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Three-year observations of halocarbons at the Nepal Climate Observatory at Pyramid (NCO-P, 5079 m a.s.l.) on the Himalayan range

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Abstract. A monitoring programme for halogenated climate-altering gases has been established in the frame of the SHARE EV-K[2]-CNR project at the Nepal Climate Laboratory – Pyramid in the Himalayan range at the altitude of 5079 m a.s.l. The site is very well located to provide important insights on changes in atmospheric composition in a region that is of great significance for emissions of both anthropogenic and biogenic halogenated compounds. Measurements are performed since March 2006, with grab samples collected on a weekly basis. The first three years of data have been analysed. After the identification of the atmospheric background values for fourteen halocarbons, the frequency of occurrence of pollution events have been compared with the same kind of analysis for data collected at other global background stations. The analysis showed the fully halogenated species, whose production and consumption are regulated under the Montreal Protocol, show a significant occurrence of "above the baseline" values, as a consequence of their current use in the developing countries surrounding the region, meanwhile the hydrogenated gases, more recently introduced into the market, show less frequent spikes.

Atmospheric concentration trends have been calculated as well, and they showed a fast increase, ranging from 5.7 to 12.6%, of all the hydrogenated species, and a clear decrease of methyl chloroform (−17.7%). The comparison with time series from other stations has also allowed to derive Meridional gradients, which are absent for long living well mixed species, while for the more reactive species, the gradient increases inversely with respect to their atmospheric lifetime. The effect of long range transport and of local events on the atmospheric composition at the station has been analysed as well, allowing the identification of relevant source regions the Northern half of the Indian sub-continent. Also, at finer spatial scales, a smaller, local contribution of forest fires from the Khumbu valley has been detected.

1 Introduction

Halocarbons (HCs) contribute to climate forcing being powerful greenhouse gases able to absorb long-wave radiation re-emitted by the Earth's surface in the 8–13 µm atmospheric window (Ramanathan and Feng, 2009). Moreover, HCs containing chlorine and bromine atoms can also influence the climate system via stratospheric ozone depletion. Due to the above mentioned impacts, many halocarbons, in particular those of anthropogenic origin, are regulated under international agreements. The Montreal Protocol and subsequent amendments (UNEP, 1987) called for a complete phase out of the CFCs and Halons in non-Article 5 (developed) countries, in January 1994, meanwhile Article 5 (developing or low emitting) countries were allowed to delay implementation of control provisions, with a complete phase out by January 2010. A slightly different schedule has been agreed for the chlorinated solvent methyl chloroform (MC) whose phase out times are 1996 and 2015 in non-Article 5 (non-A5) and in Article-5 (A5) countries, respectively. The second generation man-made products, i.e. the HCFCs, less aggressive toward the stratospheric ozone layer, have a more articulated and prolonged phase out schedule, implying their

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complete ban in 2030 (non-A5) and 2040 (A5). HFCs, not involved in any ozone depletion process, are not included in the Montreal Protocol.

On the other hand, the Kyoto Protocol (UNFCCC, 1997) called for a reduction in the collective emissions of those greenhouse gases (GHGs) in the so called Kyoto basket, including HFCs. The other man-made halogenated greenhouse gases – CFCs and HCFCs – are not included, being dealt with under the Montreal Protocol.

A few halocarbons have both biogenic and anthropogenic emission sources and their atmospheric budget is often subject to large uncertainties (Butler, 1999). This is the case for two methyl halides, CH_3Br and CH_3Cl. CH_3Br anthropogenic emissions are due to its use as a soil fumigant and to emissions from leaded gasoline; these uses are regulated under the Montreal Protocol which called for a 100% reduction of its sales and consumption in 2005 in developed countries. However, natural sources, like biomass burning (Andreae et al., 1996), oceans (Moore et al., 1996a), coastal and freshwater wetlands and peatlands (Cox et al., 2004), rice paddies (Redeker et al., 2000), and terrestrial plants, especially in the tropics (Yokouchi et al., 2002a; Rhew et al., 2001, 2010), are dominating the CH_3Br budget. As shown by levels measured in firn air (Butler et al., 1999; Trudinger et al., 2004) showing an increase of only 5–10% of its atmospheric mixing ratio in the last century, also the CH_3Cl budget is dominated by natural sources. These are tropical biomass burning (Rudolph, 1995; Andreae and Merlet, 2001), coastal wetlands (Cox et al., 2004), tropical plants (Yokouchi, 2002b; Xiao et al., 2010) and the oceans (Moore et al., 1996b). Anthropogenic sources, like coal combustion, waste incinerator, and industrial processes, account for about 5.4% of the total sources (McCulloch et al., 1999). As far as the region of interest is concerned, the measurements conducted during the INDOEX (Indian Ocean Experiment) aircraft campaign over the northern Indian Ocean in 1999 showed a strong enhancement in CH_3Cl levels likely to be attributed to the extensive use of biofuels (notably chlorine containing agricultural waste and dung) in India and Southeast Asia (Scheeren et al., 2002)

In order to assess emissions of HCs and the effectiveness of regulation under the Montreal and/or Kyoto protocols, long term measurements are needed. They are conducted on a global scale at remote stations in the frame of AGAGE (Advanced Global Atmospheric Gases Experiment), SOGE (System for Observation of Halogenated Greenhouse Gases in Europe) NIES (National Institute for Environmental Studies in Japan), and HATS (Halocarbons and other Atmospheric Trace Species) in Situ Monitoring Program of NOAA/ESRL (National Ocean Atmospheric Administration – Earth System Research Laboratory), implying high frequency measurements. Moreover, HATS Flask Sampling Program at NOAA/ESRL provides low frequency observations from a number of stations.

