Atmos. Chem. Phys. Discuss., 10, 22339–22368, 2010 www.atmos-chem-phys-discuss.net/10/22339/2010/ doi:10.5194/acpd-10-22339-2010 © Author(s) 2010. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

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

M. Maione<sup>1,6</sup>, U. Giostra<sup>2,6</sup>, J. Arduini<sup>1,6</sup>, F. Furlani<sup>2,6</sup>, P. Bonasoni<sup>3</sup>, P. Cristofanelli<sup>3</sup>, P. Laj<sup>4</sup>, and E. Vuillermoz<sup>5</sup>

<sup>1</sup>University of Urbino, Institute of Chemical Sciences, Urbino, Italy
 <sup>2</sup>University of Urbino, Dept. of Physics, Urbino, Italy
 <sup>3</sup>CNR-Institute for Atmospheric Sciences and Climate, Bologna, Italy
 <sup>4</sup>Laboratoire de Glaciologie et Géophysique de l'Environnement, Université Grenoble
 <sup>1</sup>-CNRS, Grenoble, France
 <sup>5</sup>Ev-K<sup>2</sup>-CNR Committee, Bergamo, Italy
 <sup>6</sup>CINFAI, National Consortium of Universities for Atmospheric and Hydrospheric Physics, Italy

Received: 3 August 2010 – Accepted: 3 September 2010 – Published: 28 September 2010

Correspondence to: M. Maione (michela.maione@uniurb.it)

Published by Copernicus Publications on behalf of the European Geosciences Union.



# 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 fre-
- quency of occurrence of pollution events have been compared with the same kind of analysis for data collected at other global background stations. 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
- <sup>15</sup> 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



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-

- <sup>5</sup> 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 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 <sup>15</sup> their atmospheric budget is often subject to large uncertainties (Butler, 1999). This is the case for two methyl halides, CH<sub>3</sub>Br and CH<sub>3</sub>Cl. CH<sub>3</sub>Br 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, <sup>20</sup> like biomass burning (Andreae et al., 1996), oceans (Moore et al., 1996), 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., 2002), are dominating the CH<sub>3</sub>Br 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 CH3Cl budget is dominated by natural sources. These are tropical biomass burning (Rundolph, 1995), coastal wetlands (Cox et al., 2004) and tropical plants (Yokouchi, 2002). Anthropogenic sources, like coal combustion, waste incinerator, and industrial processes, account for about 5.4% of the total sources (Mc-Culloch et al., 1999).



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) –  $\text{Ev-K}^2$ -CNR project, with the set up, in 2006, of the Nepal Climate Observatory – Duramid (NCO R) in the high Khumbu valley (Nanal) at 5070 m a al. (Rana

- vatory 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 and identify more precisely source regions and origin of halocarbons in the High Himalaya, in particular resulting from biomass burning emissions and tropical vegetation.



### 2 Methods

5

A detailed description of the site, of the measurement programme, of the meteorological characterization and of air mass circulation on a local and large scale is given in Bonasoni et al. 2010 (this issue). We therefore will limit our description to methods specifically used in the present paper.

# 2.1 Analytical Methodology

Air samples at the NCO-P are collected by drawing ambient air into stainless steel flasks by means of an ultra clean air pump, over a period of about 10 min. 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°11′ N, 10°42′ 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 optimisation of the analytical procedure in terms of efficiency, linearity, and reproducibility is reported elsewhere (Maione et al., 2004). In May 2007 the instrumentation has been upgraded with the acquisition of a new mass spectrometer (Agilent 5973). This 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 <sup>25</sup> 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 "old", well mixed, emissions of the compound of interest. In the case of halocarbons, which are normally characterised by long lifetimes, the background is built upon continuous emissions and mixing, which is more efficient the longer the atmospheric lifetime of the compound is. Those data exhibiting concentration values above the baseline can be ascribed to fresh, 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.

For each compound, the time series has been divided into two sections: one before

<sup>20</sup> and one after May 2007, when the upgrading of the analytical instrumentation has been made (see Sect. 2.1). 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 1  $\sigma$  ( $\sigma$  is standard deviation) are discarded. The iteration is stopped when skewness and kurtosis of the <sup>25</sup> time series approach 0 and 3, respectively.

