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PCBs in phytoplankton in the Odra Estuary

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Abstract

Eleven PCB congeners were determined in phytoplankton samples collected from the Odra Estuary at 9 stations in 2001–2002. The PCB concentrations were related to the temperature, turbidity, salinity, oxygen and redox potential of the water as well as to the pigment content in the samples. The results indicate that phytoplankton and the detritus derived from it play a crucial role in the distribution of PCBs, their transfer from the water column to sediments and from the Estuary to the sea. The species composition of the phytoplankton occurring in this area could also be very important as regards the sorption of PCBs.

1. Introduction

Polychlorinated biphenyls (PCBs) were found in fish tissue in Sweden in the mid-sixties (Jensen 1966). A few years later these compounds came to be regarded as posing a very serious threat to the marine environment (ICES 1970). The Helsinki Commission (HELCOM) has included PCBs among the priority pollutants of the Baltic environment ever since the Helsinki Convention was first signed in 1974. Even though PCB concentrations have been decreasing since that time, the Convention, re-signed by the Baltic states in 1992, still includes PCBs among the most hazardous substances. Recently, the EU Commission has issued a document that also places PCBs on the list of most hazardous substances and stresses the need to acquire knowledge of the distribution of these compounds and eliminate them from the natural environment (COM 2001). The document underscores the fact that data from the associated states are especially important.

Even though intensive research into PCBs in the Baltic has been carried on for over thirty years, the relevant literature deals primarily with animal organisms (fish, molluscs, birds) (HELCOM 1987, 1990, 1996, Falandysz et al. 1999). This is due to the widely-held view that these compounds are accumulated in lipid tissues, and that plants (including phytoplankton) do not contain such a large quantity of lipids. However, in the southern Baltic environment the majority of biomass consists of phytoplankton (Kowalewska 1997, Maksymowska et al. 2000). The very idea of PCB sorption by phytoplankton appeared soon after these compounds had been discovered in the natural environment (Jensen et al. 1972). Next, Olson & Sandegren (1989) put forward the hypothesis of the accumulation of PCBs by phytoplankton in the natural environment, based on the observation that otters, which are very sensitive to PCBs, survived in Sweden only in eutrophic lakes. They explained this by the 'dilution effect' of phytoplankton, i.e. by the bioaccumulation of PCBs by the algae. Nevertheless, such papers treating of PCBs in phytoplankton that have been published in the world literature tend to focus on laboratory experiments with either axenic algae cultures or plankton isolated from the sea, stressed by very high concentrations of PCBs (Moore & Harris 1972, Fisher 1975, Harding & Philips 1978a, b, Biggs et al. 1979, 1980, Hiraizumi et al. 1979, Picer et al. 1979, Stange & Swackhamer 1994, Wang et al. 1998, Wallberg & Andersson 1999). At best, the experiments were carried out in a marine microcosm (O'Connors et al. 1978, Gunarsson & Rosenberg 1996). All these conditions were quite irrelevant to the sea. It is not so easy to extrapolate even the microcosm results to real conditions in the field. Furthermore, the majority of these studies were done about twenty years ago using old analytical techniques (e.g. packed columns, Aroclor standards), and this may have been the cause of the frequently contradictory conclusions. That is why it is also difficult to compare those results with the ones obtained by modern methods.

