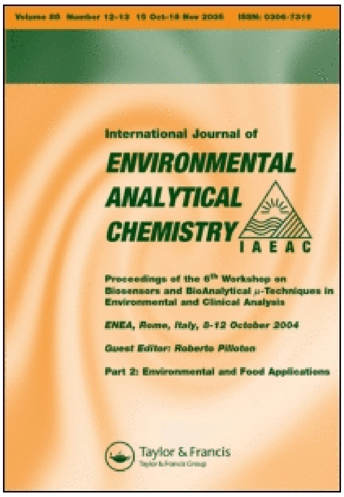

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Ten Years Monitoring of Chlorofluorocarbons at the Antarctica: Results and Perspectives

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To cite this Article Mangani, Filippo , Maione, Michela , Lattanzi, Luciano and Arduini, Jgor(2001) 'A Ten Years Monitoring of Chlorofluorocarbons at the Antarctica: Results and Perspectives', International Journal of Environmental Analytical Chemistry, 79: 4, 273 — 282

To link to this Article: DOI: 10.1080/03067310108044389

URL: http://dx.doi.org/10.1080/03067310108044389

Intern. J. Environ. Anal. Chem., Vol. 79(4), pp. 273-282
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A TEN YEARS MONITORING OF CHLOROFLUOROCARBONS AT THE ANTARCTICA: RESULTS AND PERSPECTIVES

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(Received 10 January 2000; In final form 5 May 2000)

Chlorofluorocarbons are man-made long lasting atmospheric pollutants of great environmental concern, responsible for important global change phenomena. Recently, they were replaced by hydrogenated halocarbons that, even if less persistent, do not lack in environmental impact. Atmospheric concentrations of these compounds were measured in Antarctica by gas chromatography. The extremely low atmospheric mixing ratios of these compounds require a pre-concentration step of the air sample on suitable adsorbent in order to meet the sensitivity of the analytical method. Results obtained analyzing air samples collected in Antarctica since 1988 for the determination of CFC-12 and CFC-11 are reported, together with data concerning the less abundant species.

Keywords: Chlorofluorocarbons; hydrogenated halocarbons; graphitized carbon black; gas chromatography – mass spectrometry

INTRODUCTION

Chlorofluorocarbons (CFCs) tropospheric concentrations were monitored in Terra Nova Bay Region (Northern Victoria Land-Antarctica) since austral summer 1988–1989[1]. Such study was aimed to evaluate the efficacy of restrictions on CFCs use and consumption, laid down by the *Montreal Protocol to Reduce Substances that Deplete the Ozone Layer*[2]. Since Northern Hemisphere accounts for 95% of total emissions of these anthropogenic compounds into troposphere, Antarctica can be regarded as the chosen sampling site to assess their background concentration levels.

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In the last years, our research was extended to those compounds more recently introduced as an alternative to CFCs: hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). The design of these molecules involved the introduction of hydrogen atoms, giving rise to more reactive compounds whose transport to stratosphere is made relatively inefficient[3]. For this reason, HCFCs have ozone depleting potential (ODP) values quite low, meanwhile HFCs have zero ODP. However, due to their high global warming potential (GWP), both HCFCs and HFCs were listed in *Kyoto Protocol on Global Climatic Change*[4], among those compounds responsible for global warming whose emissions must be regulated in the next years. Atmospheric lifetimes and GWP of selected hydrogenated halocarbons compared with those of CFC11 are reported in Table I.

TABLE I Atmospheric lifetimes and GWP of selected hydrogenated halocarbons compared with those of CFC11

Compound	*Atmospheric Lifetime (years)*	*GWP*
HCFC-22 (CHF_2Cl)	14	0,36
HFC-134a (CF_3CFH_2)	14	0.27
HCFC-141b ($CFCl_2CH_3$)	7	0,092
HCFC-142b (CH_3CF_2Cl)	17,8	0,36
CFC – 11	50	1,0[a]

a. *CFC 11 GWP is approximately 1300 times greater than that of CO_2

TABLE II List of tile compounds analyzed

Commercial Name	*Chemical Formula*
CFC-12	CF_2Cl_2
CFC-11	$CFCl_3$
CFC-114	$C_2F_4Cl_2$
CFC-113	$C_2F_3Cl_3$
HCFC-22	CHF_2Cl
HFC-134a	CF_3CFH_2
HCFC-142b	CH_3CF_2Cl
HCFC-141b	CH_3CFCl_2

In order to assess trends in their tropospheric mixing ratios, measurements of CFCs and their replacement compounds are recommended. However, concentration levels of HCFCs and HFCs are extremely low due both to their recent introduction and to their tropospheric reactivity. Therefore, for the simultaneous determination of different halocarbons of environmental concern, improvements of the analytical methodology previously used were necessary, especially in the sampling enrichment step and in the gas chromatographic separation.