It is worth noting that the values of  $\sigma$  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 (described in Giostra, 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 1.

Some of the compounds, being characterised by long atmospheric lifetimes, fall into the definition of "long living well mixed" (LLWM) gases showing a rather uniform background concentration on a global scale, with absence of strong seasonal cycles. On

the other hand, species characterised by relatively short lifetimes (SL) also exhibit a season cycle, 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

<sup>25</sup> consequence of their current use in A5 countries surrounding the region; (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

15

Data have been filtered in order to discriminate high or low concentration values (due to due to different air mass composition) from baseline values, following the procedure described above. As an example, the plot obtained for HFC-134 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-134 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. 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.

# 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 2, the AGAGE stations considered in the comparison and their coordinates are reported. Baseline 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, 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 1,700 years), 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 y).

For pollutants with a lifetime in the order of decades (H-1211, HFC-134, 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, as HFC-152a (1.4 y) (Fig. 5f). This is consistent with a much stronger source strength in the Northern Hemisphere, between 30–60° N. Data clearly show the existence for these compounds of a seasonal cycle driven by reaction with OH in the atmosphere.



### 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 3 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 3. 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
- <sup>15</sup> 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; Motzka et al., 2003).

#### 3.1.4 Analysis of pollution episodes

20

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

<sup>25</sup> rameters 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. How-

- ever, 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. A preliminary attempt has consisted in calculating the frequency of occurrence of pol-
- <sup>20</sup> luted trajectories as a function of all the trajectories in the considered period of the measurements. The resulting map of conditional probability, reported in Fig. 6, shows the localisation of potential sources in the domain considered. For major detail on the procedure and significance of maps of conditional probability see Maione et al. (2008).

Low spatial resolution of trajectories and the low temporal resolution of measure-<sup>25</sup> ments 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

20

- <sup>5</sup> The methyl halides CH<sub>3</sub>Br and CH<sub>3</sub>Cl show greater variability with respect to anthropogenic species that makes it difficult to identify a clear baseline, as it can be seen from time series reported in Fig. 7a and b. As a consequence no seasonal cycle, nor Meridional gradients can be identified.
- In particular, CH<sub>3</sub>Cl shows frequent occurrence of high concentration values, well above the global background of 500 to 570 ppt (Yokouchi et al., 2000), arising from the occurrence of wide areal sources ascribable to biomass burning and emission from tropical vegetation (Xiao et al., 2010). 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. For comparison, in Fig. 8 the time series of CH<sub>3</sub>Cl measured at NCO-P (full data set) is compared with baselines at three AGAGE station.

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<sub>3</sub>Cl 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



22351

The flask sampling programme obviously does not allow a high temporal resolution 25 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

#### Conclusions 4

regional-scale thermally induced circulation.

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 5 of the world.

confirming the fact that air masses reaching the station are not aged and driven by

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 LLWM species the time series data show the absence of 10 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, relevant appears the contribution of tropical vegetation and biomass burning. In fact, biomass burning emissions can significantly affect the CH3CI
- concentrations and the tropospheric composition in the South Himalayas region, as 15 observed at NCO-P during emission plume related to a forest fire episode occurred 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 North-20 ern half of the Indian sub-continent. The atmospheric circulation characterising the station does not allow the evaluation of the contribution from China. Also, at finer spatial scales, a smaller, local contribution of forest fires from the Khumbu valley has been detected, in agreement with Bonasoni et al., 2010.



Discussion Paper

**Discussion** Paper

Discussion Paper

**Discussion** Paper

Interactive Discussion



composition in a region that is of great significance for emissions of species, both anthropogenic and biogenic, relevant for the climate.