In the 1990s, papers on PCBs in phytoplankton in the natural aquatic environment started to appear; however, most of them concerned lakes and only a few the marine environment. Nevertheless, the latter were often based on the results of old analyses, done as long as 20 years ago. Thus, Schulz-Bull et al. (1991, 1995, 1998), studying the Baltic Sea and the North Sea, concluded that PCBs were scavenged along with particles from seawater, especially those containing organic matter. Their analyses of samples collected in the North Sea in 1988–1991 yielded the lowest PCB concentrations in filtered seawater during the spring phytoplankton blooms. Recently, Söderström et al. (2000) concluded from a study of a eutrophic and an oligotrophic lake in Sweden that no 'phytoplankton biomass dilution' was observed for any of the organic pollutants in the hypertrophic lake. According to these authors, the settling particle flux was higher in the eutrophic lake and, consequently, also the settling fluxes of organic pollutants. Ko & Baker (1995), who studied samples of plankton collected in 1990–1992, noted the concentration of PCBs by zooplankton only. Dachs et al. (1996), studying PCBs (Aroclor standards) in samples from the Alboran Sea (the Mediterranean, near the Strait of Gibraltar), found a negative correlation between PCBs and faecal pellet contents. This result was in direct opposition to the opinions accepted a few years earlier, that faecal pellets are the main factor responsible for PCB transfer from the water column to the sediments (Elder & Fowler 1977). Harding et al. (1997) presented a large set of results of analyses of phytoplankton samples collected in the southern Gulf of St. Lawrence (Atlantic coast of Canada) twenty years previously (1976–1977). Unfortunately, they give the sum of PCBs (calculated to wet weight) determined using Aroclor standards and glass packed columns. Bruhn & McLachlan (2002) wrote about the seasonal variation of PCBs in the water and suspended particulate matter of the southern Baltic, but did not draw any conclusions. Falandysz et al. (2002) gave the PCB content on the basis of an unknown number of phytoplankton samples collected at two stations in the Gulf of Gdańsk in an unknown way, at an unspecified time, calculated to wet weight.

Looking at the above data, one can hardly say that the problem of PCB content in phytoplankton in the marine environment has been solved. On the contrary, the data are scarce and inconsistent; indeed, they are often contradictory. Our previous studies, based on analyses of sediments, had pointed to algae as the principal factor responsible for the distribution of PCBs in the southern Baltic (Konat & Kowalewska 2001). It therefore seemed interesting to examine the PCB content in phytoplankton in seawater, in order to substantiate the previous conclusions about the part played by phytoplankton in PCB transfer in this environment. The Odra Estuary seemed especially promising as regards achieving this aim, since in comparison with other coastal regions of the southern Baltic, it has both the PCB pollution and primary production, and its other environmental parameters vary over a wide range.

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2. Experimental

The phytoplankton samples were collected in the years 2001–2002 from a boat of the Biology Department of the University of Szczecin using a 'Toń 2' type bathometer, and subsequently filtered through Whatman GF/C glass-fibre filters. After collection the samples were subjected to microscopic examination, and then HPLC-analysis for pigments in order to confirm the phytoplankton content. In 2002, the sub-samples of the water were collected and preserved for plankton species identifications. The samples were collected in the Szczecin Lagoon and at one station in the Pomeranian Bay, at the mouth of the Świna river, the main outlet of the Odra waters to the Baltic. Fig. 1 shows the location of the stations, Table 1 the co-ordinates and characteristics of the stations and the predominant phytoplankton species in 2002.



Fig. 1. Location of the sampling stations

For extraction of PCBs the method elaborated in the Marine Pollution Laboratory IO–PAS for sediments was used (Kowalewska & Konat 1999). The extracted and cleaned-up PCB fraction was analysed using GC-ECD and GC-MS, according to a procedure described elsewhere (Kowalewska

Station	Coordinates	Date of sampling	Temperature t [°C]	Salinity S [PSU]	Phytoplankton: predominant species in 2002 No. of cells [%]
38	53°57′N 14°16′E	June 2002	18.1	4.3	cyanobacteria-49 diatoms-47
J. W. 2	$53^{\circ}52'{ m N}$ $14^{\circ}24'{ m E}$	June 2002	20.8	0.5	cyanobacteria-82
J. W. 1	53°41′N 14°31′E	June 2001 June 2002	$\begin{array}{c} 15.8 \\ 20.6 \end{array}$	$\begin{array}{c} 0.6 \\ 0.5 \end{array}$	cyanobacteria-81
15	53°46′N 14°32′E	May 2001 June 2002	$\begin{array}{c} 16 \\ 19.1 \end{array}$	$\begin{array}{c} 0.9 \\ 0.5 \end{array}$	cyanobacteria-97
18	53°47′N 14°19′E	June 2002	20.6	0.5	diatoms-77
М	53°46′N 14°22′E	May 2001 June 2002	16.4 20.6	$\begin{array}{c} 0.7 \\ 0.5 \end{array}$	diatoms-84
L	53°43′N 14°26′E	May 2001 June 2002	16.3 20.8	$\begin{array}{c} 0.5 \\ 0.4 \end{array}$	diatoms-91
Κ	53°40′N 14°30′E	May 2001 June 2002	$17.1 \\ 20.5$	$\begin{array}{c} 0.4 \\ 0.4 \end{array}$	diatoms-62
R. O.	53°37′N 14°35′E	May 2001 June 2002	18.1 21.2	$\begin{array}{c} 0.3 \\ 0.4 \end{array}$	diatoms-79

