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ACCUMULATION OF CHLOROORGANIC COMPOUNDS AND HYDROCARBONS IN BALTIC SEAWEEDS

Abstract. Accumulation of chloroorganic compounds and hydrocarbons in seaweeds at the north and west coast of Estonia and in coastal waters of the islands of Saaremaa and Vormsi were studied. PCB concentrations showed a decreasing trend while DDT concentrations were relatively stable during the investigation period 1988—1989. The content of petroleum hydrocarbons in seaweeds varied more than 60 times; higher concentrations were measured in the neighbourhood of ports and urban areas.

Key words: Baltic Sea, seaweeds, accumulation, chloroorganic compounds, petroleum hydrocarbons.

Several factors such as seasonal variability, changes in pollutant content depending on growth stages, and the variation of concentration in different parts of seaweed thalli complicate the use of benthic macrophytes as pollution indicators. Relevant data are scarce due to these complications. The results of earlier investigations of the accumulation of chloroorganic compounds and petroleum hydrocarbons (PH) in samples of the Baltic Sea algae taken from the north and west coast of Estonia during 1983—1987 can be found in (Kukk et al., 1988). The following set of data characterizes the pollution of marine algae in the coastal waters of Saaremaa and Vormsi islands in 1988—1989. As a continuation of the above-mentioned work, part of the samples analysed were collected from the north and west coast of Estonia.

Methods

Phytobenthos was collected from a boat and by hand. After they were cleaned of ground particles, the samples were stored in glass containers at —20°C. The seaweeds were homogenized in the presence of Na_2SO_4 and extracted with *n*-hexane-acetone 1 : 1 v/v. Lipids were determined in an aliquot part of the extract. Another part of the extract was hydrogenolyzed with c. H_2SO_4. The analyses of PCB and DDT were made on a "Perkin-Elmer" gas chromatograph m. 3920 using a packed column 2 m with 8% OF-1 — 4% SF-96 (2 : 1) on Chromosorb Q 100—120 mesh at 190°C. Arochlor 1254 served as the reference substance for PCB determination. The analyses of DDT and metabolites were made after the dehydrochlorination with 10% KOH in methanol.

The third aliquot part of the extract was used for PH analyses. Spectrofluorometric excitation wavelength was 310 nm, emission wavelength 360 nm (Spectrofluorometer LS-3 "Perkin-Elmer"). IR-spectrophotometry was used as an alternative method for hydrocarbons determination. Absorption intensity of the extracts at 2930 cm^{-1} was compared with the absorption intensity of the mixture of *n*-hexadecane,

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isooctane, and benzene (37.5 : 37.5 : 25). Both analyses preceded the separation of the extracts on an alumina thin layer with *n*-hexane as eluent. Material with $R_f \geqslant R_f$ of crysene was taken as the hydrocarbon fraction. The gas chromatographic analysis of hydrocarbons was performed on a glass capillary 25 m, OV-101 (GC "Perkin-Elmer", m. 910).

Results

The samples of seaweeds were collected from the sites shown in Fig. 1. The results of the analyses are presented in the Table. The concentration value is the mean of two simultaneous analyses. Fig. 2 shows changes in the mean PCB and DDT concentrations in *Enteromorpha intestinalis*, *Cladophora glomerata*, and *Fucus vesiculosus* in 1983—1989. PCB concentrations decreased constantly with a slight increase in 1989, which may be due to different sampling localities. PCB concentrations were the lowest in *Furcellaria lumbricalis*, which had the lowest lipid content. The second lowest PCB levels occurred in *Fucus vesiculosus*. Besides the lipid content, the specific area is probably a factor controlling accumulation of lipid soluble contaminants in marine algae (Янковский et al., 1981).

