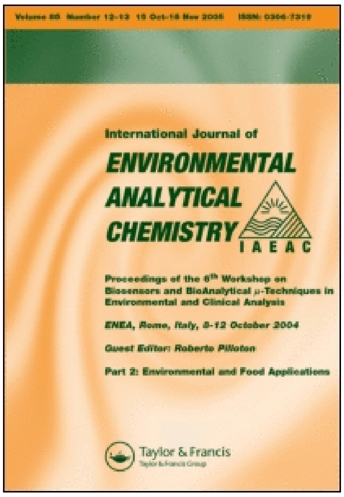

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Halocarbons in Antarctic Surface Waters

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HALOCARBONS IN ANTARCTIC SURFACE WATERS

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Surface water samples taken during the 1988–89, 1989–90 and 1990–91 Italian expeditions were analyzed for the presence of carbon tetrachloride, trichloroethylene and tetrachloroethylene. The sample analysis was carried out by solvent extraction and capillary GC-ECD-MS determination. The above-mentioned halocarbons were at ng/l level in all water samples investigated.

KEY WORDS: Antarctic waters, halocarbons, carbon tetrachloride, trichloroethylene, tetrachloroethylene.

INTRODUCTION

The evaluation of the presence, on the Antarctic Continent, of halocarbons such as carbon tetrachloride (CCl_4), trichloroethylene ($CHCl = CCl_2$) and tetrachloroethylene ($CCl_2 = CCl_2$) which are widely used in the northern hemisphere deserves particular interest. These halocarbons are indicators of the environmental contamination of remote places as the Antarctic Continent because of their long life in the environment. In this work we report the evaluation of the above-mentioned halocarbons (not previously analyzed in the Antarctica) in lake, ice and sea water samples, taken during three Italian expeditions. In the same water samples[1], chlorinated pesticides, including DDT, were not detectable.

EXPERIMENTAL

Sampling

During the 1988–89, 1989–90 and 1990–91 Italian expeditions samples of lake water, ice water and sea water were taken as reported in Table 1. Figure 1 shows the sampling sites relative to Table 1. The samples were stored at – 30°C in stainless steel containers. The containers (ten litre volume) were specially designed with screw caps and teflon gaskets.

Table 1 Samples and sampling sites for the investigated water.

Sample	*Station*	*Altitude (m)*	*Lat. S*	*Long. E*
Lake water	Carezza Lake	175	73°43′	164°01′
	Edmonson Point	190	74°20′	165°07′
	Edmonson Point	20	“”	“”
	Tarn Flat	70	74°59′	162°33′
	Inexpressible Island	100	74°55′	163°41′
	Inexpressible Island	50	74°54′	163°42′
Ice water	Corner Glacier	35	74°28′	163°34′
	Edmonson Point	190	74°20′	165°07′
	Onyx River	150	77°31′	161°40′
	Inexpressible Island	50	74°54′	163°42′
	Wood Bay	30	74°18′	165°05′
Sea water	Icarus Field Coast	0	74°42′	164°06′

Containers, caps and gaskets were carefully washed with soap and water, distilled water and with n-hexane, free of volatile halocarbons. Finally, the containers were heated (to about 100°C) and flushed with nitrogen.

Procedure

1 litre of water was extracted using halocarbon free n-hexane (1 ml). The extraction was effected by very strong mechanical agitation for about 15 minutes. After phase separation (15 minutes), the organic phase was collected with a micro separator. The organic phase was analyzed by capillary GC with ECD and by capillary GC-MS. This procedure was developed in a previous work[2].

For the analysis of water samples, carbon tetrachloride, trichloroethylene and tetrachloroethylene were dissolved in hexane, free of volatile halocarbons. A standard mixture of these compounds, analyzed by capillary GC-ECD, is shown in Figure 2. With this technique the smallest detectable amount for each halocarbon was about 0.05 pg.

Using the described procedure, the recovery from water samples was about 65% for carbon tetrachloride, about 50% for trichloroethylene and about 75% for tetrachloroethylene. Recovery was measured by adding 8 ng of each of the above-mentioned halocarbons to a 1 litre of mineral water, free of halocarbons.