Table 1. Characteristics of the sampling stations

& Konat 1999, Konat & Kowalewska 2001, Konat-Stepowicz 2002). The method of analysis was validated on certified reference sediment materials obtained from IAEA in Monaco (Nos. 383, 417). The results of the validation have been presented elsewhere (Kowalewska et al. 2002). All the results were within the confidence levels given in the relevant certificates.

Both the extraction and analysis of pigments in the phytoplankton samples were carried out according to the procedures for sediments described earlier (Kowalewska et al. 1996, Kowalewska 1997). The pigments determined included chlorins a, i.e. chlorophyll a and its derivatives (chlorophyll a', phaeophytin a, pyrophaeophytin a, phaeophorbides, steryl chlorins), chlorophylls c and β -carotene.

Chlorophyll a and β -carotene occur in almost all algae species and in higher plants, chlorophylls c in diatoms, dinoflagellates and some brown macroalgae. Phaeophorbides and pyrophaeophytin a are markers of zooplankton grazing. Chlorophyll a' and phaeophytin a are products of early chlorophyll a diagenesis.

The environmental parameters were determined using a YSI 6000 type multiparametric sonde for water quality control. These measurements included: t – temperature [°C] (sensor – thermistor, range –5 to 45°C, precision ± 0.15 C), S – salinity [PSU] (calculated on the basis of results of temperature and specific conductivity, range 0 to 70 ppt, precision ± 0.1 ppt), O₂ – dissolved oxygen [mg l⁻¹] (polarographic sensor, range 0 to 20 mg l⁻¹, precision ± 0.2 mg l⁻¹), T – turbidity [NTU] (optical sensor, range 0 to 1000 NTU, precision ± 0.1 NTU), E_h – redox potential [mV] (platinum sensor, range –999 to 999 mV, precision ± 20 mV).

3. Results and discussion

The individual PCB content in the phytoplankton was generally in the range from 0.01 to 3.5 ng l⁻¹ of water, $\Sigma 11$ PCBs from 1.7 to 12 ng l⁻¹ of water (Table 2). Only the sample collected at station R. O. in May 2001 contained, in comparison to the others, very high amounts of PCBs ($\Sigma 11$ PCBs = 62 ng l⁻¹), which implied a point source of pollution. If we assume (i) the average PCB content in plankton to be the mean of all the samples studied except for R. O. in 2001, and (ii) the Szczecin Lagoon to be 4 m deep and 466 km² in area (Majewski 1980), the average PCB content (11 congeners) in phytoplankton in the Odra Estuary would be equal to c. 13 kg in 2001–2002, which is quite a considerable amount as compared to the estimated annual load carried by the Odra to the Baltic (Kowalewska et al. 2003).

Unlike the sediments (Konat & Kowalewska 2001), the phytoplankton samples contained the smallest percentage of trichlorobiphenyls, while the congeners of average and high molecular mass (101, 153, 138, 180 and 194) made up the majority in Σ 11 PCBs. This may have been due to the fact that the heavier PCBs are more easily sorbed by phytoplankton cells than the lighter congeners. This is in agreement with the results of laboratory experiments with three phytoplankton species (Stange & Swackhamer 1994). In these laboratory experiments, Anabaena sp. displayed a lower affinity for the sum of PCBs than the other algae species tested (Seleneastrum capricornutum – green algae and Synedra sp. - diatoms), but there were also differences in the sorption of individual congeners by the various species studied. This was explained by the authors either by a different algal cellular membrane permeability or a greater affinity of the heavier congeners for dissolved organic carbon. Significant differences in the sensitivity of individual algae species to PCBs

