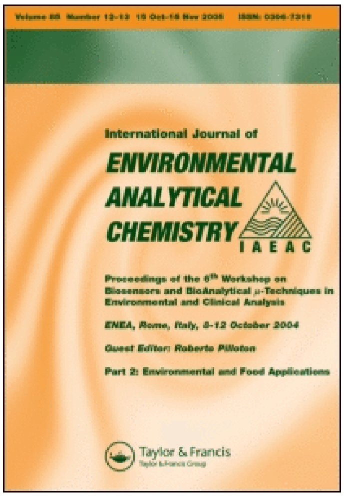

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CHLOROFLUOROCARBONS MEASUREMENT IN THE LOWER ATMOSPHERE OF THE ANTARCTICA

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Data concerning chlorofluorocarbons and other halogenated hydrocarbons concentrations in ground-level atmosphere at Antarctica are reported. Measurements were carried out during two campaigns: Austral summer 1989/90 and 1990/91. Samples collected were analyzed in the laboratory by gas chromatography-mass spectrometry and "in situ" by gas chromatography-electron capture detection. Substantial improvements in the instrumentation are also reported where for what trapping and injection of both air samples and calibration mixtures are concerned.

KEY WORDS: CFCs, air, calibration, Antarctica.

INTRODUCTION

Measurements of global distribution and trends of chlorofluorocarbons (CFCs), as well as other source gases which may directly or indirectly affect the stratospheric ozone levels (i.e. CH_4, N_2O, CO, CO_2, bromine compounds, non methane hydrocarbons, etc.) are extremely necessary, and are recommended by all of the official "ad hoc" organizations and panels[1-4] which deal with the problem of the depletion of the ozone layer. In fact, global distribution and trends allow data to be gathered on the atmospheric lifetime of these compounds or conversely, on their estimated release into the atmosphere. Thus, it is possible to calculate the total amount of atomic species immitted into the atmosphere which deplete ozone, or to check for tropospheric sinks.

CFCs are still considered to be the most potentially dangerous compounds for the ozone layer[4]. CFC11, CFC12, CFC113 together with CH_3CCl_3 and CCl_4 account for 85% of the anthropogenic organochlorine loading of the troposphere. These substances, along with CFC114 and CFC22, are the compounds monitored most often at several stations operating

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in different parts of the world. However, while most of the stations are located in the Northern Hemisphere, Antarctica is conveniently located in the Southern Hemisphere far away from large emission sources (with the exception of the local scientific bases). Therefore, Antarctica is theoretically an ideal site for the measurement of the "background" tropospheric concentration of source gases.

In the frame of the National Italian Programme for Research in Antarctica (PNRA), we started to measure the concentration of the most significant afore mentioned compounds such as CFC12, CFC114, CFC11, CFC113, CH_3CCl_3, CCl_4 during the December 1989–February 1990 expedition to Terra Nova Bay (Victoria Land, Antarctica). Measurements were repeated during the next expedition, which took place from December 1990 to February 1991. It was not possible to carry out measurements in different months of the year because of the absence of a permanent base.

Both "in situ" and non "in situ" measurements were performed. The former were based on gas chromatography- electron capture detection (GC-ECD) and "on line" sampling, while the latter were based on the gas chromatography high resolution mass spectrometry analysis (GC-HRMS) of samples collected at Antarctica. The data obtained, together with description of the methodologies used, is reported in this paper.

EXPERIMENTAL

As stated above, measurements were carried out following two different, but parallel methodologies.

The first one, widely described in several previous papers[5-10], consisted in collecting air samples in different sampling sites far away (within a 100 Km radius) from the Italian Base at Terra Nova Bay. U-shaped glass/lined stainless steel traps (30 cm long × 0.3 cm I.D.) were used. Two different types of Graphitized Carbon Black (8) were employed as adsorbing material: Sterling Ft (~10 m^2/g surface area) 800 mg, or Vulcan G (~90 m^2/g surface area) 400 mg. The choice of the type to be used was based on the volatility of the compounds to be determined. These two materials are commercially available as Carbopack C and B (Supelco, Bellefonte, PA USA) or Carbograph 1 and 2 (Alltech, Deerfield, IL USA), respectively.

Traps were connected to a portable sampler consisting of a pump equipped with an electronic transducer for flow-rate and sample volume measurements. During sampling, traps were kept at the temperature of dry ice because of the low break through volume (BTV) which most of the compounds of interest exhibit at room temperature[5]. One or two litres of air were passed through the trap, depending on the compounds to be determined. Traps were then sealed, stored and brought back to Italy, in order to be analyzed by GC-HRMS.