These programmes assure a wide spatial coverage on a global scale. However, some gaps still exist and regions like Central Asia, South America and Africa that are not covered by any network. The SHARE (Station at High Altitude for Environmental research) – Ev-K^2-CNR project, with the set up, in 2006, of the Nepal Climate Observatory – Pyramid (NCO-P) in the high Khumbu valley (Nepal) at 5079 m a.s.l. (Bonasoni et al., 2007) provided the unique opportunity to start a monitoring programme of halogenated gases, including chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs), Hydrofluorocarbons (HFCs), Halons, methyl chloroform and methyl halides. NCO-P is ideally located to obtain new information on the atmospheric background conditions of the region which is located between China and India, two of the largest and most rapidly developing countries and thus primary sources of pollution on a global scale (Ramanathan et al., 2007). This is particularly interesting as the record extends during years of the transition from the fully halogenated species to the more reactive hydrogenated compounds is occurring in A5 countries, in compliance with the Montreal Protocol.

In the following, a 3 three-year atmospheric record of 14 halogenated gases is presented. The objective of the study is to quantify trends in the atmospheric record of anthropogenic halocarbons in the High Himalaya, comparing our results with analogous trends recorded in other station to derive gradients. The obtained data could also help in identifying source regions and origin of these compounds, including halocarbons which are also originated from biogenic processes like biomass burning and tropical vegetation.

2 Methods

The Nepal Climate Observatory–Pyramid (NCO-P, 27.95 N, 86.82 E) is located at 5079 m a.s.l. in the Sagarmatha National Park, in the eastern Nepal Himalaya, at the confluence of the secondary Lobuche valley (oriented NNW-SSE) and the main Khumbu valley (oriented NE-SW). NCO-P is located away from important anthropogenic sources of pollutants, and only small villages are present along the valley, with Kathmandu as the closest major urban area located about 200 km South-West of the measurement site and more than 3.5 km lower down. The variation of meteorological conditions at the site is influenced both by the local mountain wind system (with a strong diurnal valley wind and a weak mountain night-breeze), and by the large-scale Asian monsoon circulation (Bollasina et al., 2002). In particular, besides determining the seasonal variations of meteorological parameters, the annual variations of the main synoptic circulation can also modulate the diurnal cycles characterizing the local mountain weather regime. However for a detailed description of the site and of the meteorological characterization and of air mass circulation on a local and large scale we refer to Bonasoni et al. (2010).

Table 1. Limits of detection (LOD), limits of quantification (LOQ), and percent relative standard deviation (RSD %) calculated on 25 repeated measurements of a reference mixture containing the compounds considered in this study, before and after the instrument upgrading (May 2007).

Compound	LOD ppt	LOQ ppt	RSD %	LOD ppt	LOQ ppt	RSD %
	Before May 2007			After May 2007		
CFC-11	0.29	1.0	2.0	0.13	0.4	0.3
CFC-12	0.35	1.2	1.0	0.18	0.6	0.5
CFC-115	0.42	1.4	2.0	0.15	0.5	0.8
CFC-114	0.30	0.9	2.0	0.16	0.5	1.2
H-1301	0.52	1.7	3.0	0.15	0.5	1.5
H-1211	0.29	1.0	3.0	0.12	0.4	1.5
Methyl Chloroform	0.40	1.4	1.8	0.30	0.9	1.3
HCFC-22	0.38	1.3	1.3	0.30	0.9	0.4
HCFC-142b	0.37	1.2	3.0	0.12	0.4	0.6
HFC-134a	0.55	1.8	2.0	0.14	0.5	0.6
HFC-152a	0.30	1.0	3.0	0.03	0.1	1.3
HFC-125	0.47	1.6	3.0	0.20	0.6	0.7
Methyl Bromide	0.10	0.3	3.0	0.10	0.3	1.2
Methyl Chloride	1.97	6.5	3.0	0.85	0.3	1.3

2.1 Analytical methodology

Air samples at the NCO-P are collected by drawing ambient air into 1-liter stainless steel flasks by means of an ultra clean air pump, over a period of about 10 min, reaching the pressure 1.8×10^5 Pa. Air aliquots are then analysed by gas chromatography-mass spectrometry (Agilent 6890–5972 GC-MS) equipped with an auto-sampling/pre-concentration unit (Markes International UNITY-Air Server). The system is currently operating for continuous measurements at a mountain remote site in Europe (MTC, Monte Cimone, Italy, 44.17 N, 10.68 E, 2165 m a.s.l.) (Maione et al., 2008). For the specific purpose of analysing flask samples, the GC inlet is connected to the stainless steel canister. The optimization of the analytical procedure in terms of efficiency, linearity, and reproducibility is reported elsewhere in detail (Maione et al., 2004). In Table 1, we summarize the main performance characteristics of the GS-MS system, before and after May 2007, when the instrumentation has been upgraded with the acquisition of a new mass spectrometer (Agilent 5973). As shown by data reported in Table 1, the upgrading resulted in an improved accuracy of the analytical data of the second part of the data set.

