POLISH POLAR RESEARCH	9	2–3	399—408	1988

Aleksy B. ŁUKOWSKI [1]) and Ryszard LIGOWSKI [2])

[1]) Department of Zoology and Ecology,
Institute of Zoology, University of Warsaw,
Krakowskie Przedmieście 26/28,
00-325 Warszawa, POLAND

[2]) Laboratory of Polar Biology,
Department of Invertebrate Zoology and Hydrobiology,
Institute of Environmental Biology, University of Łódź,
Banacha 12/16, 90-237 Łódź, POLAND

Contamination of Antarctic marine phytoplankton by chlorinated hydrocarbons (BIOMASS III)

ABSTRACT: In the region of Bransfield Strait and southern part of Drake Passage the highest amounts of chlorinated hydrocarbons (CHs — compounds of the DDT group, HCH isomers and PCBs) were found in the samples taken at the sampling station where the CHs bottom deposits were released to the upper layers due to the special hydrological situation at this station. Increased amounts of CHs were observed also in phytoplankton sampled close to the melting ice of glacier origin which was considered as a source of pollution. However, phytoplankton sampled from the waters covered with pack-ice exhibited the lowest rate of CHs accumulation. Slightly elevated CHs accumulation was found in sea ice diatoms. All the samples exhibited elevated amount of polichlorinated biphenyls, markedly higher than that of chloroorganic insecticides.
Key words: Antarctica, phytoplankton, chlorinated hydrocarbons, BIOMASS III.

1. Introduction

The occurrence of residual chlorinated hydrocarbons (CHs i.e. the compounds of the DDT group, HCH isomers and polichlorinated biphenyls — PCBs) in the Antarctic atmosphere and hydrosphere was reported (Tanabe, Hidaka and Tatsukawa 1983). The compounds are characterized by low water solubility and high affinity to the compounds of lipid nature. They could be accumulated by the lipids of water organisms. Particularly high

rate of CHs accumulation was found in diatoms of which reserve material are lipids (Keil and Preister 1969; Dursma and Marschand 1974). Increased accumulation of CHs by net phytoplankton (mainly diatoms) inhabiting Antarctic waters was reported previously (Łukowski and Ligowski 1987). Algae, with the diatoms as their predominating component, are able to develop inside the sea ice of polar regions being even highly abundant in some places (Garrison, Sullivan and Ackley 1986). Any data on CHs content of sea ice diatoms had appeared since now.

Atmosphere is the main route of chlorinated hydrocarbons shifting to the Antarctic region where they are accumulated also as permanent deposits inside the glaciers (Riesenbrough et al. 1976; Tanabe, Hidaka and Tatsukawa 1983). The only time of the year when direct CHs penetration to the sea waters with the atmospheric rainfall is possible seems to be summer. In winter CHs molecules are accumulated on the sea ice surface and with the delay they penetrate sea water during ice melting (Tanabe et al. 1982).

The results of previous studies (Łukowski and Ligowski 1987) on the influence of sea ice cover of the area on the level of CHs found in sea diatoms suggested them to be the direct indicator of Antarctic water local pollution rate with CHs released from melting glaciers.

During BIOMASS III expedition sea diatoms were studied as an indicator of sea water pollution with CHs. The experiments were carried out during two cruises in 1986/1987 season. The estimation of qualitative and quantitative pollution rate of phytoplankton and sea ice algae was performed in the region of Bransfield Strait and in southern part of Drake Passage in the region of Elephant Island.

2. Study area

Net phytoplankton samples were collected from the r/v "Profesor Siedlecki" in the study region of BIOMASS III expedition. Collecting was carried out at 14 sampling stations during two periods: October 22, 1986 — November 12, 1986 (Tab. 1) and January 3, 1987 — January 12, 1987 (Tab. 2).

One sample of sea ice diatoms was collected also in the region of Elephant Island on 1986.10.29 (Tab. 1).