The gas chromatograph used was a DANI 3900 (Dani Strumentazione Analitica SpA, Monza, Italy), equipped with a glass column (2m long × 0.2 cm I.D.) packed with Vulcan G 80–100 mesh coated with 0.1% SP1000.

The temperature programme was 4 min. at 40°C, then 15°C/min. up to 190°C and hold for 10 min. Samples were injected into the GC column by heating the trap at 100°C or 120°C, depending on the specific adsorbing material (Carbopack C or B respectively). Ultra High

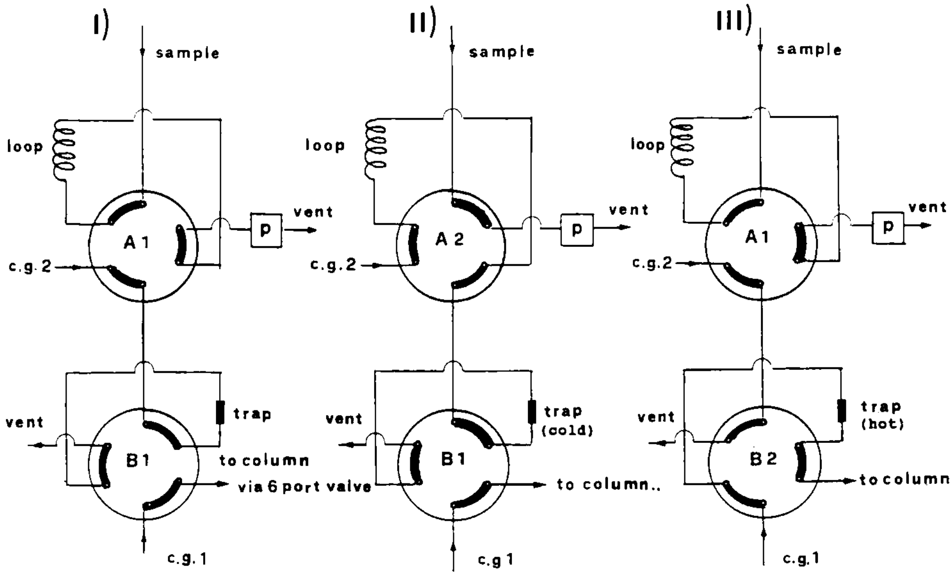
Table 1 Selected m/z values for the GC-MS analysis of Halocarbons.

COMPOUNDS	*m/z*
CFC12	84.9647, 86.9627
CFC114	84.9647, 86.9627
CFC11	100.9361, 102.9361
CFC113	100.9361, 102.9361
CH_3CCl_3	96.9612, 116.9065
CCl_4	116.9065

Purity (UHP) Nitrogen was used as carrier gas, and permeation tubes, made in our laboratory, were used as primary standard[11]. The GC was coupled to a VG 70–70H mass spectrometer (VG Micromass Ltd, Manchester GB) used in the selected ion monitoring mode (SIM) at a resolution power of 3000 (10% valley). Two characteristic m/z values were selected for each compound (except for CCl_4) in order to use the relative abundance on the basis of the isotopic ratio of ^{35}Cl and ^{37}Cl for positive identification. In Table 1 the selected m/z values are shown.

The "in situ" measurements were performed by means of a commercially available gas chromatograph, ETA 8521 Environmental Trace Analyzer (Dani Strumentazione Analitica SpA, Monza, Italy), which was located in the OASI (Infrared Submillimetric Astronomic Observatory) laboratories at Terra Nova Bay. The instrument, equipped with a device for automatic and continuous air sampling, was completely modified for our purposes.

The working mechanism of the instrument, detailed in previous papers[10,12] can be summarized in three subsequent phases: (I) air sampling, (II) sample transfer, (III) sample desorption and injection, as shown in Figure 1.



Air Sampling and Stand By

Sample Transfer to Trap

Sample Desorption and Injection

Figure 1 Diagram of the apparatus for air sampling and injection, showing the various operation steps.

(I) Air is sampled by means of a pump (P) and fills a 50 mL stainless steel loop. (II) A six-port valve (A) is switched and the sample is transferred from the sampling loop to a frozen stainless steel microtrap (5 × 0.1 cm I.D.) filled with an adsorbent material. (III) The microtrap is flash-heated and the preconcentrated sample is injected in the GC column, after switching a second six-port valve (B).