For calibration purposes, every sample run is bracketed between two working standard runs. Working standards are actual air samples in turn calibrated against the SIO2005 (Scripps Institution of Oceanography) – UB98 (University of Bristol) scales, used within the AGAGE network.

Samples have been normally collected once a week. In selected periods, in order to identify possible changes in mixing ratios due to atmospheric circulation, sampling has been performed twice in the same day in function of mountain wind regime (up-valley and down-valley conditions). Moreover, during intensive campaign periods, samples have been collected with higher temporal resolution, up to four times a day, for up to five consecutive days. Gaps in the time series are mostly due to difficulties in maintaining a regular sampling schedule at the site.

2.2 Baseline determination

Data have been analysed in order to assess background values and concentration trends as well as to perform comparisons with time series from other background stations. The identification of halocarbon background values is the first step in the data analysis. We can define as background those values representative of atmospheric composition at large spatial and temporal scales, which are ascribable to well mixed emissions of the compound of interest. Halocarbons are normally characterised by lifetimes of the order of years or decades, i.e. longer than the intra-hemispheric dispersion timescale, and the background is built upon continuous emissions and mixing. Those data exhibiting concentration values above the baseline can be ascribed to not well mixed emissions. Commonly, background values are identified through the use of meteorological filtering procedures (Ryall et al., 2001) or statistical filtering (Hastie et al., 2001). Both procedures cannot be applied to this data set due to difficulties in employing a meteorological filter in a region characterised by complex orography and due to the number of data points that is not sufficient to allow a robust statistical approach.

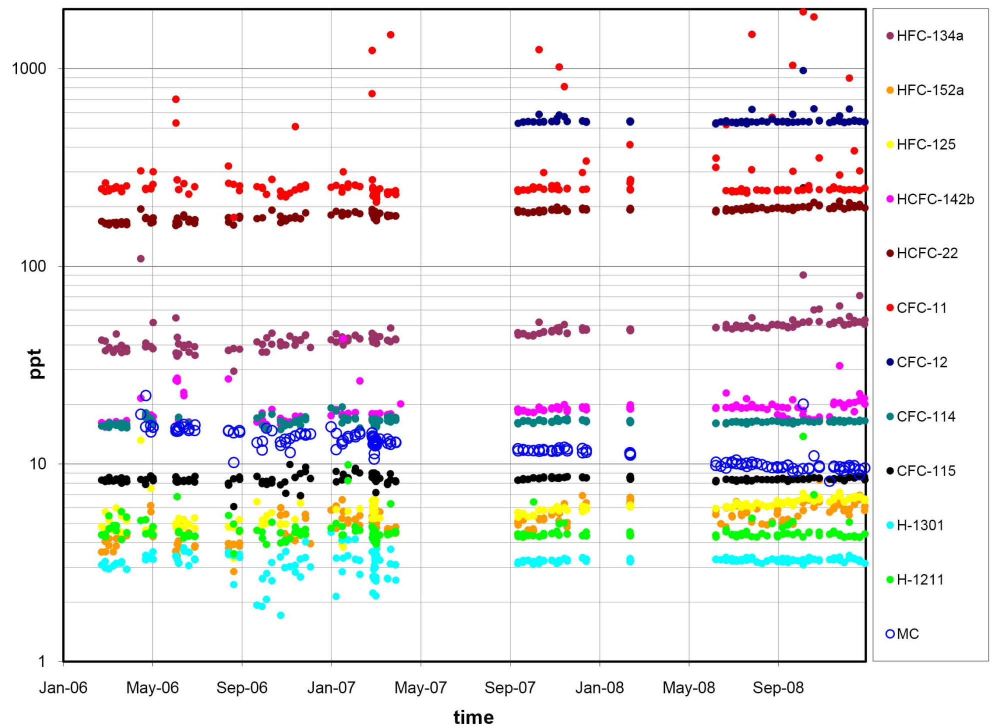

Fig. 1. Time series of 12 manmade halocarbons recorded at NCO-P.

Assuming that baseline data are distributed in a Gaussian mode, for each time series we have applied iteratively a linear regression procedure where, at each step, values with a deviation from the best fit greater than 1σ (σ is standard deviation) are discarded. Iteratively a new linear regression and a new σ are evaluated and deviations greater than 1 σ are discarded. The iteration is stopped when skewness and kurtosis of the deviations from the best fit approach 0 and 3, respectively.

For each compound, the time series has been divided into two sections: one before and one after May 2007, when the upgrading of the analytical instrumentation has been made (see Sect. 2.1).

It is worth noting that the values of σ obtained using the present simplified procedure and for a relatively low number of data (ca. 200 data points) differs only by 10% from that obtained for the Mt Cimone data set, evaluated on a 8-year time series, derived from continuous (two hours time resolution) "in situ" measurements following a more robust statistical approach (Giostra et al., 2010).