During the first sampling period the area of sampling stations was covered by ice-floes, icebergs and ice of iceberg origin to various degree. The region of sampling stations 43 and 44 was covered with drifting sea ice. The areas of sampling stations 85, 86, 87 and 88 were covered mostly by

packed ice-floes. In sampling stations 55 and 57 the ice of iceberg origin was abundant. Sea surface at the other stations was much less covered with ice. Hydrological data concerning the investigated area during the BIOMASS III Expedition are to be found in the papers by Grelowski and Wojewódzki (1988 and unpubl. data) and by Rakusa-Suszczewski (1988). Temperature and salinity in the water column at the sampling station 61 was almost uniform (Grelowski and Wojewódzki, unpubl.).

In the second sampling period the studied areas were not so heavily covered with ice and were much less diversified in this respect.

3. Material and methods

Phytoplankton samples were collected with a Copenhagen-net of natural gauze with brass tumbler and hauled in the layer between 100 and 0 meters. Mesh size of the net was 55 μm and its opening mouth area was 0.196 m^2. All 28 collected samples were composed mainly of phytoplankton. Zooplankton share in the samples was not high enough to be taken into account.

Drifting piece of sea ice was hand-collected directly from the launch, then diatoms for the study were collected after ice melting.

Each sample was placed on the glass filter (Whatman GFF) in a nutsche filter fixed into a vacuum bulb and filtered off using vacuum pump with pressure of 1 atm to get wet weight. Every sample was divided into three parts, each of them wrapped in aluminium foil washed earlier with redistilled acetone, deep freezed at −28°C and stored at applied temperature until gas chromatographic analysis.

Frozen samples were homogenized with anhydrous sodium sulfate in a porcelain mortar. Then samples were extracted 24 h in the Soxhlet aparatus with 90 ml of the following mixture: n-hexane, acetone, ethyl ether and petroleum ether (2.5:5.5:1:9). Organic extract was evaporated under a stream of nitrogen and the residue was dissolved in 1 ml of n-hexane. Obtained sample was than washed with concentrated sulphuric acid. Such purified extract again was evaporated and dissolved in 1 ml of n-hexane. 5 μl portions of prepared samples were chromatographed on Pye Unicam 104 gas chromatograph with Ni^{63} detector. Glass columns of 4 mm in diameter, 5 feet in length packed with 1.5% OV 17+1.95% OV 210 on 80—100 mesh WHP Chromosorb were applied for the GC analysis. ECD and column temperatures were 260° and 210°C, respectively. Argon was applied as carrying gas with flow rate of 60 ml/min. Chromatograms of chlorinated hydrocarbons present in the samples were compared with chromatograms of authentic standard compounds (BHC, α, β, γHCH, pp'DDD, pp'DDE, Aroclor 1242 and Clophen 60) to quantitate CHs.

Table 1

Chlorinated hydrocarbons contents (ppb of wet weight) of net phytoplankton samples collected during BIOMASS III expedition (October—November 1986) nd — not detected; $\sum$I — DDT compound group and HCH isomers.

Station	Lat. S	Long. W	Chlorinated hydrocarbons compound					Dominant species
			αHCH	γHCH	pp'DDE	$\sum$I	PCB_s	
1	2	3	4	5	6	7	8	9
5	53°34'0	50°53'5	trace	1.2	1.8	3.0	160	
43	62°22'5	56°50'9	trace	1.1	2.4	3.5	400	*Corethron criophilum* *Nitzschia* sp. (*Fragilariopsis*)
44	61°14'0	56°56'0	trace	2.7	2.7	5.4	730	*Corethron criophilum* *Nitzschia* sp. (*Fragilariopsis*)
55	61°52'9	55°40'5	nd	4.5	9.4	13.9	860	*Corethron criophilum* *Nitzschia* sp. (*Fragilariopsis*) *Rhizosolenia alata* *Chaetoceros neglectum*
57	62°18'5	57°17'5	nd	3.8	11.8	15.6	940	*Chaetoceros neglectum* *Corethron criophilum* *Nitzschia* sp. (*Fragilariopsis*) *Rhizosolenia alata*
59	62°54'8	57°09'3	nd	0.8	2.1	2.9	280	*Thalassiosira antarctica* *Chaetoceros socialis*
61	62°58'9	57°26'8	nd	9.8	41.0	50.8	1400	*Thalassiosira antarctica* *Chaetoceros socialis* *Chaetoceros neglectum*
76	63°16'6	58°16'7	nd	0.7	1.0	1.7	76	*Chaetoceros neglectum* *Thalassiosira antarctica* *Corethron criophilum*