In this paper the results of a ten years monitoring of most abundant chlorofluorocarbons (i.e. CFC-12 and CFC-11) are reported. Concentration data regarding less abundant fully halogenated species are reported as well, together with preliminary data for to the recently introduced hydrogenated halocarbons.

A comprehensive list of the compounds that were object of this study is reported in Table II.

EXPERIMENTAL

The overall analytical procedure consists of the following steps: grab sampling, sample enrichment, thermal desorption, capillary gas chromatographic analysis, mass spectrometric detection, and calibration.

Air samples were collected filling, by means of a portable ultra clean air pump (model FC-1121, Biospheric Research Corporation, Hillsboro, OR, USA), at the pressure of 3 atm, 0.85 liter Stainless Steel canisters (Biospheric Research Corporation, Hillsboro, OR, USA), following an already described procedure[1].

Particular attention was devoted to the study of an adsorbent capable of trapping at ambient temperature even the most volatile compounds. A detailed study concerning the development of an adsorption tube to be used in this kind of measurements is reported elsewhere[5]. It is a dual layer adsorption tube designed as follows: a glass tube (10 cm long x 0.3 cm i.d.) was filled with 100 mg of a graphitized carbon black, whose surface area was 90 m g^{-1} (Carbograph 1, Alltech, Deerfield, IL), and with 300 mg of Carbograph 5 (Lara Srl, Rome, Italy) with a surface area of 560 m g^{-1}. When using the dual layer adsorption tube, the air sample is passed first through the Carbograph 1 which retains the less volatile halocarbons, and then through Carbograph 5 which adsorbs most volatile compounds. Nevertheless, during the thermal desorption step, in which the carrier gas flow direction is reversed, the less volatile halocarbons are easily released by the lower surface area adsorbent, while the more volatile compounds are released from the high surface area adsorbent. The use of this adsorption tube allows enriching 200-ml aliquots of the air sample without using cryogenic fluids and at the same time allows a full release of all the compounds of interest.

The trapped analytes were released by heating the adsorption tube at 220°C for 5 minutes 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 the flow rate of 6 ml min^{-1}. Cryofocussing of the analytes on top of the column was obtained by freezing a fused silica capillary pre-column at the temperature of −150°C for 5 minutes.

The gas chromatographic column was specially made for this kind of separation requiring the efficiency and the retention capability typical of gas liquid solid capillary chromatography. It is a graphite layer open tubular column 90m long × 0.25 mm i.d., whose stationary phase is Carbograph 1 covered with AT1000 (Alltech, Deerfield, IL, USA)[6]. A HP 6890 GC system (Hewlett Packard, Palo Alto, CA, USA) was used with the following temperature programme: 10 minutes at 35°C, then 10°C/min. up to 150°C. UHP Helium was used as carrier gas.

Mass spectrometric detection was necessary due to high specificity required for this kind of determination. A HP 6890 Quadrupole Mass Selective Detector (Hewlett Packard, Palo Alto, CA, USA) was operated in electron impact and in the selected ion monitoring (SIM) mode. The SIM program is reported in Table III.

TABLE III SIM Program

Compound	*m/z (% relative abundance)*
HCFC-22	51 *(100%)*, 67 *(15%)*
HFC-134a	69 *(71%)*, 83 *(63%)*
HFC-142b	65 *(100%)*, 85 *(14%)*
HCFC-141b	81 *(100%)*, 83 *(41%)*
CFC-12	85 *(100%)*
CFC-114	85 *(100%)*, 135 *(52%)*
CFC-114a	135 *(100%)*, 101 *(84%)*
CFC-11	101 *(100%)*, 103 *(66%)*
CFC-113	101 *(100%)*, 151 *(68%)*

For quantitative purposes, calibration curves were created by loading the adsorption tubes with known volumes of gravimetrically calibrated standard gaseous mixtures, containing the analytes of interest at certified concentration levels diluted in UHP nitrogen. The mixture containing 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 pl l^{-1} by volume, respectively), meanwhile the mixture containing HCFC-22, HCFC-141b, HFC-134a and HFC-142b, was prepared at the concentration level of 101, 50, 50 and 50 $\mathrm{pl\,l^{-1}}$, respectively.

