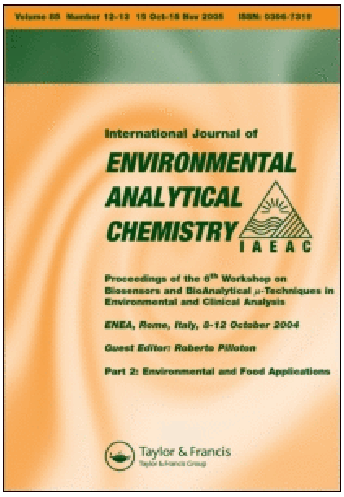

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Halocarbons in Aqueous matrices from the Rennick Glacier and the Ross Sea (Antarctica)

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HALOCARBONS IN AQUEOUS MATRICES FROM THE RENNICK GLACIER AND THE ROSS SEA (ANTARCTICA)

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Aqueous matrices from Antarctica were analysed for three volatile chlorinated hydrocarbons (VCHCs): tetrachloromethane (CCl_4), trichloroethylene (C_2HCl_3) and tetrachloroethylene (C_2Cl_4). The matrices analysed were snow from Rennick Nèvè and Rennick Glacier sampled during the Italian Expeditions of 1995/96 and 1996/97, respectively, and seawater, pack ice, sea-microlayer, subsuperficial water and freshwater, collected during the Italian Expedition of 1997/98. Extractions from the aqueous matrices were carried out in Antarctica (the laboratories of the Italian Base, Terra Nova Bay). Because of the critical space–time conditions in these laboratories, an extraction procedure was developed, suitable for large volumes of water (10 L), in order to combine the extraction of other classes of organic compounds (polychlorinated biphenyls, polycyclic aromatic hydrocarbons and chlorinated pesticides) with those of our direct interest. The VCHC organic extracts were analysed in Italy by GC-ECD and GC-MS. The analyses confirmed the presence of the three halocarbons in Antarctica in quantities ranging from units to some dozens of nanograms per kilogram. The results were evaluated with respect to the local distribution of these compounds and their diffusion on a global scale.

Keywords: Antarctica; Seawater; Snow; Halocarbons; Extraction

INTRODUCTION

In previous work [1,2] traces of volatile chlorinated hydrocarbons (VCHCs) as tetrachloromethane (CCl_4), trichloroethylene (C_2HCl_3) and tetrachloroethylene (C_2Cl_4), were found in lake water and ice samples, and also in surface and pit snow samples, collected during Italian Antarctic Expeditions. These compounds were selected as indicators of global contamination in remote areas. Due to their chemical physical properties [3–5] these compounds can diffuse from inhabited areas to remote regions such as Antarctica.

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This work reports both on the analyses of snow samples from Rennick Nèvè and the Rennick Glacier in Antarctica, collected during the Italian Antarctic Expeditions of 1995/96 and 1996/97, respectively, and on the analysis of seawater, sea-microlayer, pack ice and lake water samples, collected during the Italian Antarctic Expedition of 1997/98 (see Fig. 1). This research aims to confirm the presence of VCHCs in Antarctica and to contribute experimentally to the evaluation of the mechanisms of transport of the compounds in the study on both local and global scales.

EXPERIMENTAL

Materials and Instruments

A 10-L flat bottomed flask, a modified flask-stopper (Fig. 2) and a modified microextractor (the microextractor used in a previous work [2] was fitted to a larger flask) were employed for the extraction. A stirring device (MR 3000 D-230 V/50 Hz; Heidolph Elektro, Germany) and a stirring magnet (7SWN672 CYL 50 × 8 mm Bibby Sterilin Ltd, England) were employed to spread the organic extracting phase into the water sample. *n*-Hexane for organic residues analysis (J.T. Baker Chemical Co.) was used for extraction. All the glassware was washed with chromic mixture and distilled water, and the water residues were removed under hot air.

