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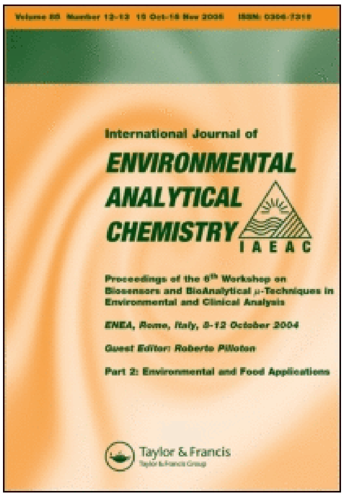

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Zoccolillo, L. , Amendola, L. and Tarallo, G. A.(1996) 'Halocarbons in Antarctic Surface Waters and Snow', International Journal of Environmental Analytical Chemistry, 63: 2, 91 — 98

To link to this Article: DOI: 10.1080/03067319608026254

URL: http://dx.doi.org/10.1080/03067319608026254

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Intern. J. Environ. Anal. Chem., Vol. 63, pp. 91–98
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HALOCARBONS IN ANTARCTIC SURFACE WATERS AND SNOW

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(Received, 4 May 1995; in final form, 16 August 1995)

Surface and pit snow samples, collected from Terranova Bay area in Antarctica during the Italian expeditions of 1991–92 and 1992–93, were analysed, for halocarbons, namely tetrachloromethane, trichloroethylene and tetrachloroethylene. The results obtained (including those related with lake and ice water samples previously reported) were evaluated with respect to the worldwide distribution of these compounds and their diffusion to a global scale. Important innovations concerning sensitivity and reproducibility of the analytical method, are also reported.

KEY WORDS: Antarctica, natural water, snow, halocarbons.

INTRODUCTION

In a previous work[1], traces of tetrachloromethane, trichloroethylene and tetrachloroethylene were found in lake and ice water samples collected in the Terranova Bay area in Antarctica during the Italian expeditions in 1988–89, 1989–90, 1990–91. The above compounds were selected as pollution indicators in remote areas because large amounts have been released into the environment over the past fifty years, and their volatility may contribute to their diffusion to a global scale. The possibility of sampling these chemicals at very low concentrations (ng/L) in natural water samples makes also attractive their determination. The present paper reports on the analysis of surface and pit snow samples collected during the Italian Antarctic expeditions of 1991–92 and 1992–93. Research on these compounds was extended to snow because this is the only compartment in which pollution is deposited on the Antarctic continent. The work also aimed at improving analytical methods, as regards sensitivity, reproducibility and sample volumes used.

EXPERIMENTAL

Sampling

Two surface snow and one ice samples were taken during the brief Italian expedition to Antarctica in 1991–92. In the 1992–93 expedition, seven snow samples were taken from a three metre pit, one sample every 0.5 m (Table 1). Stainless steel cylinders (vol = 10 L

Table 1 Samples and sampling site for Antarctic ice and snow.

Expedition	*Sample*	*Station*	*Altitude*	*Lat. S*	*Long. E*
1991–1992	Ice	Reeves Glacier	—	74° 43'	162° 45'
1991–1992	Surface snow	Priestley Glacier	—	74° 08'	162° 48'
1992–1993	Snow pit	Hercules Nevè	2960 m	74° 06'	165° 28'

and i.d. = 20 cm) were used for the snow samples (Figure1). The container lids had an internal diameter equal to the outer diameter of the containers. A silica rubber seal allowed air-tight closure of the cylinders. The shape of the cylinder allowed direct snow sampling from the pit sides. The quantity of snow taken for each container corresponded to approx. 2 L of water. The same type of container was used for surface ice, which was sampled using an ice-pick. All samples were kept at –20°C before analysis.

