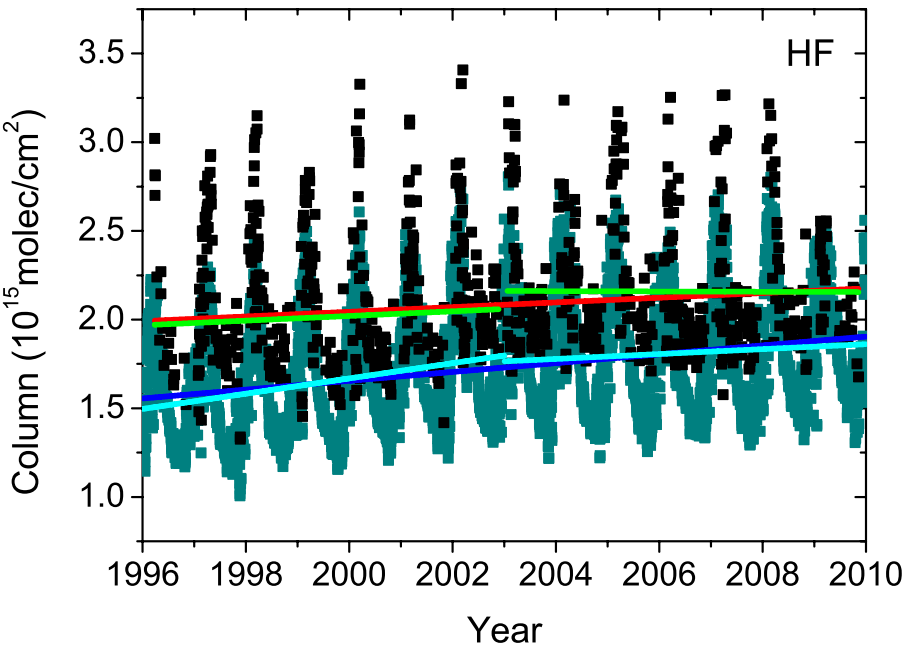


**Fig. 2.** Time series of FTIR measurements (black squares) and KASIMA model data (dark cyan squares) of hydrogen fluoride (HF) above Kiruna from March respectively January 1996 until November respectively December 2009. The red and dark blue lines represent the linear portion of the least squares fit of function (1) to the measurements and model results, respectively, from 1996 to 2009. The green and cyan lines show the fits from 1996 to 2002 and 2003 to 2009 from FTIR and KASIMA, respectively.





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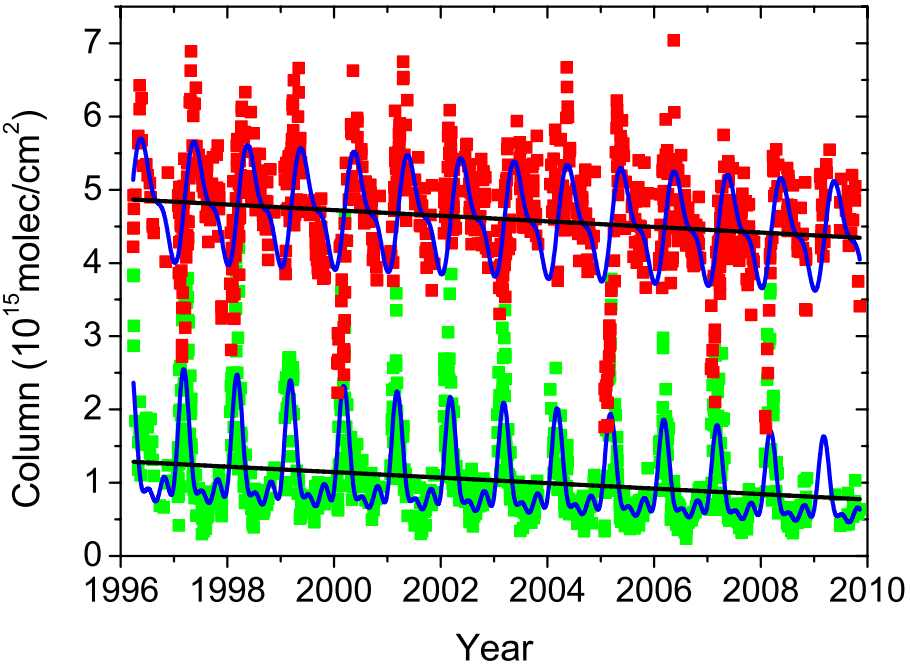


**Fig. 3.** Time series of HCl (red squares) and $ClONO_2$ (green squares) FTIR measurements in Kiruna from March 1996 until November 2009. The blue lines represent the least squares fit of function (1) to each series, the black lines show the linear part of the fit result only.