The gas chromatographic column was identical to the one described above. The temperature programme was 4 min. at 40°C then 4°C/min. to 160°C and hold for 20 min. UHP Nitrogen, further purified by means of a molecular sieve trap, was the carrier gas. A ^{63}Ni frequency modulated electron capture detector was used.

The modifications introduced essentially regard the sampling and calibration apparatus.

During the sampling step, a K_2CO_3 trap was placed at the sampling device inlet in order to eliminate water. The adsorbing material contained in the microtrap (originally active charcoal) was substituted with graphitized carbon black (Vulcan G, 50 mg). Then, several parameters were optimized experimentally: a) the microtrap temperature during the trapping process was brought down from –8 to –50°C, by means of dry ice, in order to trap the more volatile compounds; b) the time and the volume of gas necessary for a complete transfer of the sample from the microtrap to the GC column were 4 minutes and 140 mL, respectively; c) optimum temperature for complete desorption of all the compounds, with no decomposition problem (except with CCl_4) was found to be 280°C.

Table 2 shows the recoveries of the compounds of interest from the microtrap under different experimental conditions. Optimum conditions are reported in the last column.

Calibration was performed again by means of permeation tubes. In order to calibrate the instrument under the same conditions as those during the actual sampling, a third six-port valve, positioned before valve A was utilized. This valve was equipped with a 200 μL microloop and was connected to the effluent from the permeation tubes on one side, and to the 50 mL sampling loop and the frozen microtrap on the other. Calibration was performed twice a day.

Table 2 Recoveries (%) of the compounds of interest under different experimental conditions. RSD in brackets.

t_r =Transfer time; $V_{tr.g.}$ =volume of transfer gas; $T_{mt.s.}$, $T_{mt.d.}$=microtrap temperature during sample transfer and desorption, respectively.

COMPOUNDS	RECOVERIES (%)							
CFC12	0	0	0	0	0	0	3.6	100(3)
CFC114	—	—	—	—	82	80	92	92(2)
CFC11	83	78	88	76	84	93	90	94(4)
CFC113	93	91	94	94	89	88	89	94(2)
CH_3CCl_3	92	95	94	97	93	91	90	95(3)
CCl_4	32	33	35	35	41	40	27	65(5)
EXPERIMENTAL CONDITIONS								
t_r (min)	3	4.5	4	4	4	4	4	4
$V_{tr.g.}$ (mL)	102	154	140	140	140	140	140	140
$T_{mt.s.}$ (°C)	-8	-8	-8	-8	–20	–20	–35	–50
$T_{mt.d.}$ (°C)	210	210	210	100	210	280	280	280

Table 3 Halocarbons concentrations 1990/91 campaign. Laboratory measurements. N =Samples number. RSD in brackets.

COMPOUNDS	*N*	*pptv*	*RSD*
CFC12	13	452	(12)
CFC114	17	16	(6)
CFC11	18	269	(8)
CFC113	28	58	(7)
CH_3CCl_3	26	129	(15)
CCl_4	22	118	(25)

RESULTS

Laboratory measurements

During the 1990/91 campaign, 60 samples were collected at about 20 stations (Figure 2), two or three traps were sampled at each site on different days. Several traps were excluded because of contamination problems. Results are reported in Table 3. The table shown is somewhat different (except for CFC12 and CFC11) from the preliminary ones released or published in a previous paper (13). Calibration problems were encountered at the time the samples were analyzed. A recent re-evaluation of the data concerning permeation tubes led to the above reported values.

In situ measurements

These were carried out over a 20 day period (from January 15th to February 5th). The instrument was placed in the OASI laboratories, located 500 meters away from the Italian Base main body. Two or three samples were collected and analyzed every day. Unfortunately, heavy contamination was noticed at the retention time of CFC11, probably due to emission from the foam used as insulating and packing material at the base. Moreover, pollution caused by some of the base activities may have given rise to further contamination problems. These considerations may also be true for the CFC114 and CCl_4 data, which show values higher than those obtained in laboratory measurements. Such drawbacks can be overcome by arranging a monitoring station, constructed with suitable materials and built in a location free from the influence of the base, and also taking into account the main wind directions. Further improvements of the instrumentation are still in progress, with the aim of creating a monitoring station that would function almost completely unattended. In Table 4, data from the "in situ" measurements are reported. Also in this case, a re-evaluation of calibration data yielded new values for CFC113 and CH_3CCl_3.