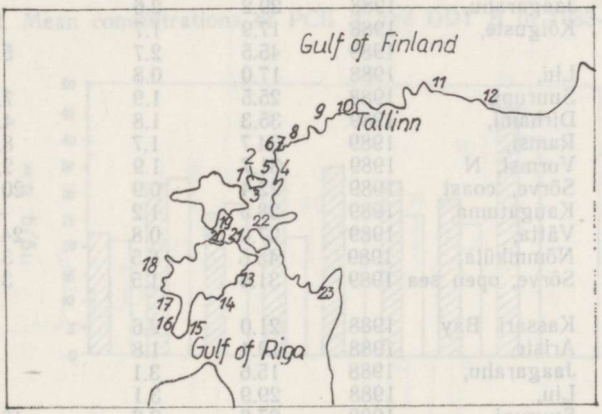

Fig. 1. Sites of the collection of seaweed samples: *1* — Vormsi North, *2* — Diibi, *3* — Sviiby, *4* — Österby, *5* — Ramsi, *6* — Dirhami, *7* — Nõva, *8* — Berta Cape, *9* — Suurupi, *10* — Kakumäe, *11* — Käsmu, *12* — Toolse, *13* — Kõiguste, *14* — Vätta, *15* — Sõrve, *16* — Ariste, *17* — Kaugatuma, *18* — Jaagarahu, *19* — Kassari, *20* — Triigi, *21* — Rannaküla, *22* — Nõmmküla, *23* — Liu.

The mean DDT concentrations showed large variability during the period of investigation. The increase in DDT concentrations in 1986—1987 and the relative stability in 1988—1989 are characteristic with the exception of *Cladophora glomerata* in which the mean concentration in 1989 was 3.7 times higher than in 1988. The increase in PCB concentrations in 1989 was the most noticeable in case of *Cladophora*. In 1989 all the *Cladophora glomerata* samples were taken from the coast of Vormsi Island. Though the number of samples was limited to eight per year, the data reflect the pollution state of this region.

Concentration of PCB, DDT, and hydrocarbons in seaweeds of different sampling sites

Species	Sampling site and time		Chloroorganic compounds, ng/g d. w.		Hydrocarbons, µg/g d. w.	
			PCB	DDT	Fluorescence spectrophotom.	IR-spectrophotom.
Cladophora glomerata	Toolse,	1988	32.6	2.63		
	Kakumäe,	1988	25.9	2.1		
	Triigi,	1988	20.0	1.5		
	Kõiguste,	1988	32.2	1.2		
	Ramsi,	1989	74.8	5.6	0.6	134.2
	Österby,	1989	53.0	6.0	3.8	448.0
	Sviibi,	1989	60.7	10.2	16.0	200.7
	Diibi,	1989	78.6	6.5	5.0	92.0
Enteromorpha intestinalis	Toolse,	1988	38.0	2.0		
	Triigi,	1988	39.7	4.4		
	Kõiguste,	1988	64.6	4.9		
	Liu,	1988	34.1	6.3		
Fucus vesiculosus	Toolse,	1988	17.2	1.0		
	Toolse,	1989	42.9	2.6	5.5	214.9
	Käsmu,	1988	27.3	3.7		
	Kakumäe,	1988	21.1	2.2		
	Triigi,	1988	18.8	0.8		
	Ariste,	1988	19.0	3.9		
	Jaagarahu,	1988	29.2	2.6		
	Kõiguste,	1988	17.9	1.7		
		1989	45.5	2.7	5.1	283.4
	Liu,	1988	17.0	0.8		
	Suurupi,	1988	25.5	1.9	7.2	124.4
	Dirhami,	1989	35.3	1.8	4.1	167.3
	Ramsi,	1989	34.7	1.7	8.6	234.4
	Vormsi, N	1989	31.7	1.9	2.7	268.7
	Sõrve, coast	1989	22.4	0.9	20.5	136.1
	Kaugatuma,	1989	28.5	1.2	—	85.4
	Vätta,	1989	27.6	0.8	24.1	172.4
	Nõmmküla,	1989	45.6	6.5	3.7	182.4
	Sõrve, open sea	1989	31.6	1.5	3.3	114.9
Furcellaria lumbricalis	Kassari Bay	1988	21.0	2.6		
	Ariste,	1988	19.4	1.8		
	Jaagarahu,	1988	15.6	3.1		
	Liu,	1988	29.9	3.1		
	Suurupi,	1988	27.6	2.6	19.1	381.6
	Dirhami,	1989	22.0	3.5	2.4	82.7
	Ramsi,	1989	22.6	2.2	1.3	31.4
	Vormsi, N	1989	25.6	0.9	1.2	34.7
	Berta Cape,	1989	22.0	1.7	0.2	14.6
	Sõrve, open sea	1989	20.9	0.8	16.2	289.8
	Kaugatuma,	1989	23.7	1.6	3.2	19.8
	Sõrve, open sea	1989	32.1	2.0	0.8	37.8
	Jaani,	1989	60.6	4.2	1.3	84.8
	Nõmmküla,	1989	39.9	8.0	8.5	94.1
Ceramium tenuicorne	Rannaküla,	1989	38.8	6.0	0.3	3.6
	Nõva,	1989	23.2	3.6	5.6	172.2
Rhodomela confervoides	Sõrve,	1989	10.8	0.5	2.3	17.9
	Nõva,	1989	55.3	4.3	20.0	539.6
Ramunculus baudotii	Käsmu,	1988	56.2	4.1		
Potamogeton filiformis	Toolse,	1988	24.7	—		
	Käsmu,	1988	32.2	1.4		