Acknowledgements. This work was carried out in the framework of the UNEP – ABC (Atmospheric Brown Clouds), and founded by Ev-K<sup>2</sup>-CNR – SHARE (Stations at High Altitude for Research on the Environment) projects. The authors would like to thank Michael Sprenger who provided the LAGRANTO back-trajectories used in this work have. Ray Weiss and the SIO2005 scale, The University of Bristol and the UB 98 scale are gratefully acknowledged, as well as the science teams of the SOGE and AGAGE consortia. Data from AGAGE stations have been downloaded from the WDCGG ftp://gaw.kishou.go.jp/pub/data/current\_archives/. The authors
 also thank Tenzing C. Sherpa, Kaji Bista, Laxman Adhikary, Pema Sherpa, Lakpa T. Sherpa, Chhimi T. Sherpa and Hari Shrestha for their support at the Nepal Climate Observatory – Pyramid.

#### References

15

Andreae, M. O., Atlas, E., Harris, G. W., Helas, G., de Kock, A., Koppmann, R., Maenhaut, W.,

Mano, S., Pollock, W. H., Rudolph, J., Scharffe, D., Schebeske, G., and Welling, M.: Methyl Halide emissions from savannah fires in southern Africa, J. Geophys. Res., 101, 23603–23613, 1996.

Bonasoni, P., Laj, P., Bonafè, U., Calzolari, F., Cristofanelli, P., Marinoni, A., Roccato, F., Facchini, M. C., Fuzzi, S., Gobbi, G. P., Pichon, J. M., Venzac, H., Sellegri, K., Villani, P., Maione,

- M., Arduini, J., Petzold, A., Sprenger, M., Verza, G. P., and Vuillermoz, E.: The ABC-Pyramid: a scientific laboratory at 5079 m a.s.l. for the study of atmospheric composition change and climate. in: Mountains witnesses of global changes research in the Himalaya and Karakoram; SHARE- Asia project, Developments in Earth Surface Processes, edited by: Baudo, R., Tartari, G., and Vuillermoz, E., Elsevier, Amsterdam, 67-73, 65, Chapter 10, 2007.
- <sup>25</sup> Bonasoni, P., Laj, P., Marinoni, A., Sprenger, M., Angelini, F., Arduini, J., Bonafè, U., Calzolari, F., Colombo, T., Decesari, S., Di Biagio, C., di Sarra, A. G., Evangelisti, F., Duchi, R., Facchini, M. C., Fuzzi, S., Gobbi, G. P., Maione, M., Panday, A., Roccato, F., Sellegri, K., Venzac, H., Verza, G. P., Villani, P., Vuillermoz, E., and Cristofanelli, P.: Atmospheric Brown Clouds in the Himalayas: first two years of continuous observations at the Nepal-Climate Observatory



22353

at Pyramid (5079 m), Atmos. Chem. Phys. Discuss., 10, 4823–4885, doi:10.5194/acpd-10-4823-2010, 2010.

- Butler, J. H., Battle, M., Bender, M., Montzka, S. A., Clarke, A. D., Saltzman, E. S., Sucher, C., Severinghaus, J., and Elkins, J. W.: A twentieth century record of atmospheric halocarbons in polar firm air Nature 399, 749–755, 1999
- <sup>5</sup> in polar firn air, Nature, 399, 749–755, 1999.
  - Cox, M. L., Paul, J., Fraser, P. J., Sturrock, G. A., Siems, S. T., and Porter, L. W.: Terrestrial sources and sinks of halomethanes near Cape Grim, Tasmania, Atmos. Environ., 38, 3839– 3852, 2004.

Clerbaux, C. and Cunnold, D.M. (Lead Authors), Anderson, J., Engel, A., Fraser, P. J., Mahieu,

