Atmospheric measurements of the halogenated hydrocarbons involved in global change phenomena

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Abstract

Chlorofluorocarbons and their replacement compounds are anthropogenic compounds of great environmental concern. For this reason monitoring their atmospheric mixing ratios on a worldwide scale is recommended. An analytical methodology for the simultaneous determination of selected chlorofluorocarbons and their replacement compounds has recently been developed. This methodology was applied in the analysis of actual air samples collected in remote and semi-remote areas located in the Northern and Southern Hemispheres. The concentration levels measured in the air samples collected in the two hemispheres are reported. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The role of chlorofluorocarbons (CFCs) in two important global change phenomena, i.e. stratospheric ozone depletion and global warming, is well known. Because of their high ozone depletion potential (ODP), and following the directives laid down by the *Montreal Protocol on Substances that Deplete the Ozone Layer* (U.N. Environmental Programme, 1987), these anthropogenic compounds have recently been phased out. Notwithstanding, the tropospheric mixing ratios of CFCs are not likely to readily decrease because of their extremely long atmospheric lifetimes. The mean change in the tropospheric mixing ratio of CFCs for a one-year interval in both hemispheres is described in a finite-increment two-box model by Elkins et al. (1993). This model shows how the emission rate of CFCs is the crucial input parameter to be considered when evaluating such a change. However, even if data concerning the production of CFCs on a worldwide scale are available (alternative fluorocar-

bons environmental acceptability study (AFEAS)), there are still many uncertainties related to their actual emission rates into the atmosphere. This is due both to the use of CFCs by non-accomplishing countries, or to their long-term release (Holmes, 1996). Therefore, in order to overcome limitations in model predictions, continuous monitoring of CFC tropospheric mixing ratios in both hemispheres is recommended. Various research groups are involved in the worldwide monitoring of the most abundant chlorofluorocarbons in sampling sites located at different latitudes (Montzka, 1996; Cunnold, 1997; Derewent, 1998). During the last decade, the interest of the scientific community has extended to those compounds that have been introduced as an alternative to fully halogenated halocarbons (alternative fluorocarbons, AFCs). The molecular design of these compounds, named hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), implies the introduction of one or more hydrogen atoms, giving rise to less stable compounds that are able to react with the OH radicals ubiquitously present in the troposphere. However, whereas the ozone depleting potential (ODP) of AFCs is very low or almost absent, they still have a remarkable global warming potential (GWP), which is associated to their capability to absorb the long-wave radiation

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re-emitted by the earth surface in the range of the atmospheric window (Wallington, 1994). Currently, the tropospheric mixing ratios of AFCs are still quite low if compared with those of parent compounds, but they are liable to increase in the next years because of the growth in their emission rates.

We have recently devised an analytical method for the simultaneous determination of selected CFCs and AFCs (Mangani, 2000). This method was applied during the analysis of air samples collected in two sites in the two hemispheres: the Terra Nova Bay Region (Antarctica) and Monte Cimone (Italy).

2. Experimental section

The overall analytical method established for the simultaneous determination of selected CFCs and AFCs has been described elsewhere (Mangani, 2000).

In brief, the air samples were collected by filling, at a pressure of 3 atm, 0.85 liters passivated stainless-steel canisters (Biospheric Research Corporation, Hillsboro, OR, USA), using a portable ultra clean air pump (model FC-1121, Biospheric Research Corporation, Hillsboro, OR, USA).

The extremely low atmospheric concentration levels of AFCs make it necessary to pre-concentrate the air samples prior to gas chromatographic separation. For this purpose, an adsorption tube capable of trapping even the most volatile compounds at ambient temperature was set up. This is a dual layer adsorption tube filled with 100 mg of Carbograph 1 (surface area 90 m g^{-1}, Lara Srl, Rome, Italy), and with 300 mg of Carbograph 5 (surface area 560 m g^{-1}, Lara Srl, Rome, Italy). When using the dual-layer adsorption tube, the air sample is passed first through the weaker adsorbent, which retains the less volatile halocarbons, and then through the stronger adsorbent, which adsorbs the most volatile compounds. Operating at ambient temperature, all compounds of interest were quantitatively trapped onto the adsorbents, as long as the enriched volume did not exceed 200 ml.

