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Cumulation of chloroorganic insecticides by Antarctic marine diatoms

ABSTRACT: In Antarctic summer 1983/1984 samples of planktonic and attached diatoms were collected in the Admiralty Bay (King George Island, South Shetland Islands) as well as samples of planktonic diatoms in the region of South Orkneys, Drake Passage and Bransfield Strait (BIOMASS-SIBEX Project). Using gas chromatography residues of chloroorganic pesticides, namely the compounds of the DDT group and HCH isomers were determined. It was found that the highest values of the content of these compounds occurred in attached diatoms coming from areas continuously washed with water from the melting glacier, in planktonic diatoms from the samples of the Admiralty Bay and from strongly glaciated regions. A hypothesis was put forward that along with the direct atmospheric transport the release of the deposits of these compounds from ice and glaciers during their melting is an additional source of input of chloroorganic biocides into Antarctic waters. Diatoms are good indicators of this process.

Key words: Antarctica, chloroorganic insecticides, diatoms.

1. Introduction

The occurrence of chlorinated hydrocarbons (CHs), including the residues of chloroorganic pesticides (compounds of the DDT group and HCH isomers) is commonly recorded in the atmosphere and hydrosphere of Antarctica (Tanabe, Hidaka and Tatsukawa 1983). It appears that atmospheric transport is the main route of CHs arrival to this region. In the Antarctic atmosphere these compounds occur mainly in form of gas and their transfer from air into water takes place with rainfall and

snowfall (Tanabe et al. 1982). This transport is possible only in Antarctic summer, in the absence of a fast ice cover on the sea surface. In winter CHs cumulate on the ice surface and are released the water with a delay, i.e. when snow and ice melt. The occurrence of CHs in Antarctic snow and ice was proved by Peterle (1969), Peel (1975) and Riesebrough et al. (1976). However, the amounts of the deposited CHs released from snow covering sea ice, from icebergs originating from continental glaciers and from the glaciers themselves are unknowm.

The HCH isomers were recorded to dominate among CHs in the Antarctic waters (Tanabe et al. 1982) being the least hydrophobic and less lipophilous compounds. The transport of HCH isomers from surface waters to deeper layers is slower, hence their presence in the euphotic zone is longer than that of clearly hydrophobic compounds (Tanabe and Tatsukawa 1983). Hidaka et al. (1984) related the lower content of highly lipophilous compounds of the DDT group in the Antarctic waters to their extremely rapid absorption from water by organic particles. One can suppose that these biocides are also cumulated by phytoplankton, mainly diatoms, which use to cumulate lipids as reserve material (Keil and Preister 1969). The accumulation value of DDT expressed by the accumulation coefficient for the diatoms ranges from 190 to 260. That means that the amount of these compounds was as many times higher in the diatoms than in the sea water in which they lived (Dursma and Marschand 1974).

In Antarctic waters, diatoms dominate both in net phytoplankton and in periphyton (Voronina 1984).

Taking into account that diatoms quickly accumulate CHs residues occurring in waters, an attempt was made at using them as indicators of secondary, local pollution of Antarctic waters with chlorinated hydrocarbons penetrating into these waters from melting ice and glaciers.

2. Study area

Samples of net phytoplankton were collected in the central part of the Admiralty Bay (King George Island) on November 24th, 1983 and in the BIOMASS-SIBEX study area on December 13th, 1983 in the vicinity of South Orkney Islands and from the 25th of December, 1983 till the 2nd January, 1984 in the southern part of the Drake Passage and the Bransfield Strait (Fig. 1). Exact position and some other data on the sampling stations are to be found in the paper by Rakusa-Suszczewski and Lipski (1985).