- E., Manning, A., Miller, J., Montzka, S. A., Nassar, R., Prinn, R., Reimann, S., Rinsland, C. P., Simmonds, P., Verdonik, D., Weiss, R., Wuebbles, D., and Yokouchi, Y.: Long-Lived Compounds, Chapter 1 in Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project report no. 50, World Meteorological Organization, Geneva, Switzerland, 2007.
- <sup>15</sup> Hastie, T., Tibshirani, R., and Friedman, J.: Data Mining, Inference, and Prediction, Springer-Verlag, New York, 2001.
  - Giostra, U.: The determination of a "European" atmospheric background mixing ratio for anthropogenic greenhouse gases: comparison of two independent methods, 2010.
- Greally, B. R., Manning, A. J., Reimann, S., Mcculloch, A., Huang, J., Dunse, B. L., Simmonds,
  P. G., Prinn, R. G., Fraser, P. J., Cunnold, D. M., O'doherty, S., Porter, L. W., Sturrock, G. A.,
  Stemmler, K., Vollmer, M. K., Lunder, C. R., Schmidbauer, N., Hermansen, O., Arduini, J.,
  Salameh, P. K., Krummel, P. B., Wang, R. H. J., Folini, D., Weiss, R. F., Maione, M., Nickless, G., Stordal, F., and Derwent, R. G.: Observation of 1,1-difluoroethane (HFC-152a) at
  AGAGE and SOGE monitoring stations 1994–2004 and derived Global and regional emission estimates, J. Geophys. Res., 112, D06308, doi:10.1029/2006JD007527, 2007.
- IPCC/TEAP: Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons, edited by: Metz, B., Kuijpers, L., Solomon, S., et al., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 488 pp, 2005.
- Maione, M., Arduini, J., Mangani, G., and Geniali, A.: Evaluation of an Automated Gas Chromatographic – Mass Spectrometric Instrumentation to be Used for Continuous Monitoring of Trace Anthropogenic Greenhouse Gases, Internat. J. Environ. Anal. Chem., 84(4), 241–253, 2004.



- Maione, M., Giostra, U., Arduini, J., Belfiore, L., Furlani, F., Geniali, A., Mangani, G., Vollmer, M. K., and Reimann, S.: Localization of source regions of selected hydrofluorocarbons combining data collected at two European mountain Stations, Sci. Total Environ., 391, 232–240, 2008.
- <sup>5</sup> Moore, R. M., Webb, M., Tokarczyk, R., and Weaver, R.: Bromoperoxidase and iodoperoxidase enzymes and production of halogenated methanes in marine diatom cultures, J. Geophys. Res., 101, 20899–20908, 1996.

Motzka, S., Butler, J., Hall, B., Mondeel, D., and Elkins, J.: A decline in tropospheric organic bromine, Geophys. Res. Lett., 30, 1826–1829, 2003.

- Ramanathan, V., Li, F., Ramana, M. V., Siva, P. S., Kim, D., Corrigan, C. E., Nguyen, H., Stone, E. A., Schauer, J. J., Carmichael, G. R., Adhikary, B., and Yoon, S. C.: Atmospheric Brown Clouds: Hemispherical and regional variations in long range transport, absorption and radiative forcing, J. Geophys. Res., 112, D22S21, doi:10.1029/2006JD008124, 2007.
   Ramanathan, V. and Feng, Y.: Air pollution, greenhouse gases and climate change: global and regional perspective, Atmos. Environ., 43, 37–50, 2009.
- Redeker, K. R., Wang, N.-Y., Low, J. C., McMillan, A., Tyler, S. C., and Cicerone, R. J.: Emissions of methyl halides and methane from rice paddies, Science, 290, 966–969, 2000.
  - Reimann, S., Schaub, D., Stemmler, K., Folini, D., Hill, M., Hofer P., Buchmann, B., Simmonds, P. G., Greally, B., and O'doherty, S.: Halogenated greenhouse gases at the Swiss High Alpine
- <sup>20</sup> Site of Jungfraujoch (3580 m asl). Continuous measurements and their use for regional European source allocation, J. Geophys. Res., 109, D05307, doi:10.1029/2003JD003923, 2004.
  - Reimann, S., Manning, A. J., Simmonds, P. G., Cunnold, D. M., Wang, R. H., Li, J., McCulloch, A., Prinn, R. G., Huang, J., Weiss, R. F., Fraser, P. J., O'Doherty, S., Greally, B. R., Stemmler,
- K., Hill, M., Folini, D.: Low European methyl chloroformemissions inferred from long-term atmospheric measurements, Nature, 433, 506–508, 2005, doi:10.1038/nature03220.
  - Rudolph, J. A., Khedim, R., Koppman, R., Bonsang, B.: Field study of the emissions of methyl chloride and otherhalocarbons from biomass burning in western Africa, J. Atmos. Chem., 22, 67–80, 1995.
- Ryall, D. B., Derwent, R. G., Manning, A. J., Simmonds, P. G., and O'Doherty, S.: Estimating source regions of European emissions of trace gases from observations at Mace Head, Atmos. Environ., 35, 2507–2523, 2001.