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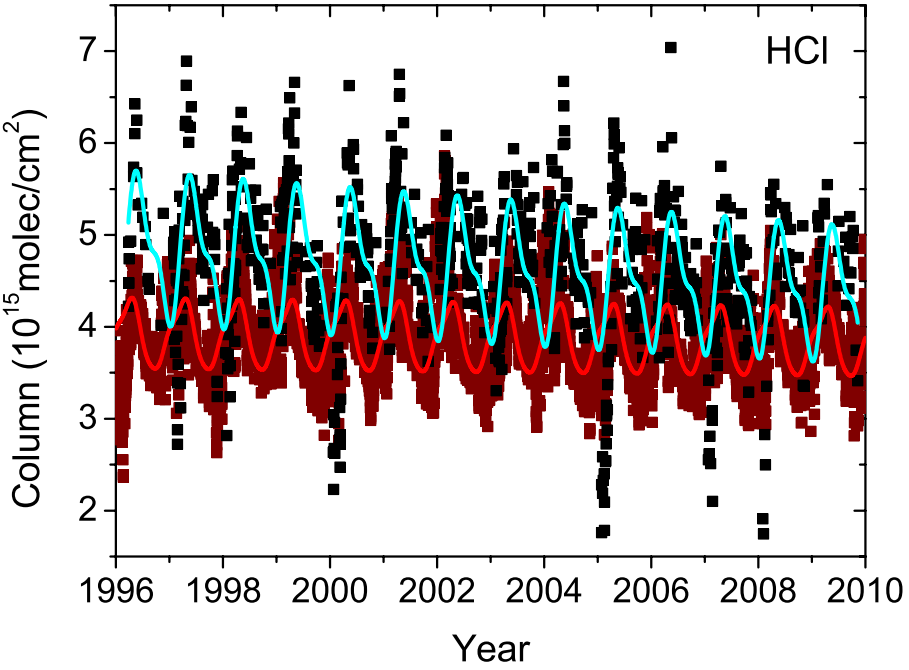


**Fig. 4.** Time series of FTIR measurements (black squares) and KASIMA model data (dark red squares) of HCl above Kiruna from 1996 to 2009 and the least squares fits of function (1) to the measurements (cyan line) and model data (red line), respectively.





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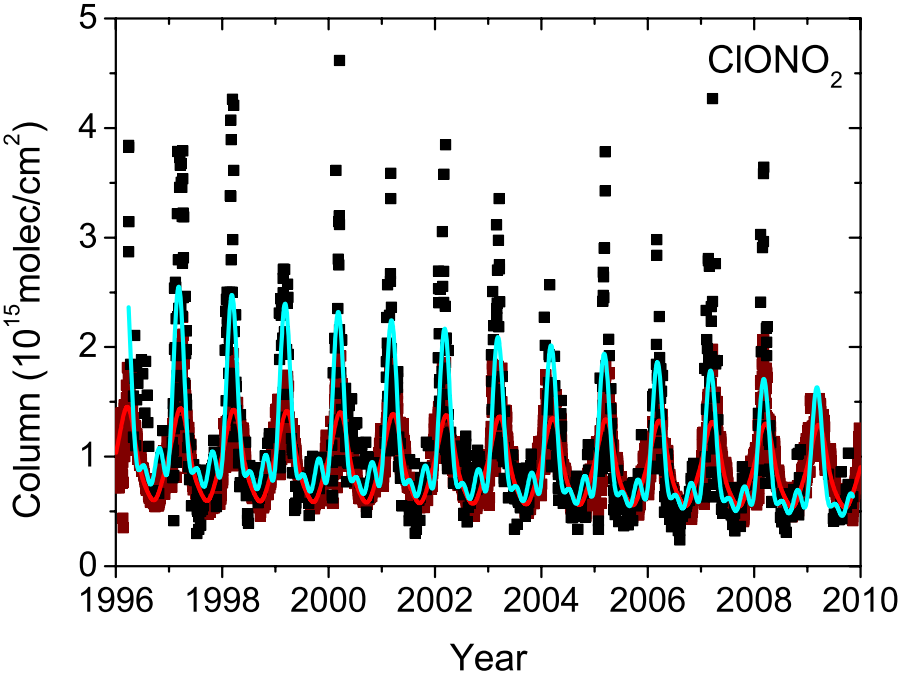


**Fig. 5.** Time series of FTIR measurements (black squares) and KASIMA model data (dark red squares) of $ClONO_2$ above Kiruna from 1996 to 2009 and the least squares fits of function (1) to the measurements (cyan line) and model data (red line), respectively.





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