Apparatus and materials

A Hewlett-Packard 5890 series II gas chromatograph was used for sample analysis. The gas chromatograph was equipped with a HP-5 capillary column (Crosslinked 5% PhMe Silica), 25 m × 0.32 mm × 0.52 μm film thickness, an on-column injector and an ECD detector. A Hewlett-Packard GC-MS 5989 system with Chemstation HP59940A was used to confirm the peak identities. n-Hexane for organic residue analysis (J. T. Baker Chemical Co.) was used for extraction, since it was free of volatile halocarbons. Tetrachloromethane, trichloroethylene and tetrachloroethylene for analysis (MERCK) were used for the standard solutions of halocarbons in n-hexane. All the glassware was washed in chromic mixture and distilled water, and the water residues were removed under hot air.

Extraction

Extraction was carried out on the melted snow and ice samples using a round flask (0.5 L) in which 0.5 L of water were extracted with 0.5 mL of hexane (Figure 2a). After 15 min of vigorous shaking using a magnetic stirrer and after separation of the phases, the organic extract was recovered using the device shown in Figure 2b. The microextractor has two parallel tubes of different diameters in the upper section. Tube A, in which the organic extract separation actually takes place, has an internal diameter of 0.5 cm and a total length of 20 cm. Tube B, with an internal diameter of 0.8 cm, is wider in the upper portion to facilitate the introduction of water to the flask. Tube B is 5 cm longer than tube A in the lower portion, so that when the microextractor replaces the flask stopper, the lower portion of tube B lies below the hexane microlayer.

The water introduced in the upper part of tube B ends up below the hexane microlayer and practically does not come into contact with it. The addition of water, free of the test substances, causes the liquid to rise until the hexane microlayer is channelled into the upper part of tube A. Alternatively, another microextractor version has been made