Materials

Particular care was devoted to the selection and testing of all materials. n-hexane for trace organic residue analysis (J. T. Baker chemical Co.) was used. This n-hexane resulted free of volatile halocarbons. Before use, all the chemical glassware was washed with chromic mixture, distilled water and n-hexane. Carbon tetrachloride, trichloroethylene and tetrachloroethylene for analysis (Merck) were used.

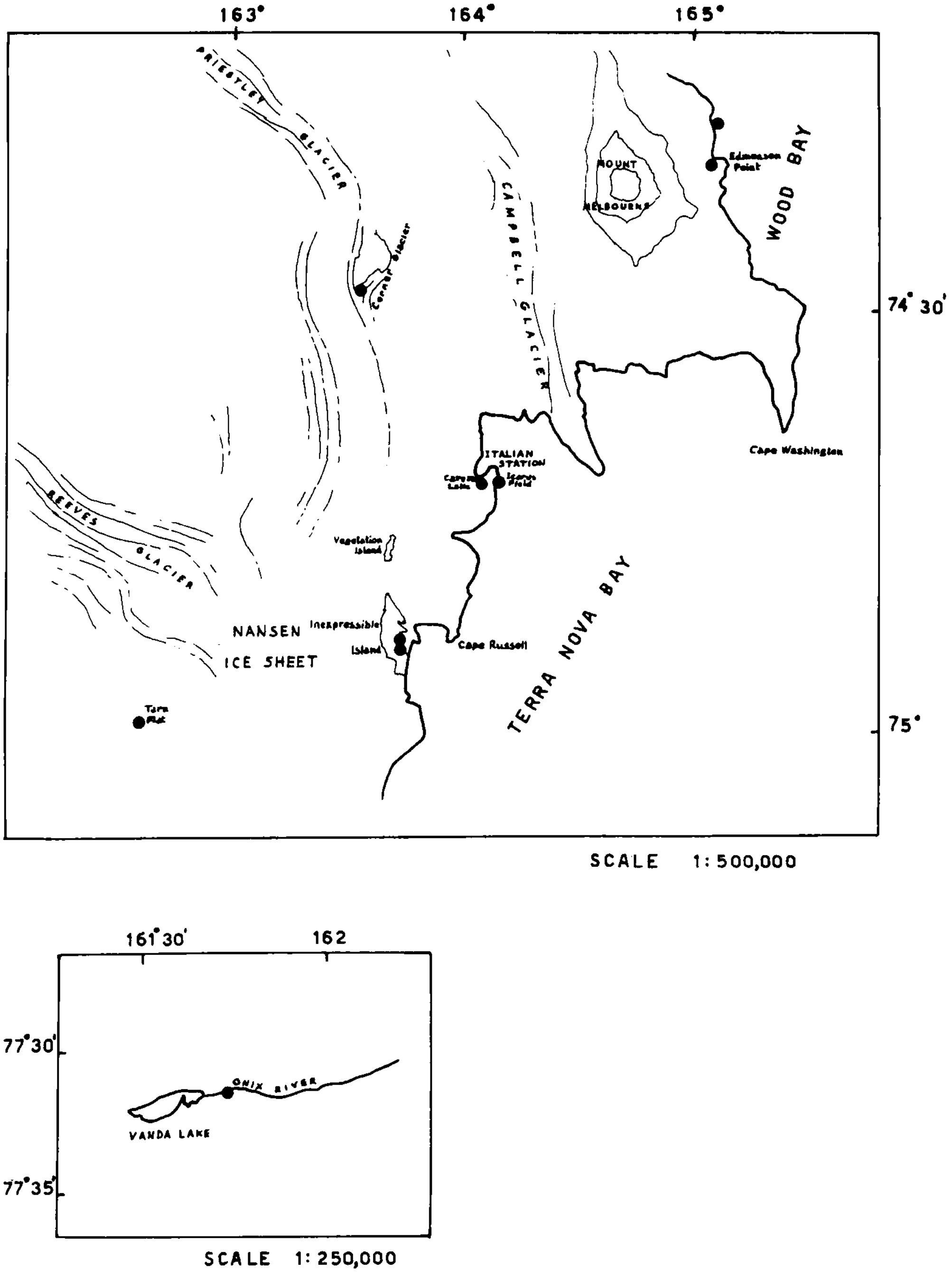

Figure 1 Sampling stations for the 1988–89, 1988–90 and 1990–91 Expeditions in Antarctica.