3 Results and discussion

Fourteen halocarbons have been taken into account in this study; of which twelve are of solely anthropogenic origin and two (methyl halides) are mainly biogenic. The main characteristics of the considered compounds are reported in Table 2.

Most of the compounds, being characterised by atmospheric lifetimes of the order of years or decades, fall into the definition of "long living well mixed" gases showing a rather uniform background concentration on a global scale, with weak seasonal cycles. On the other hand, species characterised by lifetimes of the order of one year or less also exhibit significant season cycles, mostly driven by their reactivity with OH radical, which is the main atmospheric sink for these compounds.

3.1 Anthropogenic species

In Fig. 1, an overview of the time series obtained after three years of observations, starting from March 2006 until December 2008, is given. Although the sampling shows some gaps in the period of study, nevertheless this data set can provide useful information especially because of its uniqueness.

From the plot it is also clear how the upgrading of the analytical instrumentation affected positively the quality of data, with a clear decrease of instrumental noise after the second half of 2007. However, it should be specified that the relative lower accuracy which characterise the first half of the data set, does not affect data reliability, as it will be shown in the following.

Some general considerations are: (i) the Montreal gases, especially the fully halogenated species, show a significant occurrence of "above the baseline" values, as a consequence of their current use in A5 countries surrounding the region;

Table 2. List of the halocarbons considered in this study, lifetimes and phase out schedule under Montreal Protocol and subsequent amendments.

Compound	Formula	Atmospheric lifetime (years)*	Date of phase out under Montreal Protocol in non- A5 countries	Date of phase out under Montreal Protocol in A5 countries
CFC-11	CCl_3F	45	1994	2010
CFC-12	CCl_2F_2	100	1994	2010
CFC-115	$CClF_2CF_3$	1700	1994	2010
CFC-114	$CClF_2CClF_2$	300	1994	2010
H-1301	$CBrF_3$	65	1994	2010
H-1211	$CBrClF_2$	16	1994	2010
Methyl Chloroform	CH_3CCl_3	5	1996	2015
HCFC-22	$CHClF_2$	12	2030	2040
HCFC-142 b	CH_3CClF_2	17.9	2030	2040
HFC-134a	CH_2FCF_3	14	NA	NA
HFC-152a	CH_3CHF_2	1.4	NA	NA
HFC-125	CHF_2CF_3	29	NA	NA
Methyl Bromide	CH_3Br	0.7	2005	2015
Methyl Chloride	CH_3Cl	1	NA	NA

NA. The compound is not regulated under the Montreal Protocol. * IPCC/TEAP, 2005.

(ii) on the contrary, as a consequence of a more recent introduction and a possible less frequent use in the region, the Kyoto gases show less frequent spikes if compared with those occurring in time series recorded in other remote stations located in non-A5 countries (Reimann et al., 2004; Greally et al., 2007; Maione et al., 2008).

3.1.1 Atmospheric baselines

Data have been filtered in order to discriminate high or low concentration values (due to different air mass composition) from baseline values, following the procedure described in Sect. 2.2. As an example, the plot obtained for HFC-134a is reported in Fig. 2, where red dots correspond to baseline data, whereas black dots are not baseline data. The number of iterations performed for HFC-134a have been 2 and 3 for the first and second segment of the time series, respectively.

For a quantitative evaluation of the significance of the occurrence of high concentration values in the anthropogenic gases, a comparison has been made with the time series obtained with the MTC high mountain observatory in Europe, where continuous halocarbons observations have been conducted since 2001 using the same instrumentation and calibration scale as for the flask samples collected at the NCO-P observatory.

The plot reported in Fig. 3 shows the occurrence of high concentration values as a percentage of all data points for anthropogenic HCs observed at NCO-P and at MTC.

Those compounds placed above and below the 1:1 line are characterised by a higher occurrence of high concentration values at NCO-P and MTC, respectively. It is worth noting that the compounds fall into homogeneous groups reflecting differences in production and use and therefore in regulations within the International Protocols, with most of the Montreal gases arranged above the 1:1 line and the Kyoto gases well below. Some compounds show a less extreme position. The HCFCs, with a prolonged phase-out schedule within the Montreal Protocol, still show high concentration values even in non A5 countries (Montzka et al., 2009). MC, even if phased out since 1996 and with a clear decreasing trend on a global scale, has been shown to still have European emissions higher than consumption-based figures (Reimann et al., 2005).

In order to highlight differences between the two sites, high concentration values occurrence ratios at MTC with respect to NCO-P have been calculated and they are reported in Fig. 4. For the three Kyoto gases and for those Montreal gases still having significant emissions also in Europe (HCFC-22 and MC), high concentration values are 6 to 25 times higher at MTC that at NCO-P. Conversely, the high concentration values of chlorofluorocarbons are 3 to 15 times higher at NCO-P than at MTC.