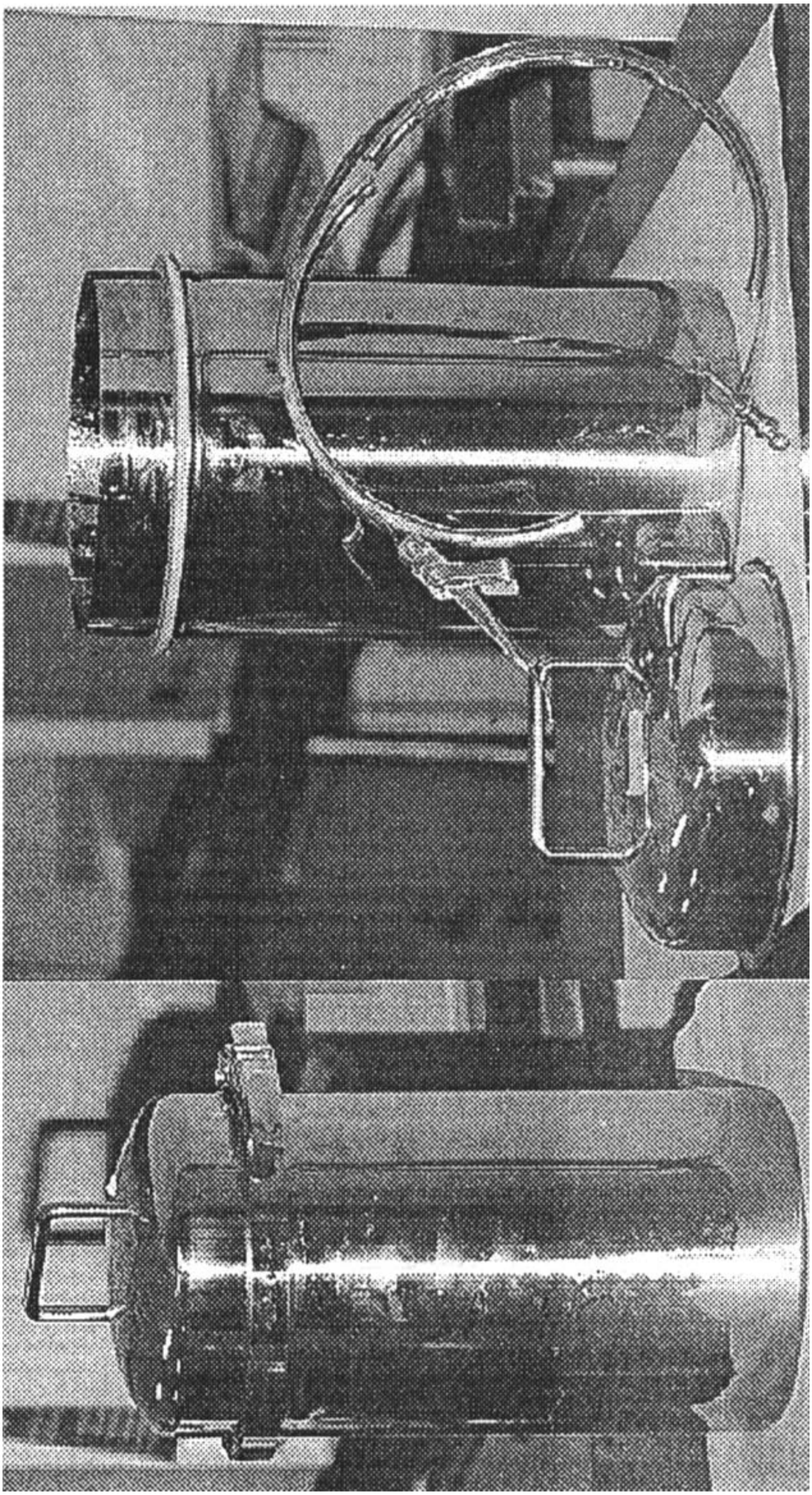

Figure 1 Stainless steel container used for ice and snow sampling (*Inox Sabat*, Bologna, Italy).