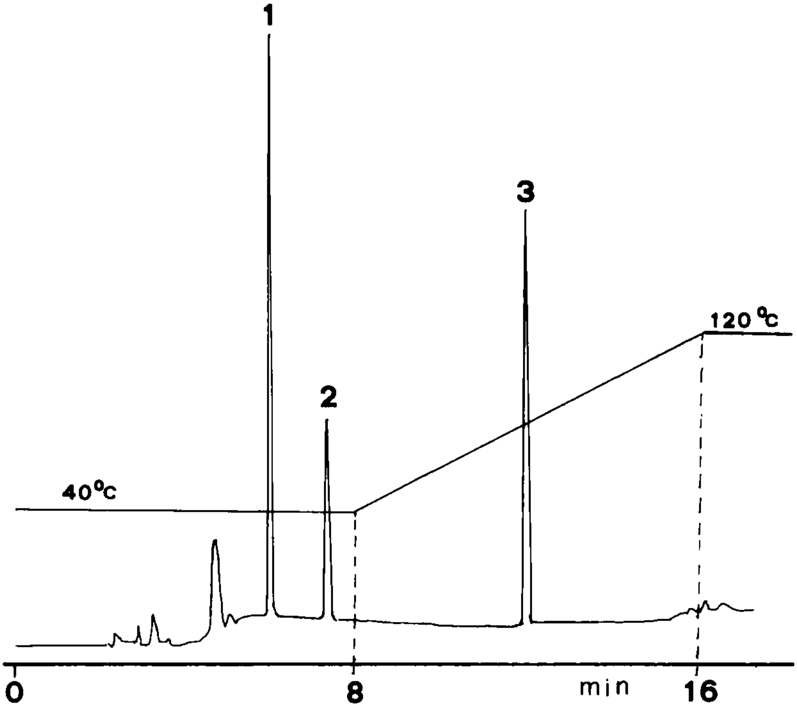

Figure 2 Chromatogram of standard mixture of the halocarbons monitored in the Antarctic water samples obtained by a Hewlett & Packard 5890 series II Gas chromatograph equipped with an "on column" injector, a fused silica capillary column (25 × 0.32 mm I. D. × 0,52µm film; Cross-Linked 5% phenyl Methyl Silicone) and a ECD detector. Carrier gas N_2. Temperature: 40°C for 8 min, 10°C/min to 120° C and hold for 1 min.
1) Carbon tetrachloride, 2) Trichloroethylene, 3) Tetrachloroethylene

Apparatus

A Hewlett Packard 5890 series II gas chromatograph was used for the sample analysis. The gas chromatograph was equipped with an "on column injector", a fused silica capillary column (25m × 0.32 mm I.D. 0,52 µm, SE54) and a ECD detector. To confirm peak identity, a Hewlett Packard 5970 MSD was used. The volume of the injected solution was 2 µl.

RESULTS AND DISCUSSION

Figure 3 reports the chromatogram of n-hexane used for the sample extraction (A) and a typical chromatogram of an Antarctic water sample (B). In chromatogram B of Figure 3, chloroform ($CHCl_3$) and 1,1,1-trichroroethane (CCl_3-CH_3) were not found. Table 2 reports the carbon tetrachloride, trichloroethylene and tetrachloroethylene concentrations (ng/l) in