Table 1 — continued

1	2	3	4	5	6	7	8	9
85	63°15′0	61°08′0	trace	0.6	trace	0.6	93	*Chaetoceros neglectum* *Chaetoceros socialis* *Chaetoceros tortissimus* *Thalassiosira antarctica*
86	63°06′5	61°09′0	nd	0.7	0.7	1.4	57	*Chaetoceros neglectum* *Chaetoceros socialis* *Chaetoceros tortissimus* *Thalassiosira antarctica*
87	62°57′3	61°07′8	nd	0.8	trace	0.8	80	*Chaetoceros neglectum* *Chaetoceros tortissimus* *Thalassiosira antarctica* *Corethron criophilum* *Nitzschia* sp. (*Fragilariopsis*)
88	62°52′0	60°16′0	nd	1.4	trace	1.4	100	*Chaetoceros neglectum* *Chaetoceros tortissimus* *Thalassiosira antarctica* *Nitzschia* sp. (*Fragilariopsis*)
91	62°23′0	58°45′0	trace	1.8	2.0	3.8	450	*Chaetoceros neglectum* *Nitzschia* sp. (*Fragilariopsis*) *Thalassiosira antarctica* *Chaetoceros tortissimus* *Corethron criophilum*
93	62°30′0	58°03′5	trace	2.8	5.9	8.7	600	*Chaetoceros neglectum* *Nitzschia* sp. (*Fragilariopsis*) *Thalassiosira antarctica* *Corethron criophilum*
B30 **(sea ice)**	60°52′0	56°04′0	trace	4.2	11.3	15.5	3730	*Nitzschia cylindrus* *Nitzschia decipiens*

Table 2

Chlorinated hydrocarbons contents (ppb of wet weight) of net phytoplankton samples collected during BIOMASS III expedition (January 1987)
nd — not detected; $\sum$I — DDT compound group and HCH isomers

Station	Lat. S	Long. W	Chlorinated hydrocarbons compound					Dominant species
			αHCH	γHCH	pp'DDE	$\sum$I	PCB_s	
1	2	3	4	5	6	7	8	9
II—4	62°35'0	57°20'0	nd	1.0	trace	1.0	70	*Chaetoceros socialis* *Chaetoceros neglectum* *Chaetoceros tortissimus*
II—6	62°36'0	57°42'0	nd	0.8	0.7	1.5	180	*Chaetoceros neglectum* *Chaetoceros tortissimus* *Chaetoceros socialis*
II—8	62°33'8	58°17'2	nd	0.8	1.5	2.3	110	*Chaetoceros neglectum* *Chaetoceros tortissimus* *Corethron criophilum*
II—9	62°24'0	58°37'0	nd	0.8	3.0	3.8	180	*Phaeocystis pouchetii* *Chaetoceros neglectum* *Chaetoceros tortissimus* *Corethron criophilum*
II—12	62°30'0	59°11'0	nd	0.4	trace	0.4	70	*Phaeocystis pouchetii* *Chaetoceros neglectum* *Corethron criophilum*
II—15	61°45'2	57°00'3	nd	1.3	4.5	5.8	200	*Chaetoceros neglectum* *Chaetoceros tortissimus*
II—21	61°45'0	56°40'0	trace	1.3	8.9	10.2	2000	*Chaetoceros neglectum* *Phaeocystis pouchetii* *Chaetoceros tortissimus* *Corethron criophilum* *Thalassiosira antarctica*

Table 2 — continued

1	2	3	4	5	6	7	8	9
II—25	61°34′0	55°18′0	3.3	0.4	0.7	4.4	1200	*Corethron criophilum* *Rhizosolenia alata* *Phaeocystis pouchetii* *Nitzschia* sp. (*Nitzschia*)
II—27	61°40′0	55°00′0	3.2	0.8	0.6	4.6	130	*Chaetoceros neglectum* *Chaetoceros tortissimus*
II—28	61°20′0	55°00′0	3.0	0.4	2.9	6.3	1600	*Chaetoceros neglectum* *Chaetoceros tortissimus* *Corethron criophilum*
II—31	61°52′1	54°18′0	3.2	1.7	8.7	13.6	2020	*Chaetoceros neglectum* *Phaeocystis pouchetii* *Chaetoceros tortissimus* *Corethron criophilum* *Thalassiosira antarctica*
II—41	60°50′0	56°23′0	0.6	1.2	0.7	2.5	130	*Corethron criophilum* *Nitzschia* sp. (*Fragilariopsis*) *Rhizosolenia alata*.
II—47	60°30′0	55°49′9	nd	1.5	3.0	4.5	180	*Corethron criophilum* *Thalassiothrix antarctica* *Rhizosolenia alata*
II—49	60°20′0	55°17′9	nd	1.7	4.3	6.0	330	*Corethron criophilum*