The trapped analytes were released by heating the adsorption tube to 220°C for 5 min in a thermal desorber (CP-4020 TCT Thermal Desorber, Chrompack International BV, Middelburg, NL), then transferring the desorbed analytes into the gas chromatographic unit at a flow rate of 6 ml min^{-1}, and reversing the flow direction with respect to the enrichment step. In these conditions, the full release of all compounds of interest was attained. Cryofocussing of the analytes on the top column was carried out by freezing a fused silica capillary pre-column at a temperature of −150°C for 5 min.

The gas chromatographic column, tailor-made for this separation, is a graphite layer open tubular (GLOT) column 90 m long × 0.25 mm i.d., with a stationary phase of Carbograph 1 covered with AT1000 (Alltech, Deer-

field, IL, USA). This column provides the efficiency and the retention capability typical of gas–liquid–solid capillary chromatography (Bruner, 1994). An HP 6890 GC system (Hewlett Packard, Palo Alto, CA, USA) was used with the following temperature programme: 10 min at 35°C, then 10°C min^{-1} up to 150°C, using UHP Helium as a carrier gas.

Mass spectrometric detection was necessary because of the high specificity required for this kind of determination. An HP 6890 Quadrupole Mass Selective Detector (Hewlett Packard, Palo Alto, CA, USA) was operated in electron impact and in selected ion-monitoring (SIM) modes, selecting two specific m/z values for each compound. For quantitative purposes, calibration curves were created by loading the adsorption tubes with known volumes of gravimetrically calibrated standard gaseous mixtures, which contained the analytes of interest at certified concentration levels diluted in UHP nitrogen. The mixture containing the fully halogenated halocarbons, CFC-12, CFC-11, CFC-113, and CFC-114, was prepared at concentration levels close to those occurring in actual air samples (i.e. 507, 301, 101 and 50 ppt by volume, respectively). The mixture containing the hydrogenated halocarbons, HFC-134a, HCFC-22, HCFC-141b, and HCFC-142b, was prepared at the concentration levels of 101, 50, 50 and 50 pptvv^{-1}, respectively.

Quantitation limits were evaluated for the single components of the standard mixture using quadrupole mass spectrometric detector, and always in the SIM mode. Enriching 200 ml of a diluted standard mixture in the dual-layer adsorption tube, the halogenated halocarbons that are subject of this research were determined beginning with a concentration of 1 pptv. In this case, the signal given by each compound was at least five times greater than the background noise.

The precision of this method was tested by performing six-fold replicate analyses on the same actual air sample. Results obtained in terms of absolute error are reported in Table 1, together with the measured concentration data.

Table 1
Measurement repeatability evaluated on six replicate analysis of an actual air sample collected in a rural site located in central Italy (Concentration data expressed in ppts (10^{-12} v v^{-1}))

Compound	Chemical formula	pptv (10^{-12} by volume)
HFC-134a	CF_3CFH_2	13.2 ± 3.1
CFC-12	CF_2Cl_2	578.6 ± 11.9
HCFC-22	CHF_2Cl	170.6 ± 9.4
HCFC-142b	CH_3CF_2Cl	12.2 ± 1.0
CFC-114	$C_2F_4Cl_2$	24.2 ± 1.7
CFC-11	$CFCl_3$	289.3 ± 11.8
HCFC-141b	CH_3CFCl_2	14.4 ± 1.0
CFC-113	$C_2F_3Cl_3$	74.9 ± 4.7

3. Results and discussion

The proposed analytical method was applied during the analysis of actual air samples collected in different regions.

Air samples were collected in the following locations: Terra Nova Bay Region (Northern Victoria Land, Antarctica), and Mount Cimone (Northern Apennines, Italy).