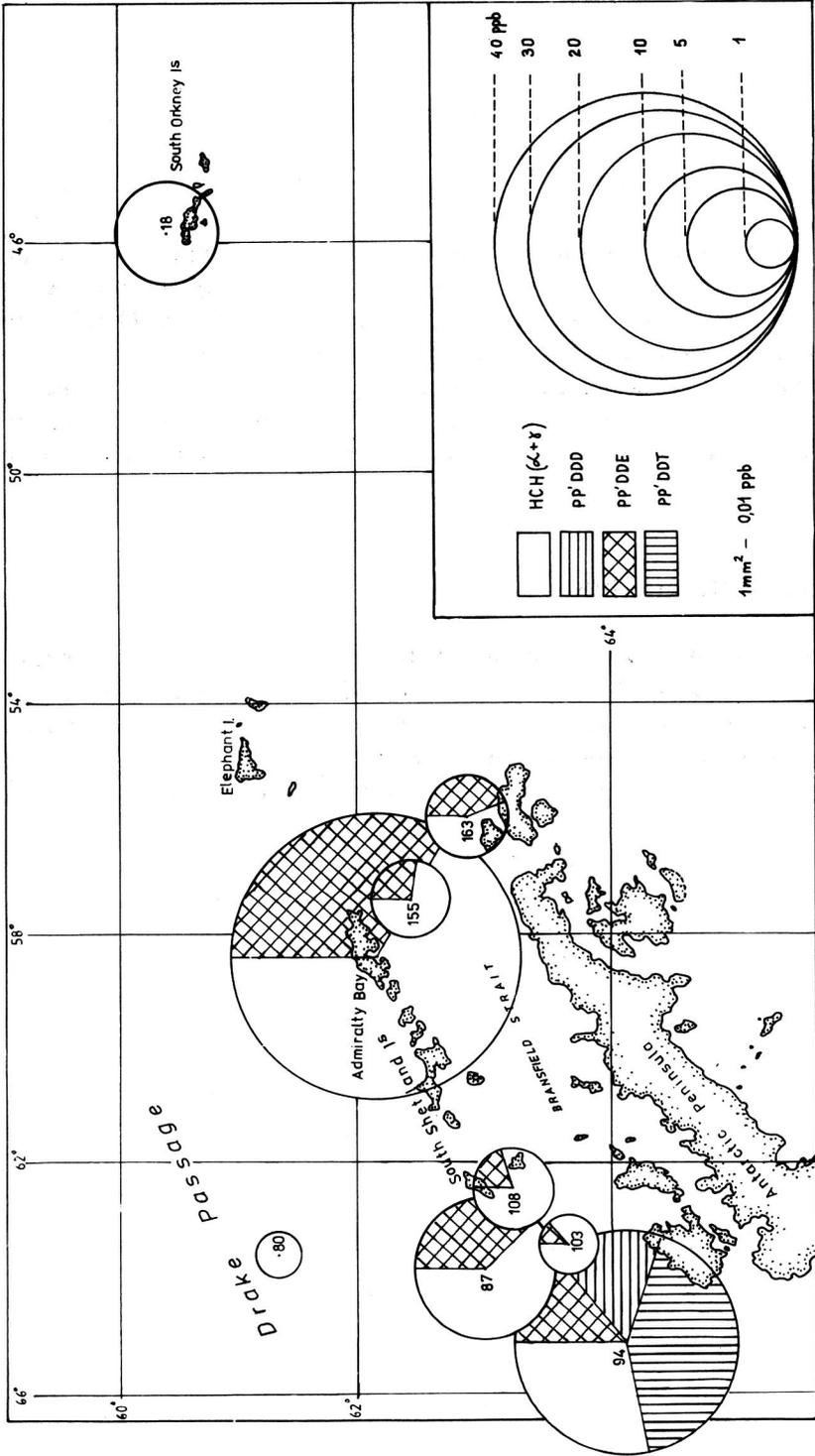In the sampling period the Admiralty Bay was under strong influence

Fig. 1. Contents of chlorinated hydrocarbons (wet weight) and their percentage share in planktonic diatoms in the Admiralty Bay and the BIOMASS-SIBEX study area

of waters from melting glaciers. The BIOMASS-SIBEX study area in which the samples were collected was covered to various degreee by icefloes and icebergs. The most extensive glaciation was observed in the south-western part of the Drake Passage (stations 87 and 94); the region of station 94 was characterized by an especially high amount of old melting icebergs. Areas close to the open ocean were completely free of ice (stations 18 and 80).