\mathbf{PCBs}
in
phytoplankton
in
the
Odra
Estuary

Station	Date						I	PCB					
	of sampling	18	31	28	52	101	149	118	153	138	180	194	$\Sigma 11$ PCBs
38	June 2002	< 0.07	< 0.09	< 0.08	0.54	0.37	0.22	0.05	0.60	0.64	1.24	1.34	5.00
J. W. 2	June 2002	0.01	< 0.09	0.06	0.64	0.73	0.52	0.15	1.31	1.36	2.74	1.84	9.36
J. W. 1	May 2001	0.41	< 0.85	< 0.8	_	0.76	< 0.77	< 0.78	0.37	2.86	0.37	< 0.09	4.77
J. W. 1	June 2002	< 0.07	< 0.09	0.13	0.67	0.63	0.45	0.08	0.88	0.99	1.76	1.52	7.10
15	May 2001	0.29	< 0.49	0.22	1.67	1.56	0.44	< 0.45	2.03	1.25	0.35	< 0.09	7.81
15	June 2002	< 0.09	< 0.12	< 0.1	0.63	0.67	0.71	0.09	1.23	1.57	3.20	2.17	10.27
18	June 2002	0.11	< 0.09	0.17	1.16	0.75	0.73	0.17	1.52	1.60	3.44	2.32	11.97
Μ	May 2001	0.37	< 0.32	< 0.3	0.09	0.76	< 0.29	< 0.29	0.10	0.37	< 0.19	< 0.06	1.69
Μ	June 2002	0.07	< 0.12	0.23	1.06	0.52	0.35	0.09	0.83	0.91	1.39	1.85	7.30
L	May 2001	0.11	< 0.32	< 0.3	0.99	1.44	0.53	< 0.29	1.22	1.19	0.75	0.01	6.23
L	June 2002	0.29	< 0.09	0.31	1.32	0.74	0.47	0.10	0.93	0.92	1.61	1.50	8.20
Κ	May 2001	0.11	< 0.32	0.45	0.24	0.94	0.17	< 0.29	0.72	1.09	1.12	0.01	4.83
Κ	June 2002	0.07	< 0.09	0.08	1.13	0.55	0.41	0.11	0.91	0.99	1.83	1.57	7.65
R. O.	May 2001	< 0.32	< 0.32	0.31	1.45	5.63	9.77	0.02	12.18	13.58	18.97	0.13	62.04
R. O.	June 2002	0.21	< 0.09	0.18	1.19	0.47	0.42	0.09	0.95	0.97	1.84	1.46	7.78

Table 2. PCB concentrations in phytoplankton [ng l^{-1}]

have been reported from laboratory experiments for many years (e.g. Moore & Harris 1972). In the marine environment Schulz-Bull et al. (1998) found that in suspended particulate matter (SPM) from the North Sea the heavier PCBs (52, 101, 118, 138, 149, 153, 180) prevailed, which dominate in technical PCB mixtures.

Considering the two sets of samples collected in the Odra Estuary, the PCB congeners of the average chlorine content (PCB 101–138) were more abundant in the samples collected in 2001. In the samples collected in 2002, there was an increase in the heaviest congeners (180, 194), the percentage of which in $\Sigma 11$ PCBs was the highest (up to 50%). This may have been due either to different sorption mechanisms and/or to the extinction of a PCB point source, or the effects of the 1997 flood, which washed primarily the light congeners out of the Lagoon . The first series of samples contained higher amounts of undecomposed chlorophylls than the second series, which proves that the former was collected in a bloom maximum.

The correlation of individual PCB with $\Sigma 11$ PCB contents is shown in Table 3. Only PCB 18 does not correlate with $\Sigma 11$ PCBs contents; the highest values of correlation coefficients with $\Sigma 11$ PCB were observed for hexachlorobiphenyls, i.e. PCB 138, 149 and 153 (r > 0.9). There is a distinct difference between correlation coefficients with individual congeners (Table 3). The lower weight congener contents correlate well with those of lower molecular weight PCB contents and similarly, the heavier congener contents correlate only with those of average and high molecular mass PCB contents. This is the evidence for different sources or, what is more probable, for a different sorption mechanism for the lighter and heavier compounds.