Table 2
Selected halocarbons tropospheric mixing ratios measured in air samples collected in the 1998/99 Antarctic expedition

Compound	Concentration ppt $(10^{-12}$ by volume)	RSD (%)
HFC-134a	7.7	10
HCFC-22	61.6	5
CFC-12	526.3	2
HCFC-142b	8.3	6
CFC-114	23.6	5
CFC-11	275.2	5
HCFC-141b	8.2	7
CFC-113	73.1	7

3.1. Antarctica

Samples from Antarctica were collected from 1988 (Mangani, 1999) for the determination of fully halogenated halocarbons, and since 1997, the research has been extended to AFCs. In actual fact, Antarctica is the chosen sampling site when background level concentrations are to be determined. Six different sampling stations, far enough from the Italian Base main body to exclude any contamination problem, were identified. The fair level of similarity among concentrations measured in samples collected in the different stations, all within the deviation inherent to the analytical method, showed that the six stations could be definitely regarded as background level sites. The concentration levels of the selected CFCs and AFCs measured during the last Antarctic campaign (austral summer 1998–1999) are reported in Table 2. Concentration data relative to the fully halogenated halocarbons were compared to those measured since 1988, and thus the 10-year trend of their atmospheric mixing ratios can be tracked (Fig. 1). Data relative to the most abundant CFCs (i.e. CFC-12 and CFC-11), when compared with those obtained by other research groups involved in the same kind of measurements (Montzka, 1996; Cunnold, 1997), show a similar trend. It can be observed that, in the last three years,
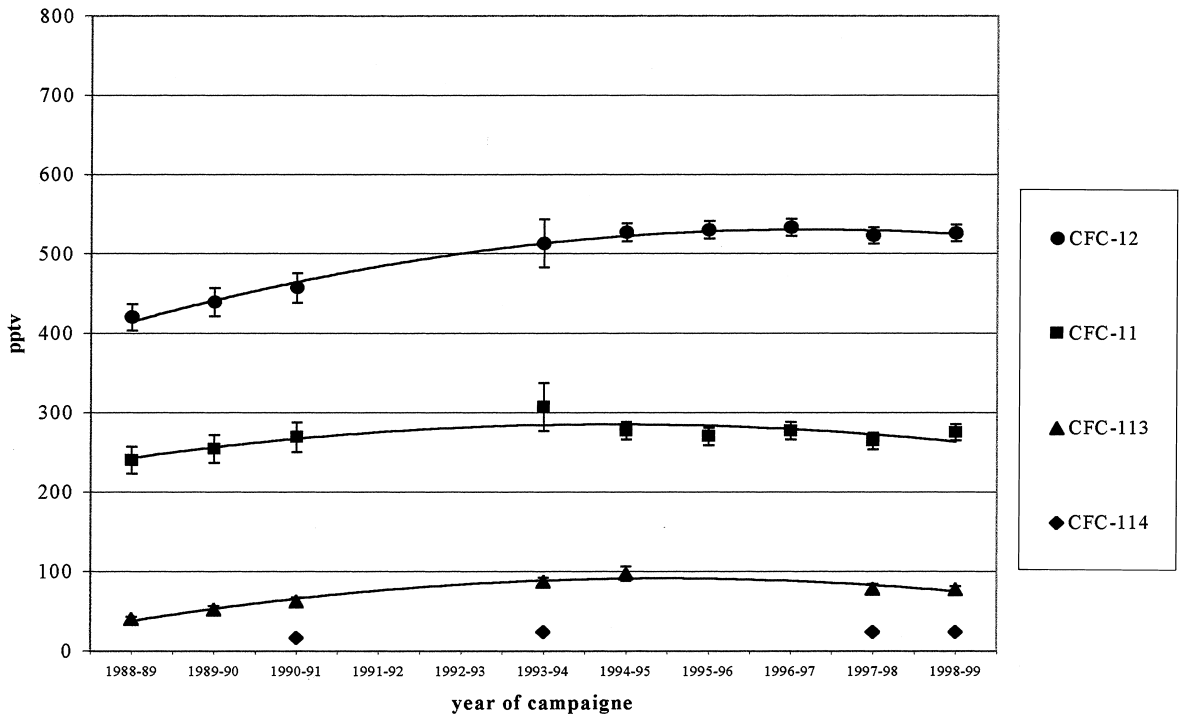