On October 10th and on November 20th, 1983 samples of attached diatoms were collected at several places of the stony bottom under the front of the Ecology Glacier in the Admiralty Bay. In October the amount of water flowing off from the melting glacier was low and it was supplied mainly by the glacier's surface layer. On the other hand, in November the amount of the melted water was much higher, and the share of water originated from the old ice crumbling at the front of the glacier was much higher.

3. Material and methods

Plankton samples were collected with a Copenhagen-net of natural gauze with a mesh size 55 µm and a 0.19625 m² opening mouth area. The net was silk in the layer hauled, 100—0 m. Phytoplankton dominated in all the plankton samples. It was estimated that the volume percentage of zooplankton was similar in all of the samples and amounted to about 10%.

Diatoms dominated in the phytoplankton samples. Data concerning volume domination of particular species are presented in Table 1.

Samples of attached diatoms were obtained by scraping them from the stones with scalpel. Immediately after collecting, samples of the diatoms were put into glass vessels washed in redistilled acetone. In October the community of the attached diatoms in 90% was composed of *Achnanthes groenlandica* (Cleve) Grun. and in November in the same percentage dominated *Amphipleura rutilans* (Trentephal) Cleve.

To calculate the wet weight a sample of diatoms was put on a filter Whatman GFF in a nutsche filter fixed into a vacuum bulb and filtered off using vacuum pump with pressure of 1 atm. A sample of 1 g was taken from the material obtained in the above described way and a total volume of phytoplankton cells was counted under a microscope after the appropriate dilution procedure. It was assumed that 1 cm³ of cells volume equaled 1 g of wet weight. The wet weight of phytoplankton weighed after the filtrating was higher by 20% than that culculated with the method of summing the cell volumes. The difference was regarded as extracellular water left after filtrating.

Table 1

CHs contents in planktonic diatoms (ppb wet weight) from the Admiralty Bay and the BIOMASS-SIBEX study area. As ∑ CHs the cumulation of CHs recalculated for wet weight with the filtrating method (A) and the method of cell counting (B) is given; nd — not determined

Stations	Chlorinated hydrocarbons recorded							∑ CHs		Volumetrically dominant diatoms	The degree of glaciation of the area
	BHC	γHCH	βHCH	HCH	pp'DDT	pp'DDD	pp'DDE	A	B		
18	nd	1.4	nd	3.3	nd	nd	bd	4.7	5.6	Chaetoceros neglectus	Free
	nd	1.2	nd	3.1	nd	nd	nd	4.3	5.1		
80	nd	0.3	nd	0.7	nd	nd	nd	1.0	1.2	Chaetoceros criophilum	of ice
87	nd	1.3	nd	3.8	trace	nd	3.1	8.2	9.8	Chaetoceros neglectus Rhizosolenia alata	Densely covered with icefloes
94	nd	2.5	nd	3.8	9.5	3.8	3.2	22.3	27.2		High number of old melting icebergs
	nd	2.3	nd	3.5	9.1	3.6	2.6	21.4	25.6	Corethron criophilum	
	nd	2.5	nd	4.1	9.4	3.3	3.3	22.6	27.1		
103	nd	0.3	nd	0.8	nd	nd	0.3	1.4	1.7		
	nd	0.3	nd	0.9	nd	nd	0.2	1.4	1.7	Chaetoceros neglectus	Low
	nd	0.4	nd	1.1	nd	nd	0.2	1.7	2.0		amount
108	trace	0.4	nd	1.7	nd	nd	0.5	2.6	3.1		of
	trace	0.6	nd	2.1	nd	nd	0.6	3.3	4.0	Chaetoceros atlanticus	ice
	trace	0.6	nd	1.9	nd	nd	0.6	3.1	3.7		
155	trace	0.4	nd	1.5	nd	nd	0.7	2.6	3.0	Chaetoceros neglectus	on
	trace	0.5	nd	1.4	nd	nd	0.6	2.5	3.0		the
163	nd	0.6	nd	1.2	nd	nd	1.4	3.2	3.8		
	nd	0.5	nd	1.1	nd	nd	1.2	2.8	3.4	Chaetoceros socialis	water
	nd	0.5	nd	1.1	nd	nd	1.2	2.8	3.4		
Admiralty Bay	nd	7.0	nd	26.0	nd	nd	14.0	47.0	56.4	Corethron criophilum	Strong inflow of water from
	nd	7.0	nd	12.0	nd	nd	12.0	31.0	37.2	Thalassiothrix antarctica	melting surface of glaciers into
	nd	8.0	nd	12.0	nd	nd	12.0	32.0	38.4		the bay

The filtrated samples were wrapped in aluminium foil washed in redistilled acetone and frozen at $-28°C$. They were kept at this temperature until analysis.