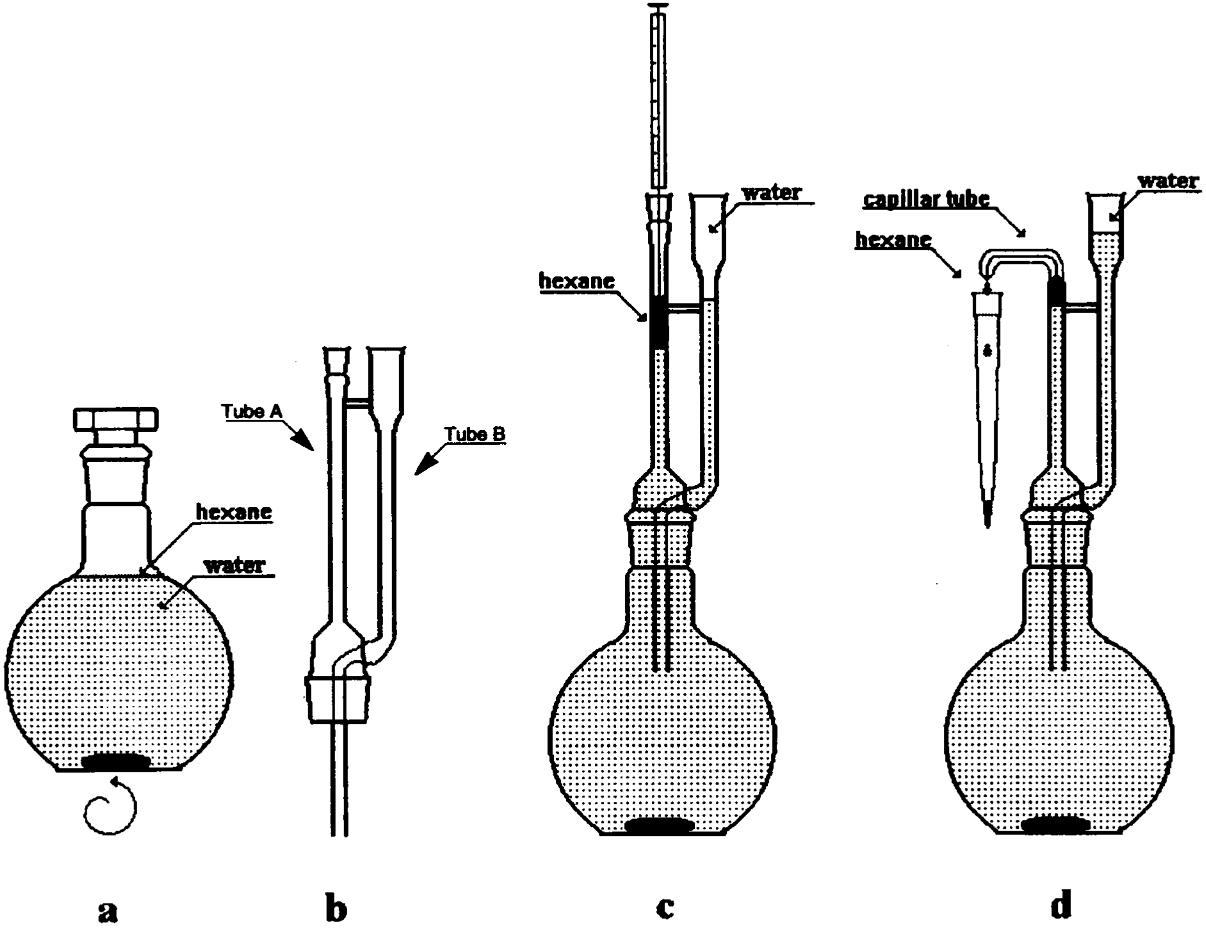

Figure 2 Microextractors used for extraction (hexane/water 1/1000); a) round flask; b) typical microextractor; c) extract sampling for direct injection in the gas chromatograph; d) extract separation for possible further extract concentration.

which allows complete recovery of the organic extract and avoids sampling using a Pasteur pipette (Figure 2d). In the new version, tube A is 5 cm shorter and ends with a U-shaped capillary. Because of the higher surface tension of water compared with hexane, when the meniscus of the water lying beneath the hexane reaches the top of the capillary the flow of liquid stops.

Without concentrating the extract, the extraction system shown in Figure 2c allows obtaining the required halocarbons in hexane at the μg/L level (measurable with GC-ECD and GC-MS) with respect to the ng/L level present in the original water sample. The microextractor in Figure 2d is useful for separating all the extract for further research of other less volatile compounds.

GC-ECD-MS analysis

Analysis of the snow and ice organic extracts was carried out using a GC-ECD apparatus (Carrier gas: N_2; 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. At least a concentration of 0.1 ng/l of tetrachloromethane, trichloroethylene and tetrachloroethylene in water is detectable using the described extraction system. The standard deviation of the halocarbons measured concentration is about 10%. A GC-MS apparatus under the EI-SIM mode, was used to confirm the peak identities (Carrier gas: He; temperature: same conditions of GC-ECD analysis). In order to allow the use of a high resolution column (0.20 mm i.d. with the on-column injector) a section of fused silica column, without fixed phase was mounted in the injector. This section had a length of 10 cm and an internal diameter of 0.53 mm, and was connected to the analytical column (0.20 mm i.d.) via a pressfit. The 0.53 mm column section acted as a microinjector suitable for conventional 0.44 mm diameter needles. Figure 3B shows a typical GC-MS in SIM chromatogram of an extract of Antarctic snow.

RESULTS AND DISCUSSION

Table 2 reports the results of the analyses carried out on the snow and ice samples from the Italian expeditions of 1991–92 and 1992–93. The results confirm the conclusions reported in a previous work[1], i.e. that the Terranova Bay area is widely polluted by tetrachloromethane, trichloroethylene and tetrachloroethylene. The presence of these halocarbons in Antarctica is a further proof of their ubiquitous occurrence in the environment and, owing to their origin in inhabited areas of the world, their diffusion at a global scale. Although a lot of natural waters (such as spring waters, tap waters and mineral waters) were analysed, no one of the three investigated species was found above the detection limit of the method.

Diffusion model at global level

The environmental behaviour of the substances analysed is well-known in temperate regions and is related to their chemical and physical properties (Table 3). Once released into the environment, the high vapor pressure of the three compounds determines their preferential distribution: in air and with only low percentages in water. Therefore, the main way they are transported over great distances is via the atmosphere. Mackay and