RESULTS AND DISCUSSION

Air samples were collected in six different sampling sites selected on the base of their distance from the "Terra Nova Bay" Italian Base main body. This was in order to avoid the contamination due not only to the base activities, but also to the base itself (i.e. CFCs emission from foams used for thermal insulation of the base facilities). In the last six years we collected the air samples in the six sampling stations listed in Table IV together with geographic co-ordinates. 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. Air samples were stored in canisters up to 10 weeks. Then, 200-ml aliquots of the sample were enriched few minutes before the GC-MS analysis. The reconstructed total ion chromatogram obtained is depicted in Figure 1. Quantitative evaluations were made on the single specific ion traces, thus elucidating the contribute of the single selected m/z values. As it can be seen from the single ion traces reported in Figure 2, this allowed overcoming problems related to the separation of the first eluting peaks that, given the considerable differences in concentrations of CFC-12 with respect to HFC 134a, HCFC-22 and HCFC 142b, is rather crucial. Mean concentration values measured in air samples collected in Antarctica during the 1998–99 austral summer campaign are reported in Table V, together with standard deviations. As it can be seen, the proposed method allows the simultaneous determination of compounds of different volatility, present at concentration levels ranging from a few up to 500 $\mathrm{pl\,l^{-1}}$ (10^{-12} v/v).

TABLE IV Sampling sites selected in Terra Nova Bay region (Northein Victoria Land, Antarctica)

Station	*Lat S*	*Long E*	*Altitude (m)*
Cape Russel	74°55′	163°90′	70
Edmonson Point	74°20′	165°07′	sea level
Kay Island	74°04′	165°19′	sea level
Mount Melbourne	74°26′	164°76′	1130
Start Nunatak	75°54′	162°33′	96
Tourmaline Plateau	74°08′	163°28′	1650

TABLE V Selected halocarbons fropospheric mixing ratios measured in air samples collected in the 1998/99 Antarctic expedition

Compound	*Concentration* pll^{-1} *(*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

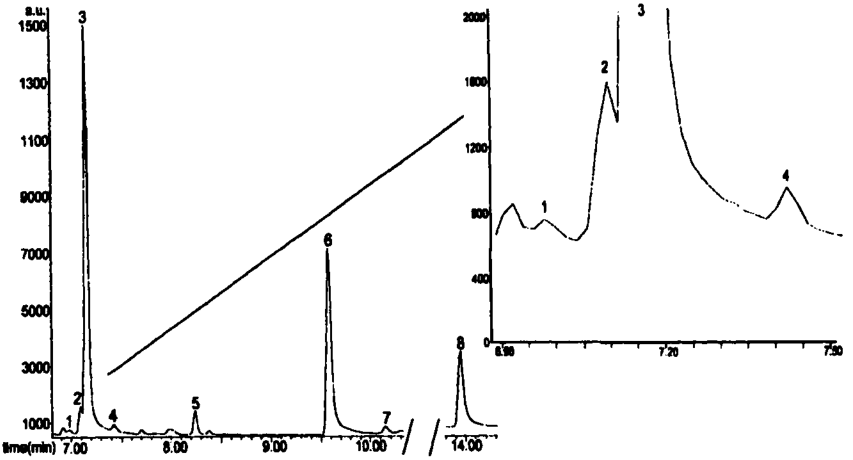

FIGURE 1 Total ion reconstructed chromatogram obtained analyzing a 200-ml air sample collected in Antarctica during the 1998–99 campaign. Peak identification: 1)HFC-134a; 2)HCFC-22; 3)CFC-12; 4) HCFC-142b; 5)CFC-114; 6)CFC-11; 7)HCFC-141b; 8)CFC-113. For chromatographic conditions see text

Since CFC-12 and CFC-11 were monitored starting from austral summer 1988–89, it is possible to observe a ten years trend of their background tropospheric mixing ratios. Concentrations measured are plotted in the graph shown in Figure 3, meanwhile Table VI reports concentration data. A continuous increase in atmospheric mixing ratios of CFC-11 can be observed until 1993, meanwhile