3.1.2 Meridional gradients

NCO-P baseline time series have been compared with baseline time series obtained in selected AGAGE stations located at different latitudes, where high frequency halocarbons observations have been conducted for several decades, using the same calibration scale as the one used for samples collected at NCO-P. In Table 3, the AGAGE stations considered in the comparison and their coordinates are reported. Baseline

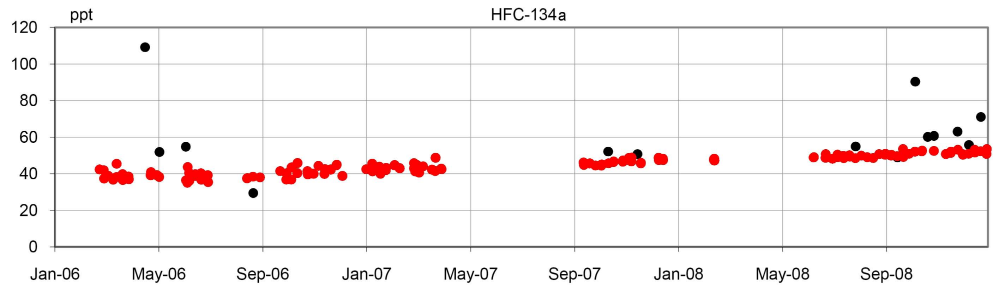

Fig. 2. Time series for HFC-134a at the NCO-P. Red dots, baseline data. Black dots, not-baseline data.

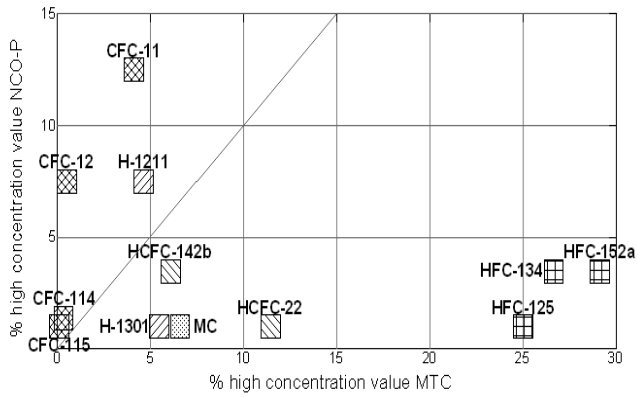

Fig. 3. Scatter plot of the percentage of occurrence of high concentration peaks at NCO-P and MTC observatories. Chemically homogeneous classes of compounds are denoted by identical shadings.

values for the AGAGE stations have been obtained using the same statistical filtering procedure applied to NCO-P data, as described above (data from AGAGE stations from WDCGG, Website: ftp://gaw.kishou.go.jp/pub/data/current_archives/).

Figures 5a to f show how the NCO-P time series are coherent with those obtained in the other stations and how they are correctly located along a Meridional gradient.

As an example of a long lived compound, the time series of CFC-115 (lifetime 1700 yr), by far the most stable of the compounds considered, clearly shows (Fig. 5a) the absence of any gradient. A quite similar behaviour is observed (Fig. 5b) for the more stable of the two Halons (H-1301, lifetime 65 yr).

For pollutants with a lifetime in the order of decades (H-1211, HFC-134a, and HFC-125) a Meridional gradient is observed (Fig. 5c to e), becoming particularly clear for compounds whose lifetime is comparable with inter hemispheric exchange (∼1 yr, Seinfeld and Pandis, 2006) , as HFC- 152a (1.4 yr) (Fig. 5f). This is consistent with a much stronger source strength in the Northern Hemisphere, between 30–60° N. The HFC-152a data clearly show the existence for these compounds of a seasonal cycle driven by reaction with OH in the atmosphere.

Table 3. Location of the three AGAGE stations considered for the comparison.

Station	Country	Coordinates
Mace Head- MHD	Ireland	53.33 N, 9.90 W
Ragged Point – RPB	Barbados	13.17 N, 59.43 W
Cape Grim, Tasmania – CGO	Australia	40.68 S, 144.69 W

3.1.3 Atmospheric trends

The three year of data can be used to attempt to derive trends in atmospheric concentrations of HCs at NCO-P. Two different approaches have been used: for compounds not showing a seasonal cycle, the best fit resulting from the linear regression analysis of the baseline data has been used; for compounds exhibiting a seasonal cycle, the same analysis has been applied to a data sub-set consisting of four months (September to December of each year), in order to overcome effects of discontinuity in the time series. In Table 4 trends, expressed in ppt per year, are reported together with the 95% confidence interval and the percent yearly trend. The four-month data sub-set are denoted by an asterisk in Table 4. Compounds are listed in order of decreasing percent trend. Compounds for which the confidence interval is well below the trend itself can be considered significant and are indicated in bold in the table, while italics denote those compounds for which the confidence interval is too close to the trend itself to be considered significant. In the first category fall all the compounds that are still emitted on a global scale, while for the fully halogenated compounds the atmospheric trend cannot be considered significant.