A Hewlett-Packard 5890 series II gas chromatograph was used for sample analysis. The gas chromatograph was equipped with an HP-5 capillary column (Crosslinked 5% PhMe Silica), 25 m × 0.32 mm × 0.52 μm film thickness and an ECD detector. A Hewlett-Packard GC-MS 5989 system with Chemstation HP 59940A (equipped with a HP-MS capillary column Crosslinked 5% PhMe Silica, 30 m × 0.32 mm × 0.52 μm film thickness) was used to confirm the peak identities. Both for GC-ECD and for GC-MS analysis an on-column injection system was set up that allowed the use of conventional syringes (needle 0.44 mm inner diameter). The microinjector was built by connecting a section of silica column without fixed phase (length 10 cm and inner diameter 0.53 mm) to the analytical column by a pressfit [2]. An improved limit of quantization was reached with the on-column microinjector.

Tetrachloromethane, trichloroethylene and tetrachloroethylene for analysis (Merck) were used to prepare standard solutions of halocarbons in *n*-hexane.

Sampling

Snow samples were taken from Rennick Nèvè during the XI Italian Expedition in Antarctica (1995/96) and from the Rennick Glacier during the XII Italian Expedition (1996/97). The snow sampling area is reported in Fig. 1A. The arrows show the sampling direction. The samples were kept at −20°C in stainless steel cylinders [2] ($V = 10$ L and i.d. = 20 cm) before melting for extraction.

Water samples were collected at different depths in the Gerlache Inlet area (station B; sites B2, B3, B4) and in the Ross Sea stations (Fig. 1B) by means of "go-flow" bottles, during the Oceanographic Campaign within the XIII Italian Expedition (1997/98). The sea-water samples were kept at −20°C in stainless-steel cylinders until extraction.

Pack ice cores were collected in the Gerlache Inlet area (sites B2, B4) and subsequently divided into two fractions, "top" and "bottom", and kept at −20°C until melting and subsequent extraction.