By comparing the data obtained for CFC11 and CFC12 during the 89/90 campaign (reported in ref. 12) with those obtained during the 90/91 campaign (Table 5), an increase in concentrations can be observed. This increase should be taken with caution and cannot be considered a trend because it is based on only two years of measurements. However, the concentration values are in good agreement with the trend that can be forecasted from the

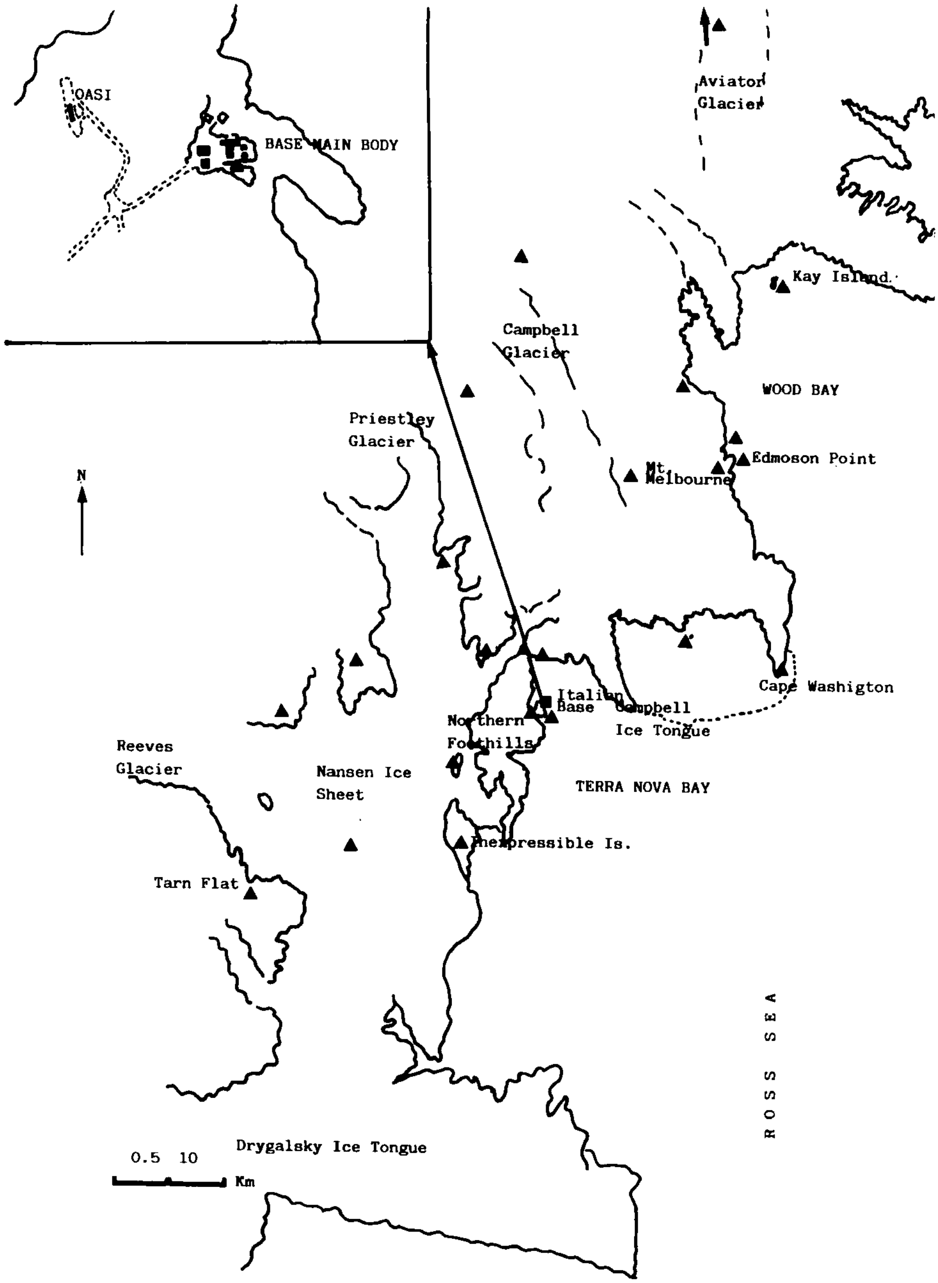


Figure 2 Sampling sites (▲) during the 1990/91 campaign.