Schulz-Bull et al. (1998) found a correlation between the PCB content in suspension and particulate organic carbon concentration. In the present work, the correlation coefficients of PCB and phytoplankton pigment contents were determined, and the latter, as was shown earlier, correlate with the organic carbon content in sediments (Kowalewska 1997). When all the samples are taken into account, there is no correlation between PCB and pigment contents in the samples studied. So the taxonomic analysis was performed on the samples collected in 2002. Examination of species has shown that the samples can be classified into two groups: one with a dominance of diatoms – the samples from stations 18, M, K, L and R.O. and another in which cyanobacteria are prevalent – the samples from stations 38, J.W.2., J.W.1, and 15. As can be seen in Tables 4 and 5, the PCB and pigment contents in these two sets of samples correlate quite differently. In the case where diatoms predominated, there was no significant correlation between

	PCB									$\Sigma 11$		
	18	31	28	52	101	149	118	153	138	180	194	PCBs
PCB18	_	_	0.72	0.63	-0.14	-0.03	-0.23	-0.23	-0.27	-0.28	-0.25	-0.01
PCB31	_	_	_	_	_	_	_	_	_	_	_	
$\operatorname{PCB}28$	_	_	_	0.79^{*}	0.17	0.06	0.13	-0.03	-0.16	-0.27	-0.05	0.18
$\rm PCB52$	_	_	_	_	0.22	0.23	0.43	0.2	0.05	-0.03	0.06	0.4
PCB101	_	_	-	_	_	0.85^{*}	0.8^{*}	0.82^{*}	0.77	0.7	0.63	0.83^{*}
PCB149	_	_	-	_	_	_	0.79^{*}	0.94^{**}	0.95^{**}	0.91^{**}	0.79^{*}	0.96**
PCB 118	_	_	_	_	_	_	_	0.91^{**}	0.8^{*}	0.76	0.7	0.89^{**}
$\rm PCB153$	_	_	_	_	_	_	_	_	0.97^{**}	0.95^{**}	0.83^{*}	0.96^{**}
$\rm PCB138$	_	_	_	_	_	_	_	_	_	0.97^{**}	0.89**	0.93^{**}
PCB180	_	_	_	_	_	_	_	_	_	_	0.83^{*}	0.88**
PCB 194	_	_	_	_	_	_	_	_	_	_	_	0.83^{*}

 Table 3. Correlation coefficients between ln of PCB contents

* p \leq 0.01; ** p \leq 0.001 – significance level.

 $\Sigma 11 \text{ PCBs}$ and pigment contents. Only for chlorophyll a' and PCB contents was the correlation coefficient high, though negative, (equal to -0.63). There was a high, positive correlation between PCB of low and average molecular mass and chlorophyll c contents (r = 0.66 - 0.90), pigments characteristic of diatoms (Table 4). There was no correlation between PCB and the markers of zooplankton grazing (phaeophorbides and pyrophaeophytin a, occurring e.g. in faecal pellets).

Table 4. Correlation coefficients between ln of PCB and pigment contents in the phytoplankton dominated by diatoms