Fig. 1. CFC concentration levels measured in Antarctica over a 10-year period.
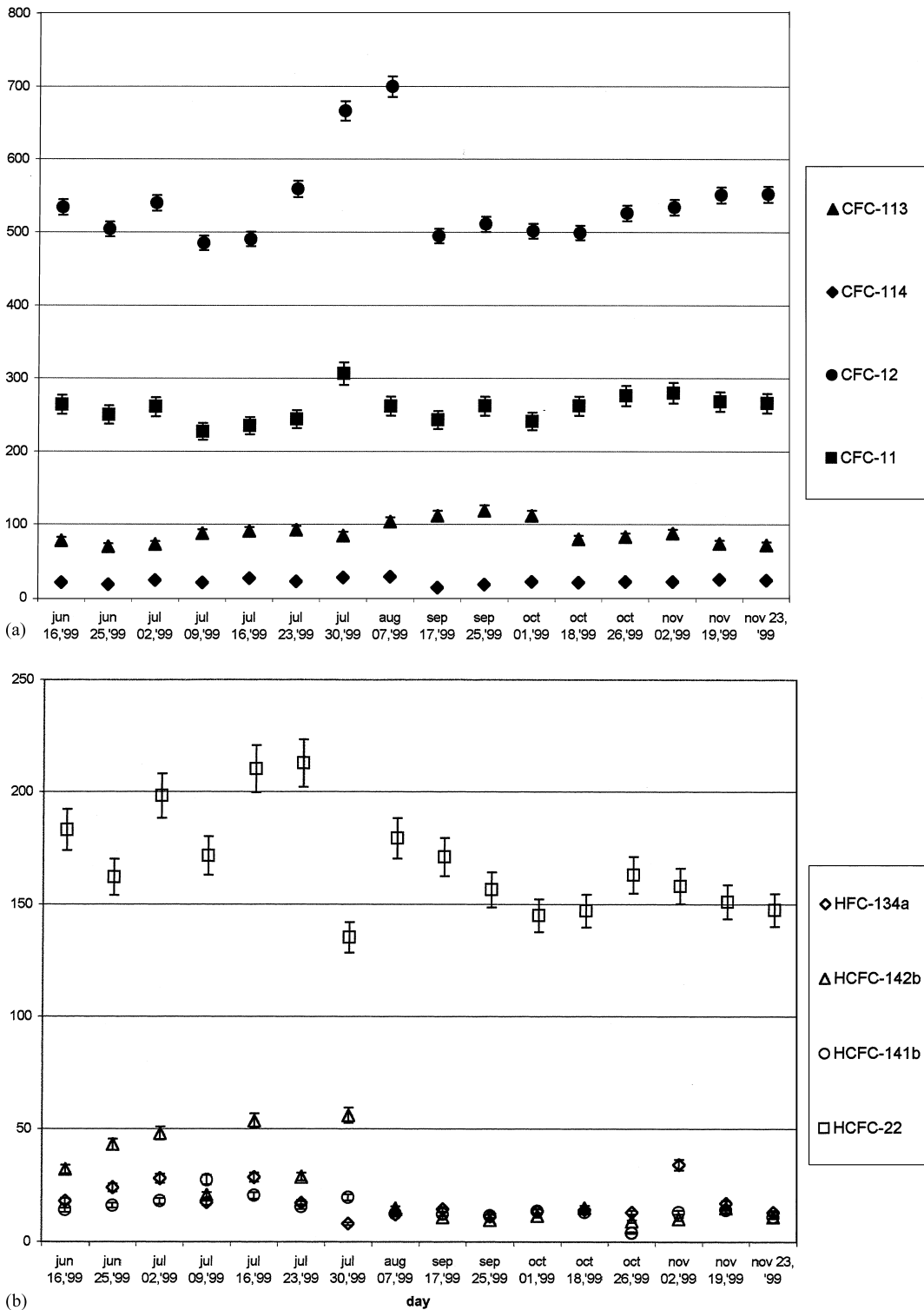
Fig. 2. (a) CFC concentration levels measured at the Mount Cimone Station from June to November 1999; and (b) AFC concentration levels measured at the Mount Cimone Station from June to November 1999.