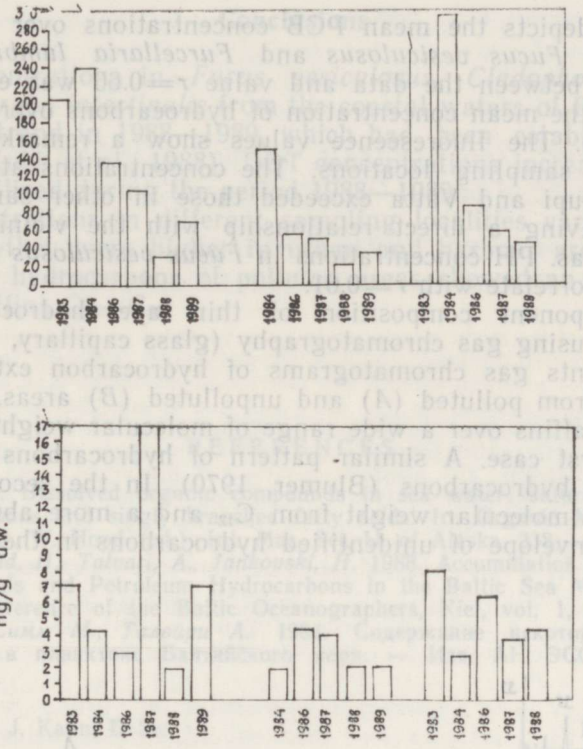

Fig. 2. Mean concentrations of PCB *A* and DDT *B* in 1983—1989.

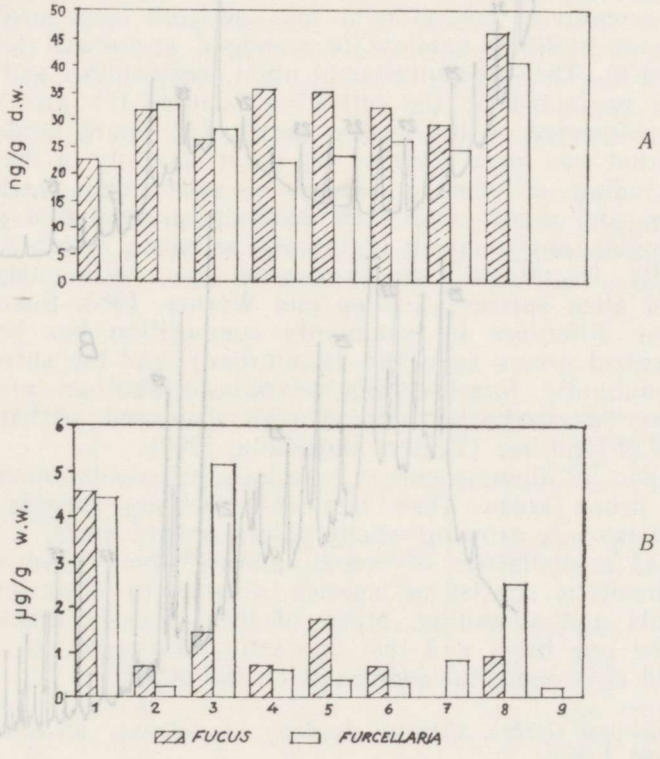

Fig. 3. Concentration of PCB *A* and petroleum hydrocarbons *B* in *Fucus vesiculosus* and *Furcellaria lumbricalis* in different sampling locations in 1989.