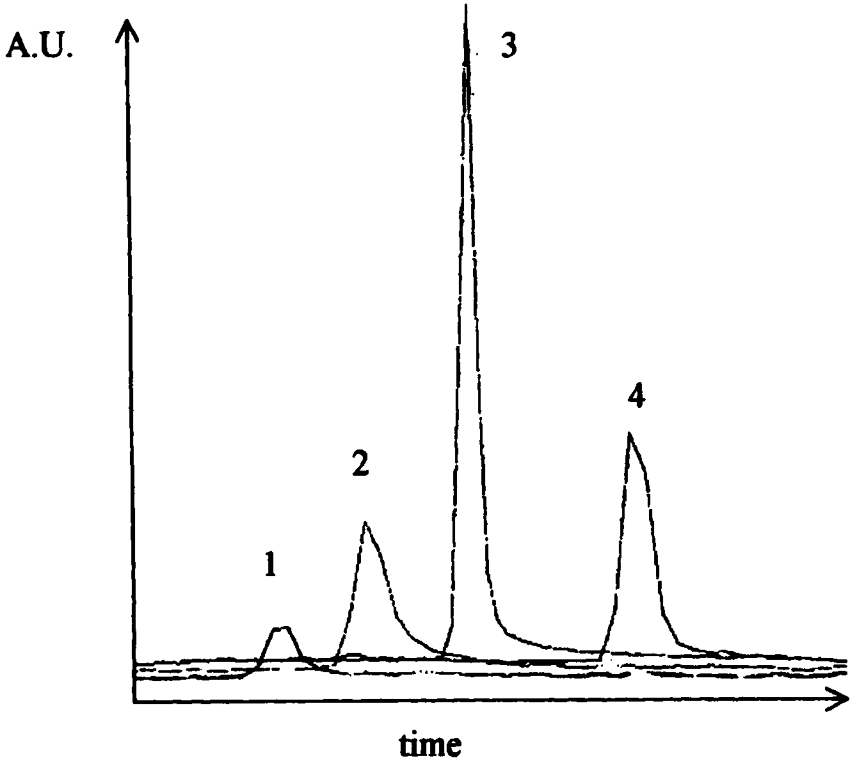

FIGURE 2 Single ion traces referred to the chromatogram reported in Figure 1. Peak identification: 1) ion 83 (HFC-134a); 2) ion 67 (HCFC-22); 3) ion 101 (CFC-12); 4) ion 65 (HCFC-142b)

starting from 1994 a decrease not only in growth rate, but also in the absolute concentration is evident. This is the consequence of the sharp decrease in CFC-11 production that took place at the end of the eighties, following the restrictions imposed by the Montreal Protocol in September 1987, that committed the 27 signatory countries to reduce its use of certain CFCs by 50 percent of their level of use in 1986 by 1999. At present, concentration levels of this compound are at the same level they had at the beginning of the nineties.

According to the finite-increment model[7] describing the mean change in tropospheric mixing ratio for a one-year interval in both hemispheres, the trend in CFC-12 concentrations slightly differs from that observed for CFC-11. In fact, mean atmospheric lifetime is one of the factors affecting such a change and for CFC-12 it was estimated to be ca. 100 years, a value that is about double if compared with that of CFC-11. As a consequence the decrease in the growth rate of

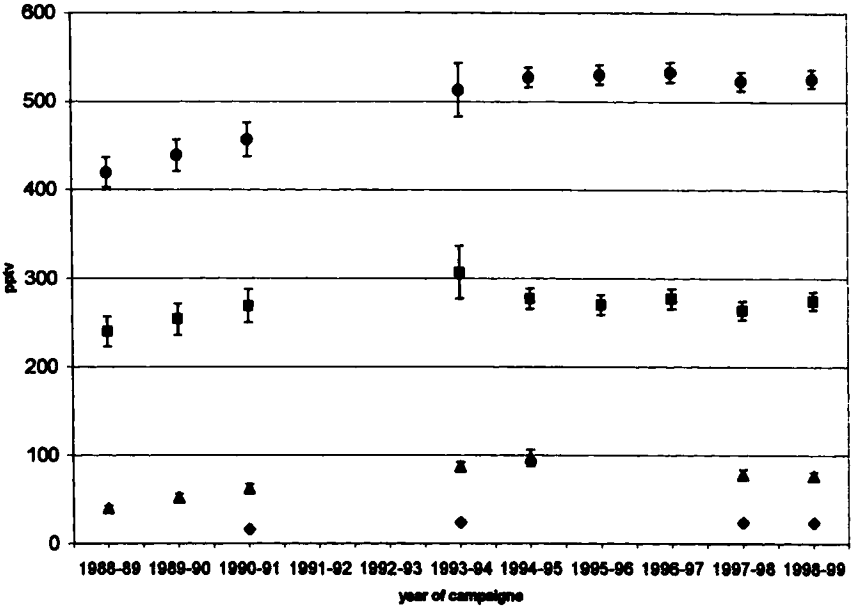

FIGURE 3 Concentration trend of selected halocarbons over a ten years period. (•) CFC-12; (■) CFC-11;(▲) CFC-113; (♦) CFC-114

CFC-12 was less pronounced, and a slight absolute decrease in atmospheric mixing ratio was observed only in the last two years.