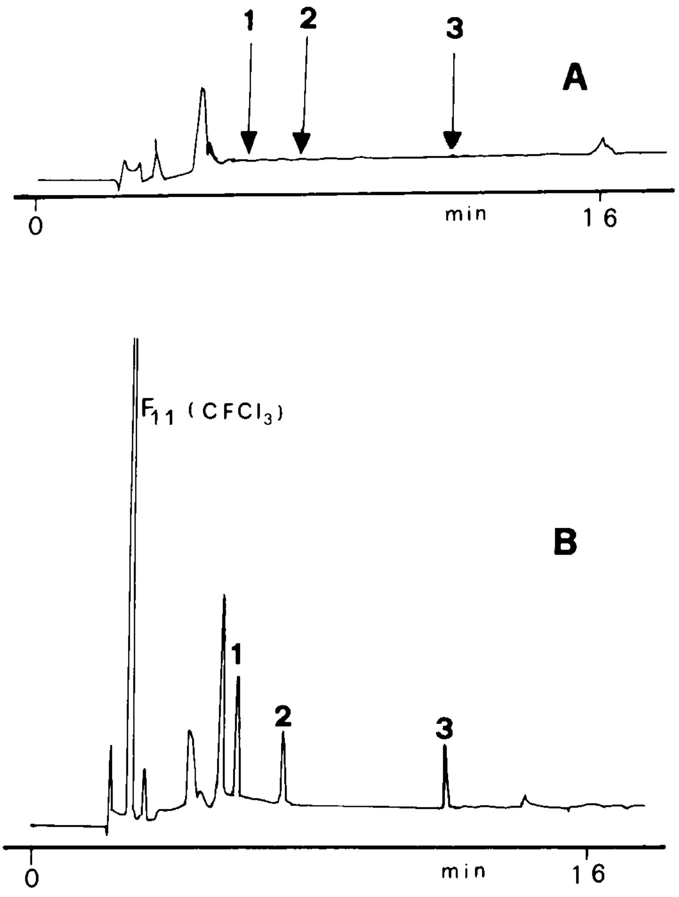

Figure 3 Chromatogram of n-hexane used for the sample extraction (A) and of a typical Antarctic water sample. Same conditions of Figure 1.
1) Carbon tetrachloride, 2) Trichloroethylene, 3) Tetrachloroethylene

the water samples of Table 1. The three halocarbons are present in all of the investigated samples; this indicates that there is diffuse contamination by the above-mentioned halocarbons in the region. It is the opinion of the authors that the presence of the monitored halocarbons in this region cannot be due to emissions from the Italian Station. In fact, higher concentration values were found in some sampling sites far from the Italian Station (Onyx River, Corner Glacier), while lower values were measured at "Carezza Lake", a sampling site near the Italian Station. The authors suggest that the differences in the halocarbons concentrations in the varius waters examined can be attributed to sampling site microclimate and to morphology.

Table 2 Halocarbons in investigated water samples (ng/l).

Compound	*Carbon tetrachloride*			*Trichloroethylene*			*Tetrachloroethylene*		
Expedition	*'88*	*'89*	*'90*	*'88*	*'89*	*'90*	*'88*	*'89*	*'90*
Lake water									
Carezza Lake	3.9	5.6	0.7	5.5	9.1	2.0	3.8	3.4	0.2
Edmonson Point (a)	-	22	3.5	-	20	9.3	-	4.3	1.1
Edmonson Point (b)	-	-	0.6	-	-	2.0	-	-	0.4
Tarn Flat	3.7	4.4	2.7	7.6	3.8	1.2	3.6	2.3	0.4
Inexpressible Island (c)	2.3	4.8	3.7	5.0	4.1	1.5	1.8	1.4	0.5
Inexpressible Island (d)	-	7.6	-	-	7.0	-	-	3.8	-
Ice water									
Corner Glacier	13	15	-	9.0	2.6	-	2.3	2.0	-
Edmonson Point	2.5	-	-	5.5	-	-	1.1	-	-
Onyx River	11	-	-	40	-	-	9.9	-	-
Inexpressible Island	-	3.2	-	-	5.3	-	-	2.9	-
Wood Bay	-	4.8	-	-	4.4	-	-	1.8	-
Sea water									
Icarus Field	-	-	1.8	-	-	3.8	-	-	0.7
Spring water Italy									
Altitude m 1000	-	-	2.3	-	-	0.1	-	-	9.2
Tap water—Rome Italy	-	-	3.5	-	-	1.0	-	-	9.9

(a) altitude m 190; (b) altitude m 20; (c) altitude m 100; (d) altitude m 50.

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