It should be noted that, notwithstanding the short time frame considered, trends are consistent with those measured on a global scale (Clerbaux and Cunnold, 2007), confirming a fast increase for the hydrogenated species, meanwhile MC shows a clear decrease, as a consequence of the phase out under Montreal Protocol (Reimann et al., 2005; Montzka et al., 2003). The only significant deviation from global mean

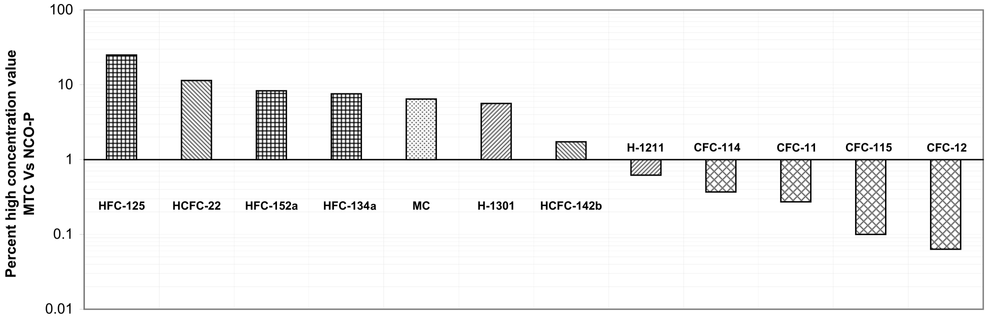

Fig. 4. Ratios of the occurrence of high concentration values at MTC with respect to NCO-P. Chemically homogeneous classes of compounds are denoted by identical shading.

Table 4. Absolute and percent atmospheric trends of HCs after three years of observations at NCO-P.

Compound	trend (ppt y^{-1})	percent trend (% y^{-1})	global mean trends (%y^{-1})[a]
HFC-125	**0.72 ± 0.07**	**12.6**	**NA**
HFC-152a	**0.59 ± 0.11**	**12.6**	**NA**
HFC-134a	**5.35 ± 0.27**	**11.9**	**NA**
HCFC-142b	**1.32 ± 0.20**	**7.2**	**3.8 ÷ 4.2**
HCFC-22	**10.0 ± 0.9**	**5.7**	**2.6 ÷ 4.4**
CFC-114	*0.08 ± 0.06*	*0.5*	*−1.2 ÷ 0.4*
CFC-115	*0.03 ± 0.04*	*0.4*	*1 ÷ 1.3*
H-1301	*0.01 ± 0.03*	*0.3*	*0 ÷ 3.2*
CFC-12[b]	*–1.03 ± 1.74*	*–0.2*	*–0.1 ÷ 0.3*
CFC-11	*–1.39 ± 1.95*	*–0.6*	*−0.7 ÷ −0.9*
H-1211	*–0.04 ± 0.02*	*–0.9*	*0 ÷ 1.9*
MC	**−2.12 ± 0.12**	**−17.7**	**−16.8 ÷ −18.7**

In bold compounds for which the trend is considered significant. In italics compounds for which the trend is not considered significant. [a] From Clerbaux and Cunnold, 2007. [b] The trend for CFC-12 has been calculated on a shorter time series.

trends reported by Clerbaux and Cunnold (2007), referring to the growth 2003–2004, are those related to the two HCFCs whose accelerated global increase from 2004 to 2008 has been reported by Montzka et al. (2009).

3.1.4 Analysis of pollution episodes

During the three years of observations, some episodes with high HCs concentrations have been identified and analysed in relation to the chemical and meteorological parameters measured at the observatory. This has been done with the aim of verifying how the emission field and the dynamic of the atmosphere can affect changes in atmospheric composition in the South Himalayan, with the intention of discriminating between the influence of local sources and that of long range transport from the polluted regions.

A first analysis has concerned possible differences in concentrations in samples collected the same day but in different hours characterized by different mountain breeze conditions, in order to ascertain if local circulation could affect the concentrations of manmade HCs at the site. In fact, as shown by Bonasoni et al. (2010), a mountain breeze system affects the high Khumbu valley where the NCO-P is located. While during summer monsoon, a valley wind is observed along the whole day, during the rest of the year, a valley wind was present during day-time with nigh-time mountain wind. However, on the basis of the available data, no significant differences have been observed, thus ruling out contribution from sources along the valley or Himalayan foothills. Even if high concentration values of the HFCs are frequently associated with valley winds, however the low number of episodes ($<$10) does not allow a reliable attribution of the source regions.

The analysis has been extended to those episodes in which at least 4 of the anthropogenic species considered simultaneously showed concentrations above the baseline. LAGRANTO 5-day back-trajectories (Wernli and Davies, 1997) of air masses reaching the NCO-P site, calculated every six hours, have been used for this purpose. The frequency of occurrence of polluted trajectories as a function of all the trajectories in the considered period of the measurements has been calculated. Let *m(i,j)* be the number of marked back-trajectories visiting the grid cell *(i,j)* over the investigated period, and let *n(i,j)* be the total number (i.e., back-trajectories