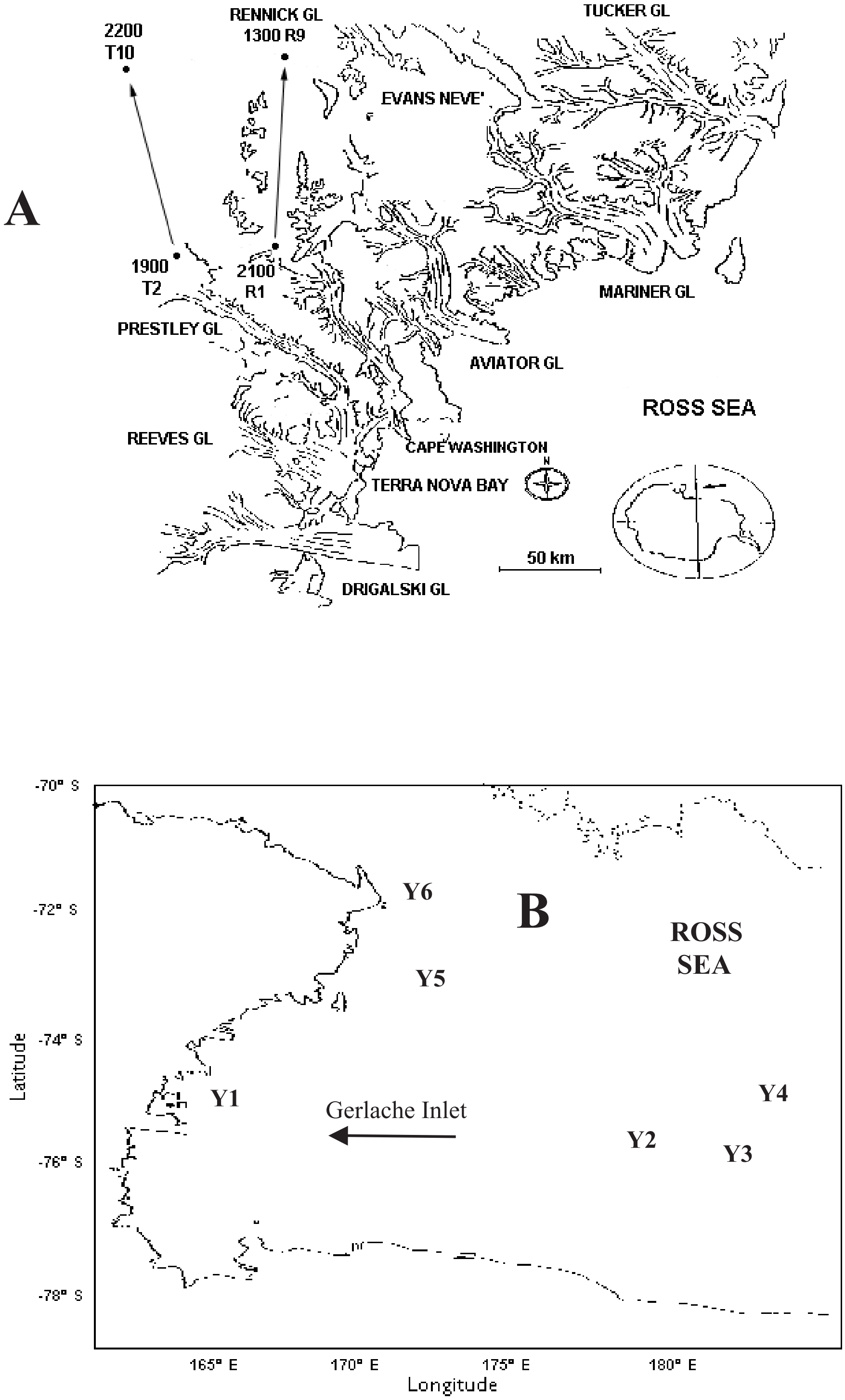

FIGURE 1 (A) Sampling sites of Rennick Nèvè (T2–T10) (XI Italian Expedition 1995/96) and Rennick Glacier (R1–R9) XII Expedition 1996/97); (B) Ross Sea and sampling sites.

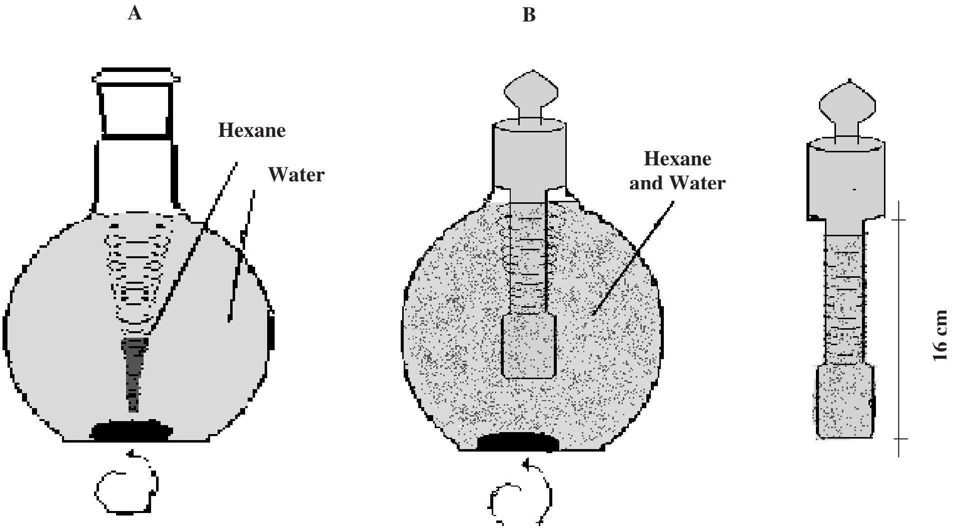

FIGURE 2 (A) Hexane distribution during the stirring phase with normal stopper. (B) Hexane distribution during the stirring phase with modified stopper.