Rudolph, J., Khedim, A., Koppmann, R., and Bonsang, B.: Field study of the emissions of



methyl chloride and other halocarbons from biomass burning in western Africa, J. Atmos. Chem., 22, 67–80,1995.

- Trudinger, C. M., Etheridge, D. M., Sturrock, G. A., Fraser, P. J., Krummel, P. B., and McCulloch, A.: Atmospheric histories of halocarbons from analysis of Antarctic firn air: Methyl
- <sup>5</sup> bromide, methyl chloride, chloroform, and dichloromethane, J. Geophys. Res., 109, D22310, doi:10.1029/2004JD004932, 2004.

UNEP (United Nations Environment Programme), The Montreal Protocol on substances that deplete the ozone layer, Montreal and subsequent amendements, 1987.

UNFCCC (United Nations Framework Convention on Climate Change), The Kyoto Protocol on Climate Change, Kyoto, 1997.

Wernli, H. and Davies, H.: A Lagrangian-based analysis of extratropical cyclones. Part I: The method and some applications, Q. J. Roy. Meteorol. Soc., 123, 467–489, 1997.

10

- Xiao, X., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Weiss, R. F., O'Doherty, S., Miller, B. R., Salameh, P. K., Harth, C. M., Krummel, P. B., Porter, L. W., Mhle, J., Greally, B. R., Cunnold,
- D., Wang, R., Montzka, S. A., Elkins, J. W., Dutton, G. S., Thompson, T. M., Butler, J. H., Hall, B. D., Reimann, S., Vollmer, M. K., Stordal, F., Lunder, C., Maione, M., Arduini, J., and Yokouchi, Y.: Optimal estimation of the surface fluxes of methyl chloride using a 3-D global chemical transport model, Atmos. Chem. Phys., 10, 5515–5533, doi:10.5194/acp-10-5515-2010, 2010.
- Yokouchi, Y., Machida, T., Barrie, L. A., Toom Sauntry, D., Nojiri, Y., Fujinuma, Y., Inuzuka, Y., Li, H.-J., Akimoto, H., and Aoki, S.: Latitudinal distribution of atmospheric methyl bromide: measurements and modelling, Geophys. Res. Lett. 27, 697–700, 2000.
  - Yokouchi, Y., Ikeda, M., Inuzuka, Y., and Yukawa, T.: Strong emission of methyl chloride from tropical plants, Nature, 416, 163–165, 2002.

Jierneeinn Da	<b>ACPD</b> 10, 22339–22368, 2010		
ner   Dieche	Three-year observations of halocarbons M. Maione et al.		
scion Dane	Page		
	Abstract	Introduction Beferences	
	Tables	Figures	
	14	۶I	
DDDr	•	•	
_	Back	Close	
	Full Screen / Esc Printer-friendly Version		
עס	Interactive	Discussion	
D			

BY

**Table 1.** 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	CCI <sub>3</sub> F	45	1994	2010
CFC-12	$CCl_2F_2$	100	1994	2010
CFC-115	$CCIF_2CF_3$	1,700	1994	2010
CFC-114	CCIF <sub>2</sub> CCIF <sub>2</sub>	300	1994	2010
H-1301	CBrF <sub>3</sub>	65	1994	2010
H-1211	CBrCIF <sub>2</sub>	16	1994	2010
Methyl Chloroform	CH <sub>3</sub> CCI <sub>3</sub>	5	1996	2015
HCFC-22	CHCIF <sub>2</sub>	12	2030	2040
HCFC-142 b	CH <sub>3</sub> CCIF <sub>2</sub>	17.9	2030	2040
HFC-134	CH <sub>2</sub> FCF <sub>3</sub>	14	NA	NA
HFC-152a	CH <sub>3</sub> CHF <sub>2</sub>	1.4	NA	NA
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	29	NA	NA
Methyl Bromide	CH₃Br	0.7	2005	2015
Methyl Chloride	CH₃CI	1	NA	NA