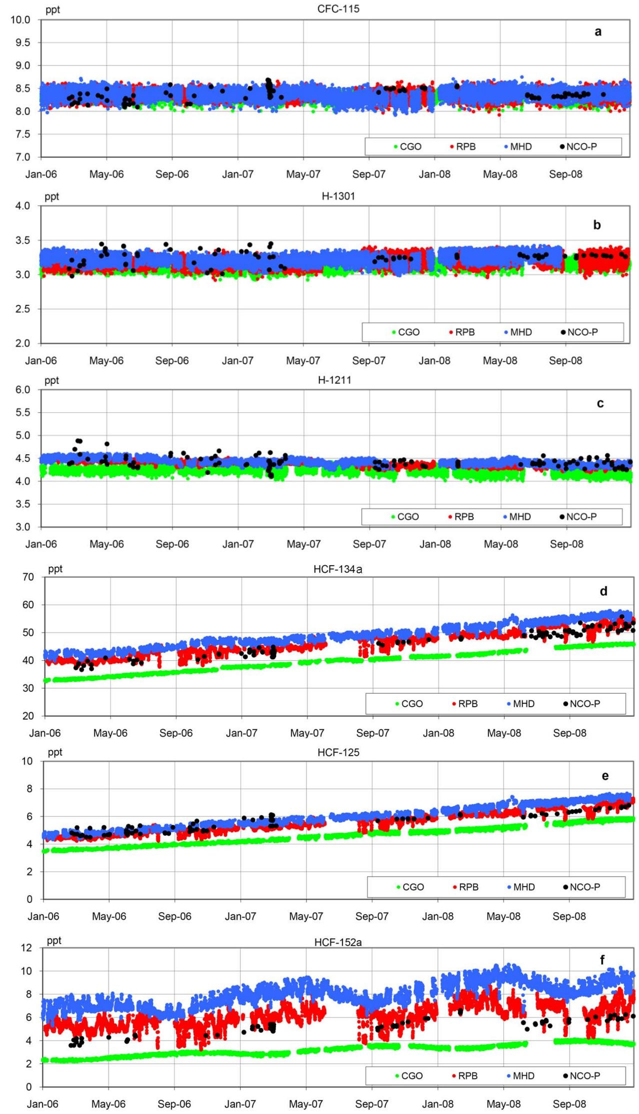

Fig. 5. Meridional gradients: time series for **(a)** CFC-115, **(b)** H-1301, **(c)** H-1211, **(d)** HFC-134a, **(e)** HFC-125 and **(f)** HFC-152 at NCO-P (black) are reported together with those obtained at MHD (blue), RPB (red) and CGO (green). Only baseline data have been considered.

associated both to above the background mixing ratios and to background values measured at receptor site) of back-trajectories visiting the grid cell *(i,j)*. In order to discard the dependency on local climatology, the conditional probability that an air parcel visits the cell *(i,j)* and arrives at the receptor with a concentration value above the background, can be defined as $P(i,j)=m(i,j)/n(i,j)$. The resulting map of conditional probability, reported in Fig. 6, shows the localisation of potential source regions in the domain considered. For major detail on the procedure and significance of maps of conditional probability see Maione et al. (2008).

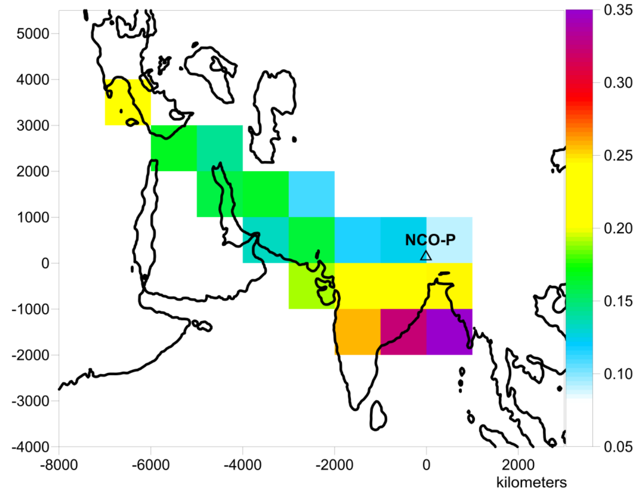

Fig. 6. Map of conditional probability of potential sources of anthropogenic halocarbons, based on observations at NCO-P observatory. The scale represents the fraction of polluted trajectories over total ones.

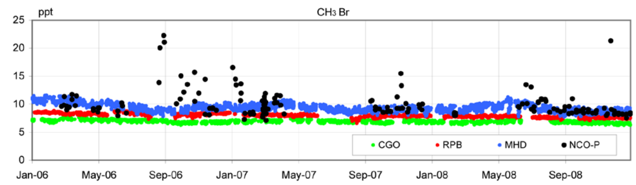

Fig. 7. CH_3Br measured at NCO-P (all data) compared with baseline data at at MHD (blue), RPB (red) and CGO (green).

Low spatial resolution of trajectories and the low temporal resolution of measurements suggest that the results should be treated with caution. Nevertheless, this preliminary analysis suggests that the grid cells especially affecting the atmospheric concentration of manmade halogenated greenhouse gases at NCO-P are those pertinent to the Northern Indian sub-continent. The atmospheric circulation characterising the NCO-P site is dominated by Westerly-South Westerly directions (Bonasoni et al., 2010). The low frequency of occurrence of transport from East-North East sectors, and the limited availability of samples, thus does not allow the characterisation of Chinese source regions in a statistically reliable way.