Freshwater samples were collected from lakes at Tarn Flat and Edmonson Point.

Microlayer samples and subsuperficial water samples were collected from Gerlache Inlet. For microlayer sampling (the sampled microlayer had a thickness around 150 μm) a Multiuse Microlayer Sampler (MUMS) equipped with a rotating glass cylinder was employed.

Extraction and Analysis

Extraction from the aqueous matrices was directly carried out in Antarctica to avoid the shipping of large-volume samples to Italy. Because of the critical space–time conditions in the laboratories of the Italian Base, an extraction procedure was developed that allowed a single extraction of a large volume of water (10 L) to enable the determination of interesting high-boiling organic compounds (PCBs, PAHs and chlorinated pesticides) as well as the three VCHCs. A large volume of sample is needed because the high-boiling organic compounds are present in Antarctic matrices at very low concentrations. An extraction system for small volumes of water (1 L), suitable for determination of VCHCs only has been well described in a previous work [2]. The increased water volume to be analysed necessitated the modification of the extraction apparatus, in order to guarantee reproducible recoveries. A stirring magnet was used to spread the organic extraction phase (10 mL hexane) into the mass of water, in order to have 1000-fold concentration enrichment. Since the stirring magnet generated a sort of whirlpool in the water (Fig. 2A) and the hexane tended to locate inside it (the effect can be visualized by adding a hydrophobic organic dye soluble in hexane), the effective contact surface area between the two phases was reduced, so that it became a critical parameter and the resulting extraction process was not homogeneous. This effect is negligible for a small sample volume (1 L), where vigorous stirring is able to break the whirlpool, but it is important for larger volumes of water. The problem was overcome by modifying the shape of the flask stopper. A stopper with a shovel-shaped end was used to close the flask, instead of a normal one (Fig. 2B). This was made by welding a glass tube of the right size to the bottom of the original stopper. During the stirring phase the new stopper prevented the formation of the whirlpool while ensuring that the extraction was running in a closed system. In addition, the power of the stirring device and the size of the stirring magnet were adapted to the increased water volume extracted.

The new method was tested in order to evaluate the reproducibility and the extraction efficiency by using distilled water previously extracted with hexane for 30 min with the modified system, so as to have a clean matrix. 10 L of this matrix were spiked with 10 mL of a 10 ppb v/v solution in methanol of the three compounds in our study and stirred to complete solubilisation, so as to have a 10 ppt v/v concentration in water. Three extractions with 10 mL of hexane were carried out for each different stirring time (5, 10, 15, 20 and 30 min). Each extract was analysed three times by GC-ECD and compared with a standard solution (10 ppb v/v in hexane). The analysis conditions were as follows: carrier gas N_2; injection temperature. 43°C; oven temperature: 40°C for 8 min, 10°C/min to 120°C, and hold for 1 min. The detection limit of the ECD detector used for the investigated species is about 0.1 pg.

Figure 3 shows that the highest recovery was reached after 30 min, 85% for tetrachloromethane, 52% for trichloroethylene and 87% for tetrachloroethylene, respectively. We found out that at longer stirring times (20–30 min) the relative standard deviation decreased. Moreover, the same extraction tests carried out without modifying the stopper gave lower extraction recoveries (30–60%), thus confirming the lower extraction efficiency already referred to above. We have chosen a stirring time of 20 min, since the extraction efficiency for the three compounds at 30 min is only 2–3% higher. The same tests were carried out in order to evaluate the extraction efficiency at different concentrations. Five solutions of the three compounds were