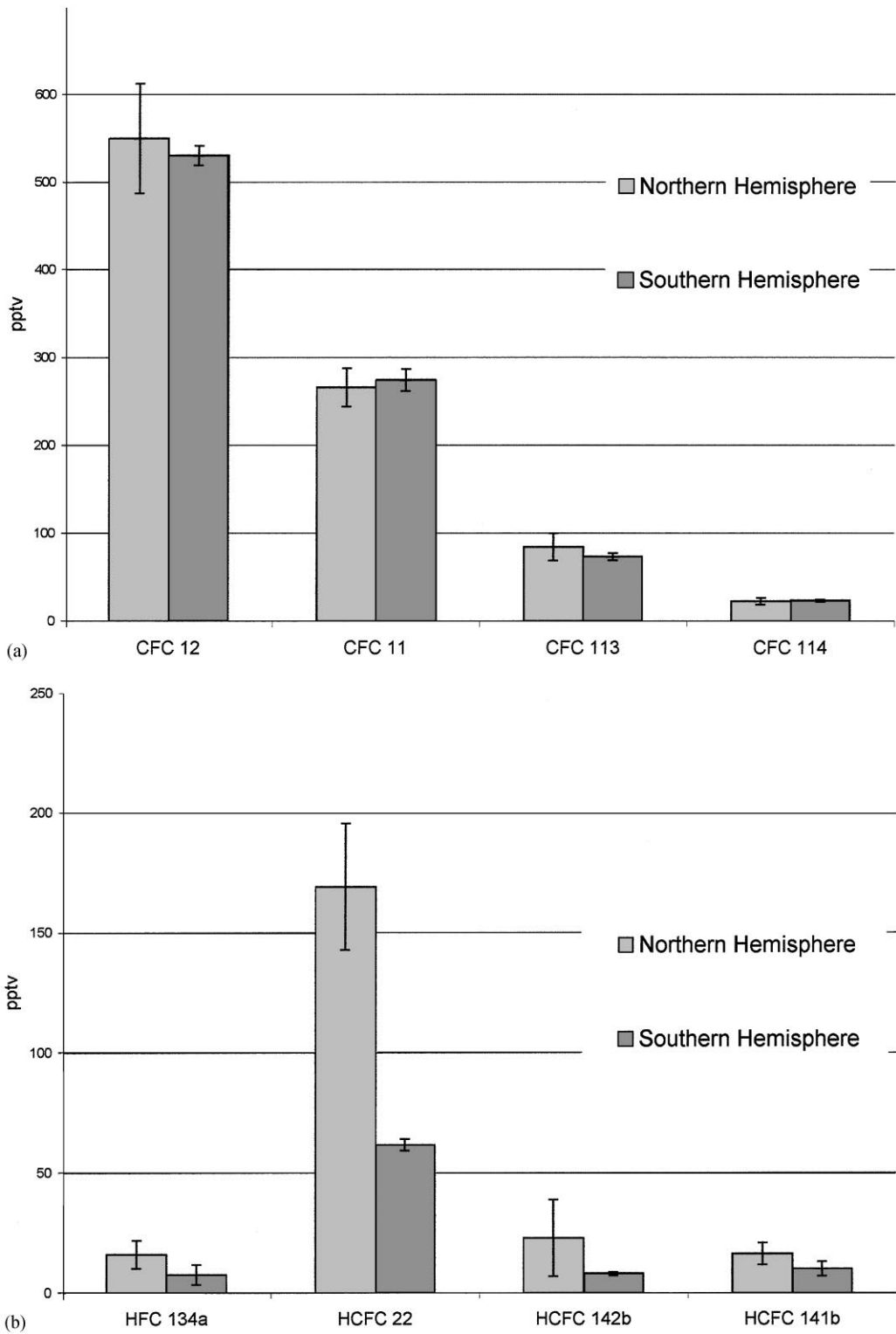
Fig. 3. (a) Comparison between average CFC concentration levels measured in the Northern and Southern Hemispheres; and (b) comparison between average AFC concentration levels measured in the Northern and Southern Hemispheres.