Fig. 3*A* depicts the mean PCB concentrations over some sampling localities for *Fucus vesiculosus* and *Furcellaria lumbricalis*. A correspondence between the data and value $r=0.66$ was established. Fig. 3*B* presents the mean concentration of hydrocarbons over the area under consideration. The fluorescence values show a remarkable variability for different sampling locations. The concentrations at the Nõva port and at Suurupi and Vätta exceeded those in other sampling stations manifold, having a direct relationship with the vicinity of harbours or urban areas. PH concentrations in *Fucus vesiculosus* and *Furcellaria lumbricalis* correlate with $r=0.61$.

The component composition of thin layer hydrocarbon fractions was studied using gas chromatography (glass capillary, 25 m, OV-101). Fig. 4 presents gas chromatograms of hydrocarbon extracts of *Fucus vesiculosus* from polluted (*A*) and unpolluted (*B*) areas. Even distribution of *n*-paraffins over a wide range of molecular weight is characteristic of the first case. A similar pattern of hydrocarbons is often found in sea-water hydrocarbons (Blumer, 1970). In the second case hydrocarbons with molecular weight from C_{12} and a more abundant complex unresolved envelope of unidentified hydrocarbons in the range C_{20}—C_{30} are present.

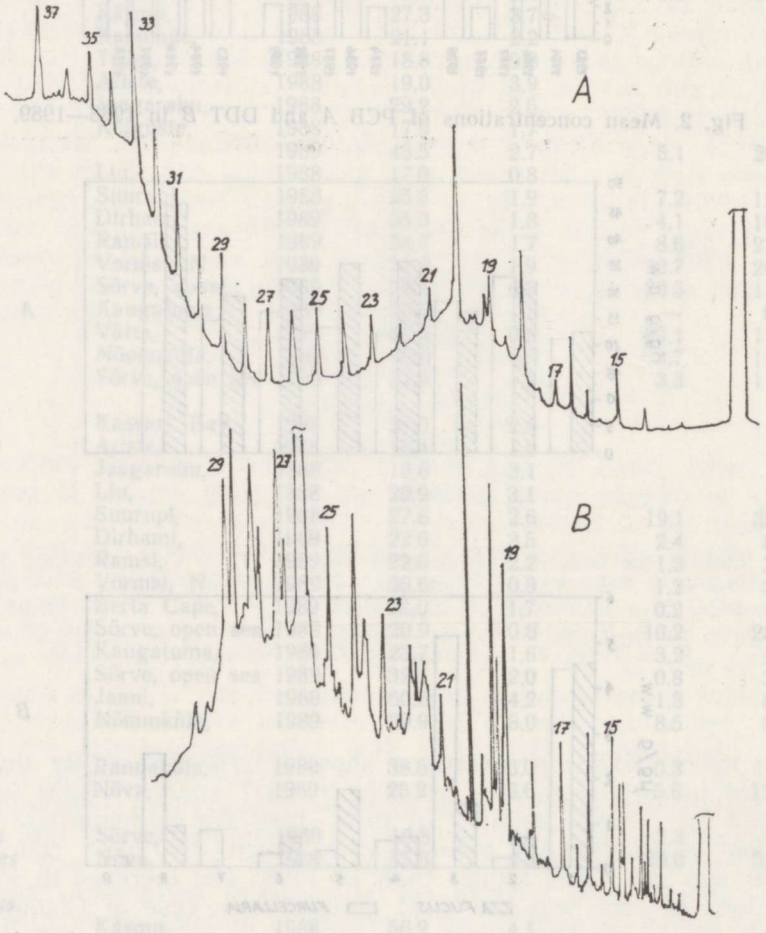

Fig. 4. Gas chromatograms of hydrocarbons of *Fucus vesiculosus* extracts: *A* — station No. 9, 19.1 μg/g d. w. and *B* — station No. 15, 3.3 μg/g d. w.

Conclusions

PCB concentrations in *Fucus vesiculosus*, *Cladophora glomerata*, and *Enteromorpha intestinalis* from the coastal waters of Estonia showed a decreasing trend in 1988—1989, which had been established also in 1983—1987 (Kukk et al., 1988). DDT concentrations increased in 1986—1987, but stabilized during the period 1988—1989.

PH concentrations in different sampling localities varied more than 60 times and they were higher in urban and harbour areas. Gas chromatograms of hydrocarbons of polluted areas showed an even distribution of *n*-paraffins C_{13}—C_{38}.

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