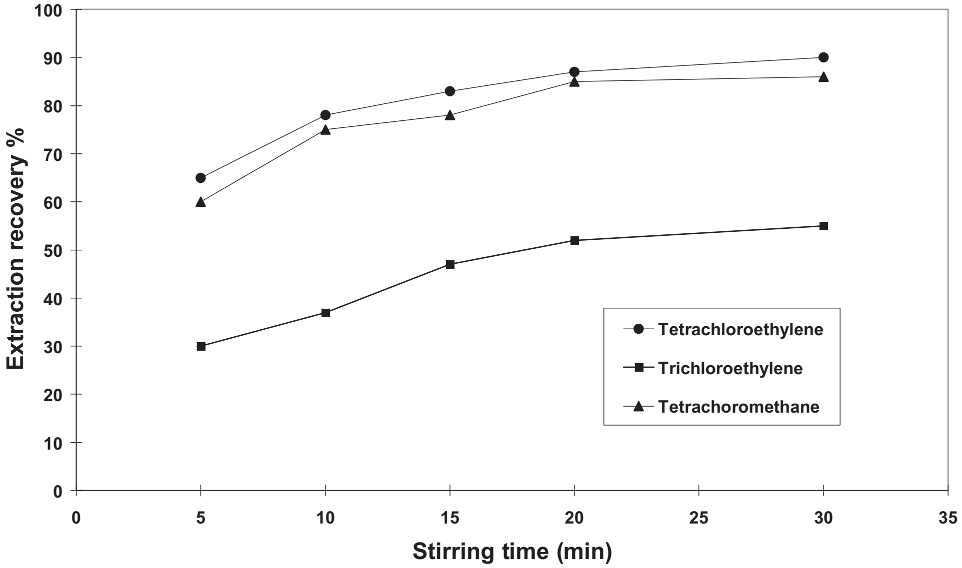

FIGURE 3 Extraction efficiency at different stirring times.

TABLE I Extraction recovery at different concentrations

VCHC	*Recovery* (%)					
	0.1 ppt	*0.2* ppt	*0.5* ppt	*1* ppt	*2* ppt	*5* ppt
CCl_4	72 ± 15	79 ± 12	83 ± 9	82 ± 5	87 ± 4	89 ± 5
C_2HCl_3	49 ± 17	55 ± 11	54 ± 12	52 ± 8	60 ± 8	57 ± 6
C_2Cl_4	76 ± 19	82 ± 13	89 ± 6	88 ± 8	90 ± 7	92 ± 4

TABLE II Sampling sites and VCHC concentrations (ng/kg) for the investigated snow samples

Site[a]	*Lat. S*	*Long. E*	*Altitude* (m)	CCl_4	C_2HCl_3	C_2Cl_4
43T02	73° 38′ 211″	160° 08′ 023″	1920	17	18	6.3
43T04	73° 23′ 124″	159° 53′ 260″	2100	13	13	6.8
43T06	73° 08′ 131″	159° 38′ 023″	2260	3.5	13	6.5
43T08	72° 53′ 23″	159° 23′ 025″	2250	20	23	7.0
43T10	72° 37′ 976″	159° 08′ 026″	2280	18	20	4.9

[a] Rennick Nèvè, XI expedition, 1995/96.

extracted with the modified device and with 20 min stirring time. Tests showed that the extraction recovery was satisfactory down to 0.2 ppt v/v, as shown in Table I. A concentration of 0.1 ppt v/v of tetrachloromethane, trichloroethylene and tetrachloroethylene in water is detectable using the described analytical procedure, but the uncertainty increases. Under these conditions the reproducibility and extraction efficiency have reached the values obtained by extraction from 1-L volumes of water as reported in the previous work [2] using the appropriately sized apparatus. With the new extraction system the standard deviation of the measured halocarbons concentration is about 10%.