V^*	chl \boldsymbol{a}	chl a^\prime	phe o \boldsymbol{a}	pyro \boldsymbol{a}	phrbs	chls c	β -car	$\Sigma{\rm chlns}~a$
PCB 18	-0.52	-0.47	-0.04	0.24	0.44	0.79	-0.43	-0.06
PCB31	_	_	_	_	_	_	_	_
$\operatorname{PCB}28$	-0.58	0.1	0.7	-0.46	-0.43	0.69	0.21	0.72
$\operatorname{PCB}52$	-0.73	-0.76	-0.02	0.08	0.44	0.9**	-0.65	-0.24
$\operatorname{PCB}101$	-0.91^{**}	-0.73	0.59	-0.69	-0.32	0.66	-0.24	0.04
$\operatorname{PCB}149$	-0.47	-0.74	0.26	-0.32	-0.07	0.26	0.01	-0.06
PCB 118	-0.36	-0.61	0.32	-0.46	-0.26	0.03	0.13	-0.05
$\operatorname{PCB}153$	-0.29	-0.59	0.25	-0.31	-0.15	0.06	0.2	0.02
$\operatorname{PCB}138$	-0.17	-0.48	0.25	-0.34	-0.23	-0.11	0.29	0.03
PCB 180	-0.17	-0.6	0.09	-0.17	-0.02	-0.06	0.14	-0.13
$\operatorname{PCB}194$	-0.14	-0.04	0.64	-0.7	-0.72	-0.24	0.64	0.44
$\Sigma PCB 11$	-0.45	-0.63	0.38	-0.42	-0.22	0.21	0.15	0.08

* V – chl *a* – chlorophyll *a*; chl *a'* – chlorophyll *a'*; pheo *a* – phaeophytin *a*; pyro *a* – pyrophaeophytin *a*; phrbs – phaeophorbides; chls *c* – chlorophylls *c*; β -car – β -carotene; Σ chlns *a* – sum of chlorins *a* (chlorophyll *a* and its derivatives).

** p ≤ 0.02 – significance level.

For the samples with dominance of cyanobacteria, as opposed to the diatom-dominated samples, there was first of all a high, positive correlation between $\Sigma 11$ PCBs and chlorophyll *a* and chlorophyll *a'* contents. There was also a high, correlation with other chlorin and β -carotene contents, though it was lower than that with the chlorophyll *a* content. The correlation between chlorophylls *c* and PCB contents was high as well, though negative, for both $\Sigma 11$ PCBs and individual PCBs, with the exception of PCB 18 and 28. The correlation of chlorophylls *c* content coefficients with these two congener contents were 0.64 and 0.79, respectively. This means that these two congeners were sorbed principally by diatoms (also present in the samples), and the heavier PCBs (52–194) were sorbed

\mathbf{V}^*	chl a	chl a'	pheo a	pyro a	phrbs	chl s \boldsymbol{c}	β -car	$\Sigma{\rm chlns}~a$
PCB18	0.05	-0.52	-0.55	-0.21	-0.74	0.64	-0.65	-0.48
PCB31	—	_	_	_	_	_	_	_
PCB28	-0.08	-0.38	0.36	0.38	0.01	0.79	0.1	0.3
$\rm PCB52$	0.54	0.61	0.92^{**}	0.98**	0.86	-0.17	0.91^{**}	0.98**
$\operatorname{PCB}101$	0.71	0.88	0.83	0.93^{**}	0.88	-0.57	0.95^{**}	0.94**
$\operatorname{PCB}149$	0.92^{**}	0.92^{**}	0.58	0.89	0.63	-0.62	0.77	0.77
PCB 118	0.48	0.86	0.8	0.72	0.92^{**}	-0.72	0.94^{**}	0.84
$\operatorname{PCB}153$	0.77	0.99***	0.64	0.78	0.76	-0.81	0.85	0.78
$\operatorname{PCB}138$	0.9**	0.98**	0.53	0.8	0.64	-0.77	0.76	0.72
PCB 180	0.89	0.99***	0.45	0.72	0.58	-0.84	0.71	0.65
$\operatorname{PCB}194$	0.94^{**}	0.96**	0.3	0.65	0.43	-0.82	0.58	0.52
$\Sigma PCB 11$	0.87^{*}	0.98**	0.57	0.82	0.67	-0.76	0.79	0.75

Table 5. Correlation coefficient between ln of PCB and pigment contents in phytoplankton dominated by cyanobacteria

*V – chl *a* – chlorophyll *a*; chl *a'* – chlorophyll *a'*; pheo *a* – phaeophytin *a*; pyro *a* – pyrophaeophytin *a*; phrbs – phaeophorbides; chls *c* – chlorophylls *c*; β -car – β -carotene; Σ chlns *a* – sum of chlorins *a* (chlorophyll *a* and its derivatives).