The frozen samples were homogenized with anhydrous sodium sulfate in a porcelain mortar. They were then put into the Soxhlet apparatus and extracted by 24 hours using 90 cm^3 of a mixture of n-hexane, acetone, ethyl ether and petroleum ether (2.5:5.5:1:9). The extract obtained was condensed under a nitrogen jet and purified by the shaking with dipping acid. The purified sample was evaporated till the solvents were removed under a nitrogen jet and the rest was dissolved in 1 cm^3 of n-hexane. 5 μl of such samples were injected into the column of a Pye Unicam 104 gas chromatograph with an ECD Ni^{63} detector. The columns (5 feet in lenght, 4 mm in diameter) were filled with 1.5% OV 17 + 1.95% OV 210 on 80/100 mesh WHP chromosorb. The ECD temperature was 260°C; column temperature 210°C; argon was the carrier gas, its flow was 60 cm^3/min.

The contents of chlorinated hydrocarbons were determined by the comparison of the chromatographs obtained with standard chromatographs of the following compounds: BHC, α, β, γ HCH, pp'DDT, pp'DDD, pp'DDE.

4. Results

In all samples the presence of α and γ HCH and absence of β HCH isomers was recorded. Also, in the majority of the samples the most stable metabolite of DDT, namely pp'DDE (Tab. 1) was detected.

The highest CHs content values were recorded in phytoplankton samples collected in the Admiralty Bay and in the southern part of the Drake Passage (stations 94 and 87). The lowest values occurred in the most northern region of the Drake Passage, in station 80 (Fig. 1).

In the phytoplankton, various share of particular CHs forms were recorded (Fig. 1). As a rule, lindan (γ HCH) and α HCH, were the dominant compounds. In regions closest to the open ocean (stations 18 and 80) the HCH isomers constituted 100% of CHs contents in the samples. In contrast, compounds of the DDT group were always recorded in samples from the southern part of study area. The highest percentage of these compounds was recorded in the region of station 94. They constituted 70% of all CHs content in samples collected there. It was also the only region where all the determined forms of DDT, i.e. pp'DDT, pp'DDD and pp'DDE with the domination of non-metabolized pp'DDT, were found.

The content of CHs in attached diatoms collected at the front of the glacier in the Admiralty Bay in October (Table 2). Was higher than

Table 2

CHs contents in attached diatoms (ppb, wet weight) from the Admiralty Bay. As ΣCHs the cumulation of CHs recalculated for wet weight with the filtrating metod (A) and the method of cell counting (B) is given; nd — not determined

Sampling data	Chlorinated hydrocarbons recorded							ΣCHs		Volumentrically dominant diatoms	The degree of glaciation of the area
	BHC	αHCH	βHCH	γHCH	pp'DDT	pp'DDD	pp'DDE	A	B		
10.10.1983	5	25	27	52	nd	nd	7	64	76.8		Water inflow from the melting surface of the glacier
	3	9	20	29	nd	nd	2	34	40.8	Achnanthes groenlandica	
	5	8	26	34	nd	nd	4	46	55.2		
	x̄ = 4.7	x̄ = 14.0	x̄ = 24.3	x̄ = 39.3	nd	nd	x̄ = 4.3	x̄ = 48.0	x̄ = 57.6		
20.11.1983	21	1	10	11	22	nd	24	98	117.6		Water inflow from deeper layers of the melting glacier
	18	9	12	21	27	nd	26	93	111.6	Amphipleura rutilans	
	44	17	19	36	31	nd	57	168	201.6		
	x̄ = 27.7	x̄ = 9.0	x̄ = 13.7	x̄ = 22.7	x̄ = 26.7	nd	x̄ = 35.7	x̄ = 119.7	x̄ = 143.6		

that in planktonic diatoms (Table 1), except two cases (station 94 and the Admiralty Bay). In November the content of CHs in attached diatoms was 2.5 times higher than that in October.