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

	ACPD		
	10, 22339–22368, 2010		
J			
-	Three-year observations of halocarbons		
	M Maione et al		
1	Title Page		
	Abstract	Introduction	
	Conclusions	References	
	Tables	Figures	
J	14		
	•	•	
	Back	Close	
!	Full Screen / Esc		
	Drinter (c)		
•	Printer-frier	aly version	
J	Interactive Discussion		
	$\overline{\mathbf{c}}$	<b>O</b> BY	

Discussion Paper

Discussion Pape

Discussion Paper

Discussion Paper

**Table 2.** Location of the three AGAGE stations considered for the comparison.

Station	Country	Coordinates
Mace Head – MHD	Ireland	53.3° N, 9.9° W
Ragged Point – RPB	Barbados	13.2° N, 59.4° W
Cape Grim, Tasmania – CGO	Australia	40.7° S, 144.7 E

Compound	trend (ppt $y^{-1}$ )	percent trend (% y <sup>-1</sup> )
HFC-125	$0.72 \pm 0.07$	12.6
HFC-152a	$0.59 \pm 0.11$	12.6
HFC-134	$5.35 \pm 0.27$	11.9
HCFC-142b	$1.32 \pm 0.20$	7.2
HCFC-22	$10.0 \pm 0.9$	5.7
CFC-114	$0.08 \pm 0.06$	0.5
CFC-115	$0.03 \pm 0.04$	0.4
H-1301	$0.01 \pm 0.03$	0.3
CFC-12 <sup>A</sup>	$-1.03 \pm 1.74$	-0.2
CFC-11	$-1.39 \pm 1.95$	-0.6
H-1211	$-0.04 \pm 0.02$	-0.9
МС	$-2.12 \pm 0.12$	-17.7

**Table 3.** Absolute and percent atmospheric trends of HCs after three years of observations at NCO-P.

<sup>A</sup> The trend for CFC-12 has been calculated on a shorter time series.

	Discussion Paper	22368, 2010 			
t	_	haloca	halocarbons		
	Discussio	M. Maio	M. Maione et al.		
	n Pap	Title	Page		
	ber	Abstract	Introduction		
	_	Conclusions	References		
	)iscu:	Tables	Figures		
	ssion Pa	I4	۶I		
	per	•	•		
	—	Back	Close		
	Discus	Full Screen / Esc			
	ssion	Printer-frier	Printer-friendly Version		
	Pap	Interactive	Discussion		
	er		<b>B</b> Y		





















**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.

<b>Discussion</b> Pa	AC 10, 22339–	ACPD 10, 22339–22368, 2010 Three-year observations of halocarbons M. Maione et al.		
tper   Discussion	Three observa haloca M. Maio			
ר Pape	Title Page			
Ð	Abstract	Introduction		
	Conclusions	References		
iscussi	Tables	Figures		
on P	I	►I		
aper	•	•		
	Back	Close		
Discu	Full Screen / Esc			
ssior	Printer-frie	ndly Version		
n Pap	Interactive	Interactive Discussion		
Der		$\bigcirc$		

 $\mathbf{O}$ 

BY



Discussion Paper **ACPD** 10, 22339-22368, 2010 **Three-year** observations of halocarbons **Discussion** Paper M. Maione et al. **Title Page** Introduction Abstract Conclusions References **Discussion** Paper **Tables Figures** .∎. ►T. ► Back **Discussion Paper** Full Screen / Esc **Printer-friendly Version** Interactive Discussion

**Fig. 5.** Meridional gradients: time series for **(a)** CFC-115, **(b)** H-1301, **(c)** H-1211, **(d)** HFC-134, **(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.



Fig. 5. Continued.











Fig. 7. Time series for  $CH_3Br$  (a) ant  $CH_3Cl$  (b) at NCO-P.





**Fig. 8.** CH<sub>3</sub>Cl measured at NCO-P (all data) compared with baseline data at MHD (blue), RPB (red) and CGO (green).





Fig. 9. Behaviour of  $CH_3CI$ , BC and ozone at NCO-P during a fire episode along the Khumbu valley.