** p ≤ 0.05 ; *** p ≤ 0.001 – significance level.

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PCB	$\begin{array}{c} Temperature \\ t \\ [^{\circ}C] \end{array}$	Turbidity T [NTU]	Salinity S [PSU]	$\begin{array}{c} Oxygen \\ O_2 \\ [\%] \end{array}$	$\begin{array}{c} {\rm Redox\ potential} \\ {\rm E_h} \\ [mV] \end{array}$
PCB18	0.53	0.29	-0.47	0.24	-0.41
PCB31	_	_	_	_	_
PCB28	0.71	-0.79	-0.66	0.65	-0.88^{*}
$\rm PCB52$	0.97^{**}	0.8	-0.98^{**}	0.14	-0.5
$\rm PCB101$	0.61	0.6	-0.66	0.57	-0.71
$\operatorname{PCB}149$	0.74	0.72	-0.75	0.29	-0.52
PCB 118	0.7	0.73	-0.74	0.28	-0.49
$\rm PCB153$	0.65	0.7	-0.66	0.28	-0.47
$\operatorname{PCB}138$	0.61	0.7	-0.63	0.24	-0.43
$\operatorname{PCB}180$	0.44	0.49	-0.46	0.15	-0.27
$\operatorname{PCB}194$	0.38	0.71	-0.4	0.48	-0.57
$\Sigma11~\rm PCB$	0.75	0.77	-0.76	0.34	-0.57

 Table 6. Correlation coefficients between ln of PCB contents and parameters characterising the environment

* p ≤ 0.02 ; ** p ≤ 0.001 – significance level.

mainly by cyanobacteria, but also by the phytoplankton detritus and products of zooplankton grazing. Interestingly, the correlation of PCB and phaeophorbide contents was not so significant. The highest correlation was that of PCB with chlorophyll *a* and the chlorophyll *a* early diagenesis product contents, which implies that sorption by phytoplankton cells is the primary stage in the process of removing PCBs from the water column and digestion by zooplankton is the secondary mechanism. Knickmeyer & Steinhart (1989) reported that in two species of copepods from the northern North Sea, *Calanus finmarchicus* and *Temora longicornis*, the patterns of PCB congeners are dominated by low chlorinated congeners. These also confirm the above conclusions, as in the North Sea diatoms are predominant in the phytoplankton biomass.

The correlation coefficients between PCB contents and the parameters characterising the environment under investigation, i.e. temperature, turbidity, salinity, redox potential and oxygen in water, are shown in Table 6. There was a negative correlation between $\Sigma 11$ PCBs and almost all the individual congener contents with salinity and redox potential (E_h) values in the water column. For temperature and turbidity this correlation was significant and positive, but there was no correlation for oxygen values in the water column and both $\Sigma 11$ PCB and the majority

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of individual congener contents. The correlations with the salinities in the water column confirm the previous conclusion for sediments (Konat & Kowalewska 2001) that the river water is the PCB source for the basin. The high correlation coefficients for PCB contents with temperature values and the correlation between PCB and individual pigment contents in the plankton samples are also in agreement with previous observations for sediments. There, the correlation with the total phosphorus content in near-bottom water implied a relation between PCB geochemistry and cyanobacteria (Kowalewska et al. 2003). Their blooms occur in summer, when the temperature is high and these algae, unlike diatoms, can also grow in anoxic conditions.

4. Conclusions

- Phytoplankton plays an important role in the transfer and distribution of PCBs in the Odra Estuary. These compounds are sorbed from the water column by phytoplankton or the detritus derived from it, and then, directly after the death of the cells or together with the products of zooplankton grazing, are transferred to sediments.
- The congeners of average and high molecular mass, i.e. 101, 153, 138 and 180, made up the highest percentage in the sum of PCBs sorbed by phytoplankton.
- Sorption of PCBs from the water column seems to depend strongly on the taxonomy of phytoplankton there. Lighter congeners (18, 28, 52) are sorbed mainly by diatoms and the heavier ones (101–180) by cyanobacteria and the detritus derived from both.

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