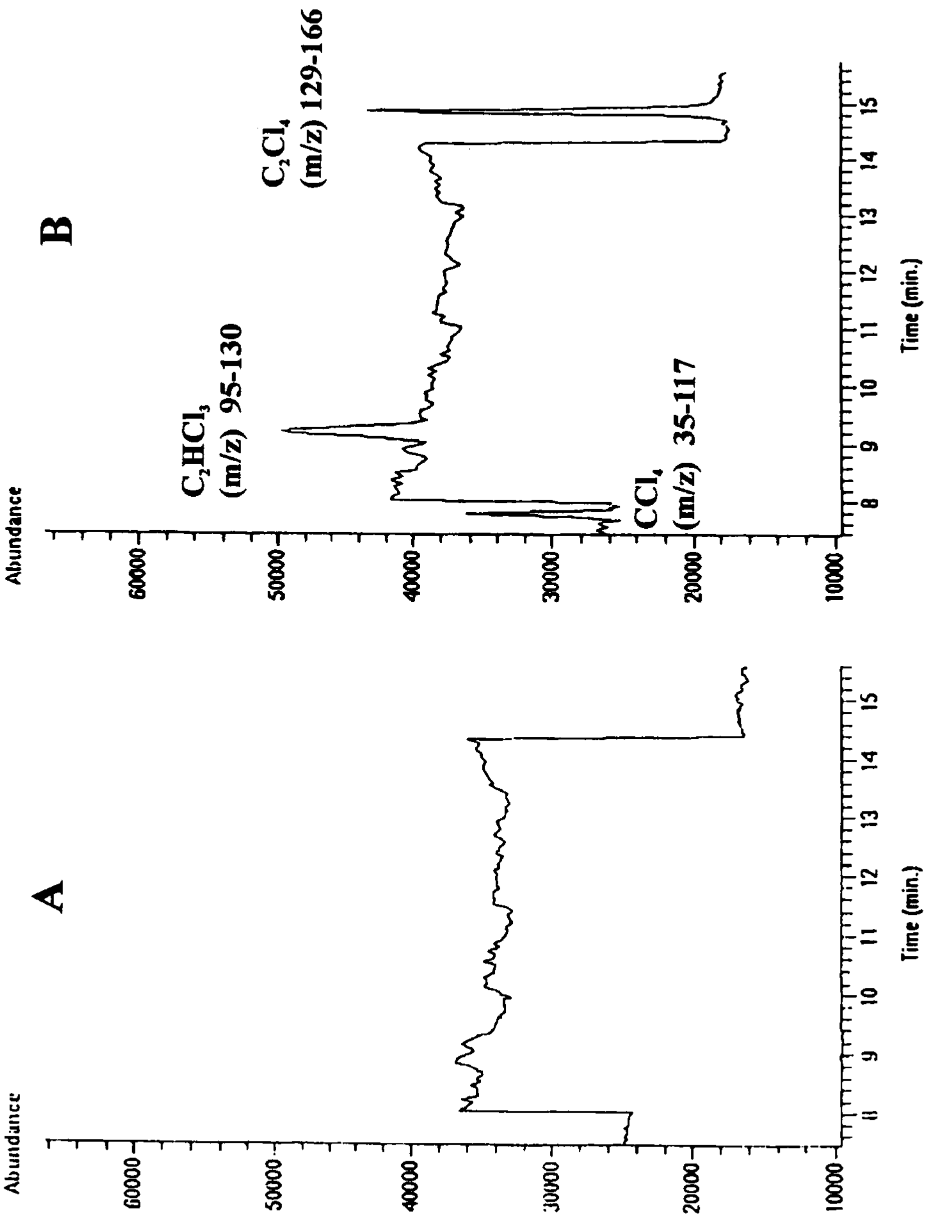

Figure 3 SIM-GC-MS chromatogram: A) n-hexane used for extraction; B) typical Antarctic snow extract.

Table 2 Halocarbons in antarctic ice and snow samples (ng/L).