3.2 Methyl halides

The methyl halides CH_3Br and CH_3Cl show greater variability with respect to anthropogenic species that makes it difficult to identify a clear baseline, as it can be seen from graphs reported in Figs. 7 and 8, where the full time series of the two methyl halides at NCO-P are reported together with baselines at three AGAGE sites. As a consequence no seasonal cycle, nor Meridional gradients can be identified.

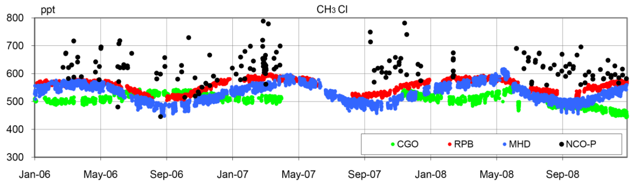

Fig. 8. CH_3Cl measured at NCO-P (all data) compared with baseline data at at MHD (blue), RPB (red) and CGO (green).

In particular, CH_3Cl shows frequent occurrence of high concentration values, well above the global background of 500 to 570 ppt (Yokouchi et al., 2000), reaching values as high as 800 ppt, comparable with the 750 ppt measured in 1999 during the INDOEX campaign (Scheeren et al., 2002). Such high values are due to the occurrence of wide areal sources ascribable to biomass burning as well as by the extensive use in the region of chlorine containing biofuels (Scheeren et al., 2002). During the infrequent periods when elevated concentrations are not measured, the minima in the data set are very similar to the baseline values at the AGAGE stations.

It should be specified that values measured at NCO-P are comparable in magnitude with data above the baseline measured at the Irish station of Mace Head, where there is a strong local contribution mainly due to emissions from coastal wetlands (Cox et al., 2004).

A further analysis concerned biogenic sources and in particular emissions from wild fires which could affect the behaviour of biogenic halocarbons. In particular, during the field campaign in February 2008, more frequent sampling was carried out, involving the collection of air samples every third hour on a day, during the occurrence of wild fires along the Khumbu Valley. Meanwhile for the anthropogenic HCs no deviations were observed from the baseline, the increase of CH_3Cl at the station was clearly correlated with the increase of black carbon (BC) and anti correlated with ozone (see Fig. 9), as expected due to the titration effect of NO emitted during the combustion process, and confirming the fact that air masses reaching the station are not aged and driven by regional-scale thermally induced circulation.

4 Conclusions

The NCO-P is located on the southern slope of Mount Everest close to Himalayan glaciers in a very strategic site nearby the largest and most rapidly developing countries of the world.

Halocarbons measurements at the site provide a different picture with respect to time series from other global background stations, still showing significant contributions from fully halogenated Montreal Gases and only minor contributions from the most recently introduced HFCs. For the long living species the time series data show the absence of a Meridional gradient, while the gradient for the more reactive species increases inversely with respect to their atmospheric lifetime. For those compounds characterised by strong biogenic sources, particularly relevant appears the contribution of biomass burning, both wild fires and use of biofuels. In fact, biomass burning emissions can significantly affect the CH_3Cl concentrations and the tropospheric composition in the South Himalayas region, as observed at NCO-P during emission plume related to a forest fire episode occurred along the Khumbu valley.

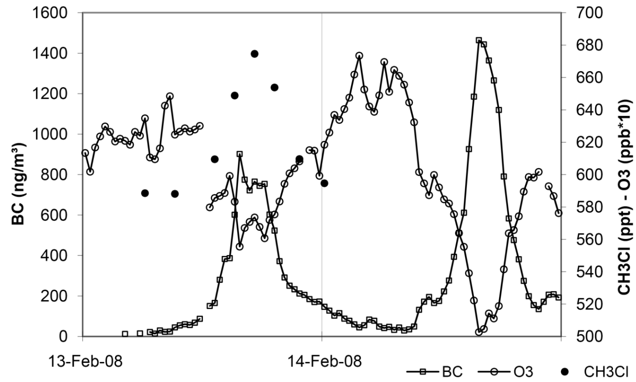

Fig. 9. Behaviour of CH_3Cl, BC and ozone at NCO-P during a fire episode along the Khumbu valley.

Atmospheric trends for all pollutants, even if derived by relatively short time series, are significant and consistent with those recorded at other global sites.

The data available so far allow the identification of relevant source regions the Northern half of the Indian subcontinent, notably the dense populated Indo Gangetic Plains. The specific atmospheric circulation characterising the station during the sampling does not allow the evaluation of the contribution from China.

The flask sampling programme obviously does not allow a high temporal resolution and sometimes implies discontinuity in the time series. However, the monitoring activity of halocarbons at NCO-P can offer important insights on changes in atmospheric composition in a region that is of great significance for emissions of species, both anthropogenic and biogenic, relevant for the climate.

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Website: ftp://gaw.kishou.go.jp/pub/data/current_archives/). The authors also thank Tenzing C. Sherpa, Kaji Bista, Laxman Adhikary, Pema Sherpa, Lhakpa T. Sherpa, Lakpa T. Sherpa, Chhimi T. Sherpa and Hari Shrestha for their support at the Nepal Climate Observatory-Pyramid.

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