Our data concerning less abundant fully halogenated halocarbons, i.e. CFC-113 and CFC-114, are lacking. However, changes in their tropospheric concentrations are reported in Figure 3 as well. The trend of CFC-113 is substantially similar to that observed for the most abundant species. CFC-114, the less abundant among the fully halogenated halocarbons considered, is one of the most persistent species with high values of GWP and ODP. Measurements concerning its atmospheric mixing ratio are rare, since it is not monitored by those groups involved in global measurements of ozone depleting substances. Our data are obviously insufficient for a correct evaluation of the atmospheric trend. However, we measured substantially steady levels of CFC-114 in the last years.

When comparing our data with those obtained, in the same time interval, by other research groups involved in the monitoring of the halogenated hydrocarbons[8], we observe not only a similar trend, but also quite similar absolute concentration values.

Two years measurements of the atmospheric mixing ratio of hydrogenated halocarbons constitute the starting point for future evaluations. A comparison between data obtained analyzing air samples collected during two subsequent Antarctic campaigns (1997–98 and 1998–99) is reported in Table VII. Concentration value for HFC·134a measured in samples collected during the 1997–98 campaign are not reported, because underestimated.

TABLE VI Fully halogenated halocarbons concentrations measured since 1988. Concentrations are expressed in $pl\,l^{-1}$

Year of Campaign	*CFC-12*	*CFC-114*	*CFC-11*	*CFC-113*
1988–89	420 ± 10%		240 ± 7%	40 ± 7%
1989–90	439 ± 10%		254 ± 7%	52 ± 8%
1990–91	457 ± 10%	16 ± 6%	269 ± 7%	62 ± 8%
1993–94	513 ± 7%	24 ± 8%	307 ± 10%	87 ± 6%
1994–95	527 ± 6%		277 ± 4%	97 ± 9%
1995–96	530 ± 6%		270 ± 4%	
1996–97	533 ± 6%		277 ± 4%	
1997–98	523 ± 6%	24 ± 8%	264 ± 4%	78 ± 8%
1998–99	526 ± 6%	24 ± 4%	275 ± 4%	77 ± 5%

TABLE VII Hydrogenated halocarbons concentrations measured in two subsequent campaigns

Compound	$pl \cdot l^{-1}$		
	1997–98	*1998–99*	*RSD%*
HCFC-22	76,7	61,6	5
HFC-134a	–	7,7	10
HFC-142b	7,9	8,3	6
HCFC-141b	7,3	8,2	7

We compared the hydrogenated halocarbons concentration data with those obtained by other researchers that monitored these compounds in air samples collected in the Southern Hemisphere[9] from 1991 to 1996. Concentration data relative to HFC-134a HCFC-141b are consistent with the annual increase estimated for these compounds, meanwhile data relative to HCFC-22 and HCFC-142b are slightly lower with respect to those reported in the above cited paper[9]. However, since the considered concentrations are extremely low, the differences observed are in the range of a few parts per trillion. On the other hand, a comparison with data obtained analyzing air samples collected in the

Northern Hemisphere is meaningless. In fact, due to tropospheric reactivity of the hydrogenated halocarbons, their background levels are likely to strongly differ from concentrations measured close to the emissions sources, meanwhile atmospheric mixing ratios of the fully halogenated more persistent species, at the moment, do not show strong differences between the two hemispheres[10].

To conclude, it should be remembered that, even if mathematical models able to predict the change in the atmospheric mixing ratio of the compounds considered are available, a continuos monitoring of these compounds is still recommended. Firstly because of the many uncertainties concerning the emissions of such compounds[11,12], then because experimental concentration data constitute a useful tool for validation of models themselves.

Acknowledgements

The present study was carried out in the frame of the Italian National Programme for Research in Antarctica (PNRA). Authors are indebted to Mauro Montagnoli (National Research Council, Institute for Atmospheric Pollution, Rome, Italy) for collecting air samples during the 1997–98 and 1998–99 campaigns.

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