RESULTS AND DISCUSSION

Tables II–X show that all the matrices investigated are contaminated with the VCHCs of interest. This evidence confirms the diffusion of the investigated compounds from inhabited areas to remote ones, including Antarctica. Certainly the atmosphere and its air-mass movements represent the main vehicle for the global diffusion of VCHCs, because of their chemical physical properties and according to predictive models of environmental distribution for temperate regions [4]. Our research group is studying the Antarctic air-sample analysis, and the measurement of the "air/snow" concentrations ratio for the investigated compounds will probably confirm the above reported statements.

Variations in concentration trends with site positions and period of sampling are due to the microclimate and to the correlated phase modifications of the aqueous matrices (snow, ice and pack ice). Although the results here presented refer to matrices collected over a three-year period (XI, XII, XIII Italian Expeditions in Antarctica), it is noticeable that the trichloroethylene concentration in seawater, pack ice and lake water samples is always higher than that measured in snow samples from Rennick; an opposite behaviour is observed for tetrachloromethane. No significant variations were registered

TABLE III Sampling sites and VCHC concentrations (ng/kg) for the investigated snow samples

Site[a]	*Lat. S*	*Long. E*	*Altitude* (m)	CCl_4	C_2HCl_3	C_2Cl_4
43R1	73° 19′ 51″	162° 29′54″	2200	10	2.2	2.8
43R3	73° 04′ 66″	162° 38′ 39″	2000	7.6	1.4	3.6
43R5	72° 49′ 01″	162° 38′ 66″	1800	29	3.3	1.7
43R7	72° 33′ 47″	162° 46′ 63″	1600	221	3.2	1.9
43R9	72° 19′ 49″	162° 26′ 26″	1350	259	2.7	1.2

[a] Rennick Glacier, XII expedition 1996/97.

TABLE IV Sampling sites and VCHC concentrations (ng/kg) for the investigated seawater samples

Site[a]	*Date*	*Lat. S*	*Long. E*	*Depth* (m)	CCl_4	C_2HCl_3	C_2Cl_4
Y1 (Drygalsky Basin)	7/12/1997	75° 04′	164° 13′	25	1.5	37	4.1
		75° 04′	164° 13′	80	1.3	37	3.1
		75° 04′	164° 13′	250	1.3	35	3.0
Y2 (Ross Bank)	13/12/1997	76° 09′	179° 57′	25	1.6	38	3.1
Y3 (Challenger Basin)	14/12/1997	75° 54′	177° 34′	25	1.5	44	4.3
		75° 54′	177° 34′	140	1.4	39	6.6
Y4 (Challenger Basin)	13/12/1997	75° 06′	176° 50′	25	1.3	35	2.9
Y5 (Joides Basin)	18/12/1997	74° 00′	174° 48′	90	1.8	37	3.7
Y6 (Cape Adere)	28/12/1997	72° 02′	172° 15′	25	1.6	38	6.1

[a] Ross Sea.

TABLE V VCHC concentrations (ng/kg) for the investigated seawater samples (Gerlache Inlet, Station B, Site B2)[a]

Depth (m)	*Sampling 1* *14/11/1997*			*Sampling 2* *24/11/1997*			*Sampling 3* *16–17/12/1997*			*Sampling 4* *7/2/1998*		
	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4
2	1.8	61	38	1.9	44	47	1.8	41	9.1	n.c.	n.c.	n.c.
4	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.5	32	2.6
10	n.c.	n.c.	n.c.	1.9	46	60	2.1	43	10	n.c.	n.c.	n.c.
25	1.7	54	61	1.8	61	68	1.7	41	10	1.4	31	2.9
50	n.c.	n.c.	n.c.	1.8	47	47	1.9	52	5.5	n.c.	n.c.	n.c.
100	1.5	59	57	2.0	42	71	1.8	39	4.5	1.6	28	2.2
200	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	1.6	40	4.7	n.c.	n.c.	n.c.
380	2.5	292	62	1.7	60	48	1.5	41	3.9	1.4	32	2.3

n.c. – no sample collected.