4. Results

In all studied samples polichlorinated biphenyls (PCBs) of industrial origin were found. Among residues of chloroorganic insecticides lindan (HCH) was present in all the samples. During the first period of study (26.10.1986 — 12.11.1986) αHCH isomer was found in trace amounts only in few samples, however, in the second period of the study (3.01. — 17.01.1987) measurable amounts of this compound appeared more often in samples. βHCH isomer was never observed in the samples.

Among detected residues of DDT only the most stable pp'DDE was present in all the samples. pp'DDT and pp'DDD were never found.

During the first period of the study the highest amounts of residues of CHs were characteristic for the phytoplankton collected at sampling stations 61, 57, 55. In contrast, the lowest amounts of these compounds were found in the samples collected at 85, 87, 86, 88 sampling stations (Tab. 1).

During the second period of study the contents of chlorinated hydrocarbons in the phytoplankton was found to be less diversified in most of the samples except relatively high values of CHs level found in the samples collected at the stations 31 and 22 (Tab. 2).

Sea ice derived diatoms exhibited much higher contents of PCBs comparing with the other samples. However the value of ΣI was found to be almost the same as that found in sea water diatoms.

5. Discussion

Tanabe et al. (1982) presented qualitative composition of chlorinated hydrocarbons in Antarctic waters of which α, γHCH isomers and pp'DDE dominated. The same groups of chloroorganic insecticide residues (HCH and pp'DDE) were found in Antarctic phytoplankton (present paper) as well as in Antarctic diatoms (Łukowski and Ligowski 1987). These last authors have found the correlation between the level of CHs accumulation of the ice derived diatoms and the amount of melting iceberg ice in the sampling area. It was concluded that the glacier ice is a kind of stock of CHs deposits in Antarctica. Both study periods during BIOMASS III expedition were characterized by increased CHs contents found in the phytoplankton collected in the areas heavily covered with the glacier ice.

However, the highest contents of CHs was recorded in phytoplankton collected at the sampling station 61 and especially pp'DDE contents was the most pronounced. The station was situated at the edge of the shelf of the Antarctic Peninsula (413 m in depth). Diatom frustules of benthic origin were found in net phytoplankton samples hauled at this station from the

0—100 m layer (Ligowski, unpubl.). A very homogenous water column found at the station suggests an intensive mixing (Grelowski and Wojewódzki, unpubl.) causing benthic sediments appearence in the upper layers. According to Tanabe and Tatsukawa (1983) DDT residues remain in the euphotic layer for a short period of time; a part of these compounds is accumulated by the phytoplankton lipids with the relatively high rate due to the lipophilic character of the molecules; the other part of molecules aggregate with the organic particles and is transported to the bottom forming benthic deposits. The same phenomenon was also described by Dursma and Marschand (1974) for the temperate seas, and by Opaliński and Łukowski (1979) for the Antarctic seas. Hydrological conditions at the station 61 could be a possible reason of such a high level of pp'DDE accumulation in phytoplankton of the 0—100 m water column. Tanabe, Hidaka and Tatsukawa (1984) observed that CHs content of water from under the shelf ice was markedly lower when compared with the CHs level of water of melting ice edge. In the course of our studies at the stations covered with the pack-ice layer we also recorded there the lowest CHs contents in the phytoplankton among all samples collected elsewhere. This confirms that the ice cover inhibits the direct penetration of CHs into the water and the pack-ice is not a source of water pollution at that time. Moreover, the fact of the high contents of CHs found in the diatoms inhabiting the sea ice suggests a high rate of the compounds accumulation in this environment.