concentration levels of CFC-12 are substantially stable. However, the most challenging data are those concerning CFC-11, for which, beginning from the 1994–1995 campaign, a decrease in the absolute atmospheric concentration values has been observed. Nonetheless, it should be pointed out that the lowest concentration values, within the relative standard deviation ($\pm$ 10%), measured in the 1993–1994 samples, are close to the highest values of subsequent measurements. Furthermore, the lack of data concerning two consecutive campaigns (1991–1992, 1992–1993), when it was not possible to receive any air sample from Antarctica, is of crucial importance when evaluating the trend of subsequent concentration values. Nevertheless, CFC-11 concentration levels measured in air samples collected in subsequent campaigns confirm this trend.

Unfortunately, our data for CFC-113 and CFC-114 are insufficient. CFC-113 shows the same decrease in growth rate as the two most abundant species. CFC-114, of which measurements on a worldwide scale are rare, seems to be present at a substantially steady level over the past years.

3.2. Mount Cimone

Mount Cimone (2165 m above sea level) is the highest peak in the Northern Apennines, and is located on the borderline of two different climatic regions: continental Europe in a northerly direction, and the Mediterranean Basin in a southerly direction. Mount Cimone is among the windiest of the Italian meteorological stations, with prevailing winds blowing from SW and NE. On the peak of Mount Cimone, adjacent to the Italian Air Force Meteorological Observatory, is the "Ottavio Vittori" CNR (Italian National Research Council) Station, where since June 1999 weekly grab air samples are collected for the analysis of CFCs and AFCs. Figs. 2a and b report the atmospheric concentration levels of fully halogenated and hydrogenated halocarbons, respectively. Error bars represent deviations in replicate analyses of the same sample ($N = 5$). Measurements were performed from 16 June to 23 November 1999.

The interest of such measurements lies in the fact that Mount Cimone is, at the moment, the only station in Italy, and in the whole Mediterranean area, where AFC tropospheric levels are routinely monitored.

The availability of meteorological data, back-trajectories, and concentration data relative to other chemicals at the Mount Cimone station will allow future distinguishing, after proper studies, between polluted and unpolluted air masses.

Comparison between concentration levels measured in air samples collected in the two hemispheres for fully halogenated and hydrogenated halocarbons is reported in Figs. 3a and b, respectively, where error bars represent deviations among measurements performed on different days. As expected, for the phased-out and long-lasting compounds (i.e. the fully halogenated species) the inter-hemispheric exchange has led to substantially similar concentration levels in both hemispheres. However, broader deviations among concentrations measured in the Northern hemisphere with respect to those measured in Antarctica, show that, even if the use and consumption of CFCs has been prohibited since January 1996 in the countries that adhered to the Montreal Protocol, local emission sources are present. As can been seen from the plots reported in Fig. 2a, for selected compounds, concentration levels approximately 40% above average values were occasionally measured.

Inter-hemispheric exchange of the hydrogenated species is less efficient because of the short atmospheric lifetime and the fast growth rates of these compounds in the troposphere. Therefore, differences among concentrations measured in the two hemispheres are evident, together with higher deviations among measurements performed in the Northern hemisphere.

4. Conclusions

The variability in CFC concentrations measured in the site located in the Northern hemisphere shows that the influence of local emission sources is still evident, even after the restrictions on CFC use and consumption imposed by the Montreal Protocol. Therefore, continuous monitoring of these compounds is still necessary in order to correctly evaluating the actual emission rates into the atmosphere of these chlorine-containing compounds. Furthermore, measurements of AFCs are recommended in relation to the increase in their production and consumption and to their possible environmental impact.

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