In the first period (October) HCH isomers (α, γ, β) dominated in attached diatoms. No pp'DDT and low amounts of the most stable metabolite, pp'DDE, were recorded. In November the mean content of HCH isomers decreased almost twice. In contrast, the amount of the compounds of the DDT group increased 14 times. A high share (over 40%) of these compounds constituted the non-metabolized form — pp'DDT.

5. Discussion

In the literature devoted to the pollution of Antarctic ecosystem with residues of CHs there is no information on the cumulation of these compounds both in planktonic and attached diatoms from Antarctic waters. The present data on phytoplankton correspond with those of Tanabe et al. (1982) concerning the distribution of CHs in Antarctic waters, in respect to the ratios of particular compounds. The concentration of CHs recorded by these authors in the water is similar to that recorded in diatoms coming from areas free of ice, whereas the amount of CHs in diatoms from ice-covered areas was many times higher (up 70x). According to Tanabe et al. (1982) the dominant residues of pesticides in Antarctic waters are the isomers of HCH, mainly α and γ HCH. On the other hand, the content of the compounds of the DDT group in Antarctic waters was much lower. A similar proportions of CHs content was found also in samples of planktonic diatoms in the present study. According to Tanabe et al. (1982) the higher content of HCH isomers than that of the compounds of the DDT group was related to their different solubility. The HCH isomers of higher solubility remain longer in the euphotic water layer. In contrast, DDT that easily forms aggregates with organic particles and of extremely high solubility in lipids is relatively quickly bounded by organic particles (Hidaka et al. 1984) and by phytoplankton (Dursma and Marschand 1974). This phenomenon is also confirmed by the present results. According to Tanabe and Tatsukawa (1983) residues of DDT remain for a relatively short time in the euphotic layer of the Antarctic Ocean water, sometimes for about dozen days, and then are transported downwards with organic particles.

It is worth noticing that we have not found any DDT residues in plankton samples taken from the open ocean completely free of ice. This indicates the lack of transport of these compounds via atmosphere

in the period directly preceding the investigations, assuming that the theory of short occurrence of DDT group compounds in the euphotic zone is correct (Tanabe and Tatsukawa 1983) and that atmospheric precipitation was the only source of pollution. In contrast, phytoplankton samples from the regions where ice was present showed usually higher levels of CHs cumulation and always contained DDT residues. Samples from the areas with many melting icebergs had higher contents of the DDT group compounds than of the CHC isomers. Moreover, in these samples the occurrence of pp'DDT was recorded, whereas Keil and Priester (1969) proved experimentally that this compound is never formed in diatoms as a result of metabolic processes. This would imply that pp'DDT was of extern origin. Note that out of all samples of planktonic diatoms the highest level of CHs contents was recorded in those from the Admiralty Bay, fed by the water from melting glaciers during the period of the present study.

This would imply that along with the atmosphere Antarctic ice is an additional source of pollution constituting a specific "bank" of CHs compounds. This refers particularly to DDT residues, the only source of which in the study period seemed to be waters from the melted deeper layers of glaciers. The authors mentioned in the introduction and particularly Riesebrough et al. (1976) have found that the highest amounts of total DDT occurred in ice layers from 1.5 to 6.0 m from the surface downwards, i.e. in the ice which was formed in the sixties, in the period of maximal DDT consumption in the world. In this period the maximal transport of this compound to Antarctica took place via atmosphere. Tanabe, Hidaka and Tatsukawa (1983) recorded as well the highest DDT content in the ice strata ranging from 2 to 6 m. These authors observed also that the level of CHs contents in water under shelf ice was much lower than that in samples collected at its melting edge.