Compound (Expedition)	*Tetrachloromethane*		*Trichloroethylene*		*Tetrachloroethylene*	
	'91–'92	*'92–'93*	*'91–'92*	*'92–'93*	*'91–'92*	*'92–'93*
Surface snow (Priestley Glacier)	4.6	-	14	-	15	-
Snow (depth 0.5 m) (Priestley Glacier)	2.5	-	8.5	-	5.0	-
Surface ice (Reeves Glacier)	3.3	-	11	-	7.5	-
Snow pit (depth 0.0 m) (Hercules Nevè)	-	12	-	5.7	-	7.4
Snow pit (depth 0.5 m) —	-	7.9	-	2.9	-	2.5
Snow pit (depth 1.0 m) —	-	8.8	-	8.3	-	5.7
Snow pit (depth 1.5 m) —	-	12	-	8.9	-	7.2
Snow pit (depth 2.0 m) —	-	6.3	-	3.9	-	3.7
Snow pit (depth 2.5 m) —	-	14	-	8.0	-	3.6
Snow pit (depth 3.0 m) —	-	9.8	-	9.0	-	6.6

Table 3 Selected chemical-physic properties of tetrachloromethane, trichloroethylene and tetrachloroethylene.

Compound/Property	CCl_4	$CHCl = CCl_2$	$CCl_2 = CCl_2$
Vapor pressure	11.94 kPa (20°C) (4)	5.8 kPa (20°C) (5)	1.3 kPa (14°C) (4)
Solubility in H_2O	0.8 g/L (25°C) (4)	0.2 g/L (20°C) (4)	0.2 g/L (25°C) (4)
k_{OH}	$<10^{-15}$ cm^3s^{-1} (5)	$2.2*10^{-12}$ cm^3s^{-1} (6)	$1.7*10^{-13}$ cm^3s^{-1} (6)
Lifetime	47 y (6)	0.021 y (6)	0.43 y (6)

Paterson[2,3] have established a behavioural model for temperate regions applicable to trichloroethylene. This model shows that, once released into the atmosphere, 92% of the trichloroethylene is carried in the air and only 8% in water. 54% of the trichloroethylene present in the air is then eliminated by OH radicals and UV radiation while the remaining 46% is carried by air currents to nearby regions. Because tetrachloromethane and tetrachloroethylene have similar chemical and physical properties to trichloroethylene, their environmental behaviour will be similar except for their lifetimes in the troposphere (Table 3), according to their reactivity with the OH radical (k_{OH}) (Table 3).

A chemical compound may be carried by the atmosphere as a vapor or through an atmospheric particulate matter in which the substance is adsorbed. The adsorbed percentage of the chemical substance in the particulate matter is mainly determined by its vapor pressure. Since chemical substances with vapor pressures greater than 1.3 10^{-2} kPa, are completely in the air phase[7] and considering the specific values of the three compounds studied (Table 3), the atmosphere can only carry the substances in the vapor state.

The phenomena regulating deposition of pollutants from air to snow are extremely complex and may be divided into two groups: wet and dry deposition[8–10]. In the former case, there is an equilibrium state between air and water phases on the water microlayers present, in summertime, on surface snow crystals or on atmospheric particulate matter. Dry deposition, on the other hand, occurs when snow forms, a very rare phenomenon in Antarctica, and via direct deposition onto the snow surface. In the latter case, the main factors which determine the deposition rate are: the surface area exposed, roughness of surfaces, and wind speed above these surfaces. Since Antarctica has a vast uneven, air permeable, snow surface and has winds that may exceed 100 km/h, dry deposition on the snowpack is certainly an important phenomenon in the accumulation of pollutants. Because the three halocarbons studied are present in the troposphere as vapors, it is likely that the main way they are deposited in snow is by dry deposition. The presence of the three halocarbons in pitsnow of up to 3 m deep at uniform concentration levels, within the experimental errors (Table 2) would confirm the predominance of dry deposition on snow surfaces. Up to a depth of three metres, permeability of snow to air is practically the same in Antarctica.

The halocarbon concentrations found in the water samples are similar and, in some cases, even greater than those found for the three substances in water samples taken from areas in Italy that are very remote from sources of pollution[1]. This may be explained by the very efficient deposition and accumulation mechanism in Antarctica that is favoured by the specific environmental characteristics, despite the fact that atmospheric concentrations of the three halocarbons are much lower than for inhabited areas of the world.

Acknowledgement

This work was performed in the framework of "Environmental Contamination Project-National Research Program in Antarctica", Italy.

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