Table 4 Halocarbon concentrations 1990/91 campaign. In situ measurements. N = Samples number. RSD in brackets.

COMPOUNDS	*N*	*pptv*	*RSD*
CFC12	16	462	(10)
CFC114	14	34	(8)
CFC11	—	—	—
CFC113	18	66	(7)
CH_3CCl_3	14	131	(14)
CCl_4	12	160	(21)

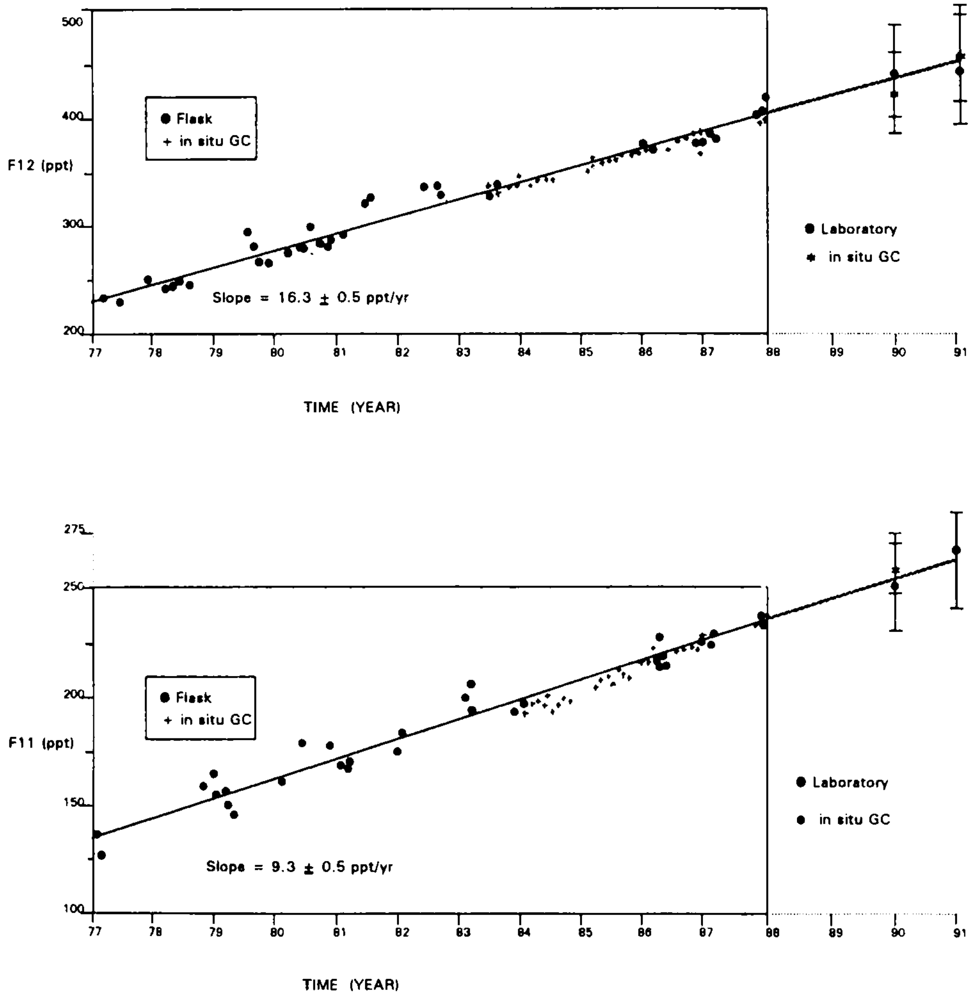


Figure 3 CFC11 and CFC12 concentration trends in Antarctica, from reference 14 (in pptv)

Table 5 Comparison between the halocarbon concentrations in Antarctica during the 1989/90 and the 1990/91 campaigns.

Compound	*Average Concentration (pptv)* 1989/90	1990/91	*estimated increase*
CFC12	439	457	18
CFC114	—	16	—
CFC11	254	269	15
CFC113	52	62	10
CH_3CCl_3	125	130	5
CCl_4	—	118	—

measurements carried out by other research groups over the last 15 years in the Antarctic environment as shown in Figure 3[14].

It is worth pointing out that the high sensitivity of the method allows the determination of compounds such as CFC114 and CFC113, the measurement of which is very rare because of their low concentration levels in the troposphere.

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