[a] Latitude 74° 41′ S; Longitude 164° 11′ E (XIII Italian Expedition, 1997/98).

for tetrachloroethylene concentrations in the different matrices analysed, except for seawater near the coast, in the period of glacier surface melting. The different distribution of tetrachloromethane among snow samples from the internal zones of the Antarctica and seawater samples from the Ross Sea probably depends on its higher volatility and lower solubility in water than trichloroethylene [5]. Tetrachloromethane deposition

TABLE VI VCHC concentrations (ng/kg) for the investigated seawater samples (Gerlache Inlet, Station B, Site B3)[a]

Depth (m)	*Sampling 1* *20/11/1997*			*Sampling 2* *3/1/1998*			*Sampling 3* *30/1/1998*		
	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4
4	1.8	47	47	1.8	44	4.4	1.7	42	3.1
25	1.6	48	39	1.8	47	4.9	1.6	55	2.3
100	1.7	55	41	1.7	44	4.6	1.7	54	0.2

[a] Latitude 74° 40′ S; Longitude 164° 13′ E (XIII Italian Expedition, 1997/98).

TABLE VII VCHC concentrations (ng/kg) for the investigated seawater samples (Gerlache Inlet, Station B, Site B4)[a]

Depth (m)	*Sampling 1* *15/11/1997*			*Sampling 2* *26–27/12/1997*			*Sampling 3* *3/2/1998*		
	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4	CCl_4	C_2HCl_3	C_2Cl_4
2	1.8	36	38	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
4	n.c.	n.c.	n.c.	1.8	40	5.9	1.6	34	3.2
25	1.8	40	48	1.9	47	6.2	1.5	36	2.4
100	1.8	44	30	1.8	45	5.6	1.3	33	0.3

n.c.: no sample collected.

[a] Latitude 74° 42′ S; Longitude 164° 09′ E (XIII Italian Expedition, 1997/98).

TABLE VIII VCHC concentrations in pack ice (ng/kg)

Site[a]	*Date*	*Ice core*	CCl_4	C_2HCl_3	C_2Cl_4
B2	8/11/1997	Top fraction	1.4	72	7.8
		Bottom fraction	0.8	50	11
	19/12/1997	Top fraction	1.2	137	5.2
		Bottom fraction	0.8	692	5.8
B4	11/11/1997	Top fraction	0.8	64	2.7
		Bottom fraction	0.7	61	2.9
	29/12/1997	Top fraction	1.2	87	3.8
		Bottom fraction	1.3	199	4.6

[a] Station B, Site B2 (Gerlache Inlet). Latitude 74° 41′ S; Longitude 164° 11′ E. Station B, Site B4 (Gerlache Inlet). Latitude 74° 42′ S; Longitude 164° 09′ E.

from atmospheric fallout in the internal Antarctic regions is probably due to the very low local temperatures. The variations in concentrations for trichloroethylene and tetrachloroethylene (more relevant for tetrachloroethylene) (Tables V–VII and Fig. 4) observed in the temporal profiles which were carried out in the Gerlache Inlet over a three-month period, can very probably be attributed to glacier surface melting and subsequent dilution in the sea. In fact during the ‘‘Antarctic night’’ the very low temperatures promote deposition on the snow/ice surfaces with a consequent accumulation of VCHCs.

TABLE IX VCHC concentrations (ng/kg) in microlayer and subsuperficial seawaters[a]

Matrix	*Date*	*CCl_4*	*C_2HCl_3*	*C_2Cl_4*
Microlayer	20/02/1998	0.7	54	2.2
	21/02/1998	0.7	84	2.1
	22/02/1998	2.6	66	2.0
Subsuperficial water	20/02/1998	1.2	40	2.6
	21/02/1998	1.1	46	2.6
	22/02/1998	1.4	41	1.7

[a] Station B, Site B2 (Gerlache Inlet). Latitude 74° 41′ S; Longitude 164° 11′ E.