A relatively high rate of polichlorinated biphenyls (PCBs) accumulation, exceeding many times the contents of residues of chloroorganic insecticides was also recorded for the samples of net phytoplankton as well as for the sea ice algae. Recently the inflow of the above mentioned compounds was found to exceed the penetration of the Antarctic region by residues of chloroorganic insecticides. It seems that PCBs deposits are formed in the ice. The suggestion seems to be confirmed by the finding that their highest contents was found also in the regions covered with the old ice.

The studies were carried out during the Expedition of the Polish Academy of Sciences, BIOMASS III, managed by prof. S. Rakusa-Suszczewski. The work was performed under the project C.P.B.P.03.03.A.

6. References

Dursma E. K. and M. Marschand. 1974. Aspects of organic marine pollution. — Oceanogr. Mar. Biol. Ann. Rep., 12: 315—431.

Garrison D. L., C. W. Sullivan and S. A. Ackley. 1986. Sea ice microbial communities in Antarctica. — BioScience, 36(4): 243—250.

Grelowski A. and T. Wojewódzki. 1988. Hydrography of the region between the King George and Elephant Islands (BIOMASS III. October—November 1986). — Pol. Polar Res., 9: 165—180.

Keil J. E. and L. E. Priester. 1969. DDT uptake and metabolism by the marine diatom. — Bull. Environ. Contamin. Toxycol., 3: 169—173.

Łukowski A. B. and R. Ligowski. 1987. Cumulation of chloroorganic insecticides by Antarctic marine diatoms. — Pol. Polar Res., 8: 167—177.

Opaliński K. W. and A. B. Łukowski. 1979. DDT in Antarctic sediments. — Pol. Arch. Hydrobiol., 26: 579—582.

Rakusa-Suszczewski S. 1988. Coarse-scale structure of the water column between King George and Elephant Islands (BIOMASS III, October—November 1986). — Pol. Polar Res., 9: 181—194.

Riesenbrough R. W., W. Walker, T. T. Schmidt, B. W. de Lappe and C. Connors. 1976. Transfer of chlorinated biphenyls to Antarctica. — Nature, 264: 738—739.

Tanabe S., H. Hidaka and R. Tatsukawa. 1983. PCBs and chlorinated hydrocarbons pesticides in Antarctic atmosphere and hydrosphere. — Chemosphere, 2: 277—288.

Tanabe S. and R. Tatsukawa. 1983. Vertical transport and residence tissue of chlorinated hydrocarbons in the open ocean water column. — J. Oceanogr. Soc. Japan, 39: 53—62.

Tanabe S., R. Tatsukawa, M. Kawano and H. Hidaka. 1982. Global distribution and atmospheric transport of chlorinated hydrocarbons HCH (BHC) isomers and DDT compounds in the Western Pacific, Eastern Indian and Antarctic Oceans. — J. Oceanogr. Soc. Japan, 38: 137—148.

Received February 13, 1988
Revised and accepted April 3, 1988

7. Streszczenie

W rejonie Cieśniny Bransfielda i południowej części Cieśniny Drake'a w czasie dwóch rejsów (październik—listopad 1986 i styczeń 1987) pobrano próby fitoplanktonu sieciowego i próbę glonów z lodu morskiego. Metodą chromatografii gazowej oznaczono w próbach zawartość chlorowanych węglowodorów (CHs — produkty rozpadu pestycydów z grupy DDT, izomery HCH i PCBs).

Największą zawartość CHs znaleziono w fitoplanktonie pobranym ze stacji, gdzie okrzemki z osadów dennych występowały w kolumnie wody od 0 do 100 m, co sugeruje naruszenie dennego depozytu CHs Podwyższoną zawartość CHs stwierdzono także w próbach pobranych w sąsiedztwie topniejącego lodu lodowcowego, który wydaje się być źródłem lokalnego zanieczyszczenia wody. Najniższą zawartość CHs wykazano w fitoplanktonie z rejonu pokrytego warstą lodu. Zwarty pak lodowy uniemożliwia bezpośrednią penetrację wody przez CHs, które pochodzą z atmosfery. Zaobserwowano podwyższoną kumulację CHs w okrzemkach rozwijających się w lodzie morskim. We wszystkich próbach oznaczona zawartość PCBs wielokrotnie przekraczała ilość insektycydów chloroorganicznych.