The above cited data combined with the present results of CHs study in planktonic diatoms clearly indicate that the source of secondary, local pollution of Antarctic water, especially in summer, is a release of CHs deposites both from sea ice covered with snow and from glaciers. The degree of the pollution seems to be related to ice and iceberg amount and the rate of their melting.

This conclusion seems to be more justified after analysing CHs contents in periphyton diatoms overgrowing the stony bottom, which as significantly affected by water from the melting Ecology Glacier. A characteristic qualitative and quantitative differentation of CHs cumulated by attached diatoms in two sampling periods compared was observed. In the first period in October, the intensity of the melting of the glacier was lower and the melting occurred mainly in its surface layer. Consequently,

lower values of CHs contents in diatoms were recorded in comparison with those found in November. Quantitatively, HCH isomers dominated in attached diatoms, whereas the compounds of the DDT group were represented only by its most stable metabolite namely by pp'DDE. Such situation seems to reflect the actual state of atmospheric pollution as a source of the pollution of Antarctica. This is also indicated by the results of Tanabe et al. (1982), who have found that isomers of HCH dominated in the atmosphere over oceanic waters, including those of Antarctica. This seems to reflect the world wide tendency to substitute the previously used DDT by these insecticides.

In November, an intensive melting of deeper glacial layers was recorded. However, the main source of glacier water were big pieces of ice from its crumbling front. This resulted in a release of older, more deeply situated deposits of CHs. This, in turn, was reflected in the analized attached diatoms in higher CHs contents, with the domination of the DDT group compounds (including the non-metabolized pp'DDT from), which were commonly used till the seventies. It seems that attached diatoms in favourable geomorphological and glaciological conditions are a kind of filter cumulating residues of CHs from the water of melting glaciers. This is indicated by many times higher rates of cumulation of these compounds by attached diatoms in comparison with planktonic diatoms, particularly those from the areas free of ice.

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7. Streszczenie

W Zatoce Admiralicji (Wyspa Króla Jerzego) oraz na obszarach o różnym stopniu zalodzenia w rejonie badań BIOMASS-SIBEX (Rys. 1) pobrano siecią kopenhaską próby okrzemek planktonowych. Natomiast pod czołem Lodowca Ekologii w Zatoce Admiralicji zebrano w dwóch okresach (październik i listopad) próby okrzemek osiadłych. Metodą chromatografii gazowej oznaczono w okrzemkach zawartość pozostałości pestycydów z grupy DDT i izomery HCH. Najwyższe wartości CHs w okrzemkach planktonowych (Tabela 1) stwierdzono w próbach pochodzących z Zatoki Admiralicji i z terenów silnie zalodzonych. Z reguły w próbach tych dominowały izomery HCH (α i γ). Na obszarach niezalodzonych stanowiły one 100% wszystkich CHs. W próbach planktonowych z terenów silnie zalodzonych zawsze stwierdzano obecność pp'DDE, a z rejonów z dużą ilością topniejących starych gór lodowych stwierdzono wszystkie oznaczane związki z grupy DDT. Sytuacja taka wskazuje, że obecnie dodatkowym, lokalnym źródłem zanieczyszczenia wód antarktycznych (oprócz atmosfery) są lody i lodowce, które stanowią swoisty "bank" CHs skumulowanych tam w okresie wcześniejszym. Dotyczy to szczególnie związków z grupy DDT. Stwierdzenie takie potwierdza porównanie wyników oznaczeń zawartości CHs w okrzemkach osiadłych (Tabela 2) z dwóch okresów (październik i listopad), w których intensywność dopływu wód z lodowca na teren poboru prób, jak również ich pochodzenie było różne. W październiku, przy dopływie wód z powierzchniowo topniejącego lodowca, w okrzemkach osiadłych dominowały izomery HCH i niewielkie ilości pp'DDE. W listopadzie natomiast poziom sumarycznej kumulacji CHs był wyższy w porównaniu z okresem wcześniejszym, a związkami dominującymi były insektycydy z grupy DDT (pp'DDE i pp'DDT). Teren poboru prób w tym okresie był pod silnym wpływem wód pochodzących z głębokich warstw lodowca, w których zdeponowane zostały pozostałości pestycydów stosowanych wcześniej na świecie.