TABLE X VCHC concentrations (ng/kg) in water samples from Tarn Flat

Site	*Date*	*CCl_4*	*C_2HCl_3*	*C_2Cl_4*
Tarn Flat[a]	9/1/1998	2.1	28	4.1
	29/1/1998	1.6	37	3.4
Edmonson Point[b]	9/1/1998	1.8	30	2.8
	29/1/1998	1.6	28	2.3

[a] Station 12, Site 12a, Lake 20, Latitude 74° 58′ S, Longitude 162° 30′ E.
[b] Station 8, Site 8b, Lake 15a, Latitude 74° 18′ S, Longitude 165° 04′ E.

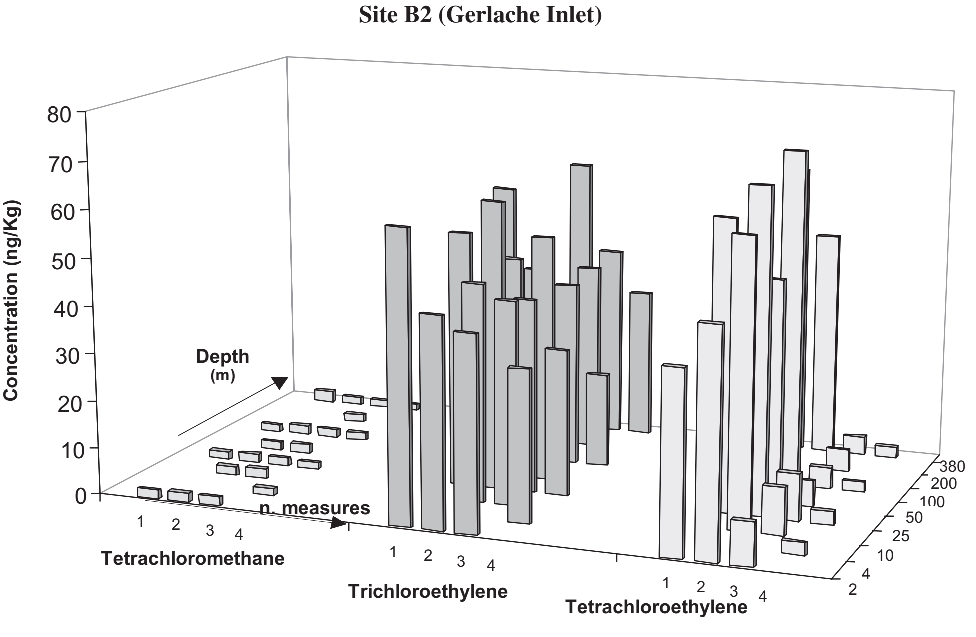

FIGURE 4 VCHC concentrations (ng/kg) for the investigated seawater samples (Gerlache Inlet, Station B, Site B2). Latitude 74° 40′ S; Longitude 164° 13′ E (XIII Italian Expedition 1997/98).

CONCLUSION

Aqueous matrices from Antarctica were analysed for three volatile chlorinated hydrocarbons (VCHCs): tetrachloromethane (CCl_4), trichloroethylene (C_2HCl_3) and tetrachloroethylene (C_2Cl_4). Extractions from the aqueous matrices were carried out in Antarctica (laboratories of the Italian Base at Terra Nova Bay). The organic extracts were analysed in Italy by GC-ECD and GC-MS. The analyses confirmed the presence of the three halocarbons in Antarctica in quantities ranging from units to some dozens of nanograms per kilogram.

The atmosphere and its air-mass movements represent the main vehicle for the global diffusion of VCHCs, because of their chemical and physical properties. The variations in concentration trends with site positions and period of sampling are due to the microclimate and to correlated phase modifications of the aqueous matrices (snow, ice and pack-ice). During the ‘‘Antarctic night’’ the very low temperatures promote deposition on the snow/ice surfaces with a consequent accumulation of VCHCs.

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