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Ott ROOTS

POLYCHLORINATED BIPHENYLS AND THEIR COMPONENTS IN THE BALTIC SEA

(Presented by U. Kirso)

Polychlorinated biphenyls (PCB) and chlororganic pesticides attract attention, first of all, due to their long-term existence in the surrounding environment and their ability to accumulate in living organisms. In our earlier work we have analyzed the concentration of PCBs and summary DDT in the Baltic water [1], plankton [1, 2], fish [1, 3], molluscs [4] and algae [5]. The coefficients characterizing the bioaccumulation of PCB and summary DDT from seawater into hydrobionts (plankton, dwarf herring) were calculated as well [6]. In 1981 the studies were commenced on PCBs sorption processes and decomposition kinetics in the Baltic Sea water. Our laboratory experiments showed that the PCBs volatilize selectively (from sea water), the components with the chlorine atoms below 5 volatilized and the process itself showed a pronounced temperature dependence [7].

Experimental

However, more than in volatile PCB components the author was interested in those which would remain for a long time in sea water (or are adsorbed on the glassware).

For determining the chlororganic substances the water samples were extracted with hexane (the solvent was distilled before the analyses). Extraction and purification methods for the PCB and chlororganic pesticides from water and biological objects samples have been worked out in our earlier works [3]. The chromatography was carried out on a Perkin-Elmer chromatograph (Model 3920B) with a detector of electron capture on a glass column of 2 m length, the inside diameter was 2 mm. Gas-chrom Q (80—100 mesh) served as a stable carrier with a stationary phase SF−96+QF−1. The temperature conditions were as follows: the temperature of the injection 220 °C, the detector 325 °C and that of the column 185 °C [2, 3].

Results and discussion

Fig. 1 presents the chromatograms for a 1095-days stored water sample (collected by the author in October 1981 from the area of the Gotland Deep, salinity 7.5‰, water temperature 20—22 °C during the experiment). Clophen A-50 as a PCB standard was added to this water sample. Proceeding from S. Jensen's work [8] it was possible to determine on the basis of retention times which PCB components had remained in sea water after 1095 days. The Table shows the international notation and structure of PCB components. From above it follows that these are mainly penta- (105, 110), hexa- (128, 138, 149, 153, 156) and hepta- (170, 180, 183) chlorobiphenyls. The PCBs detected in sea water and those adsorbed on glassware did not differ in composition (Fig. 1.).

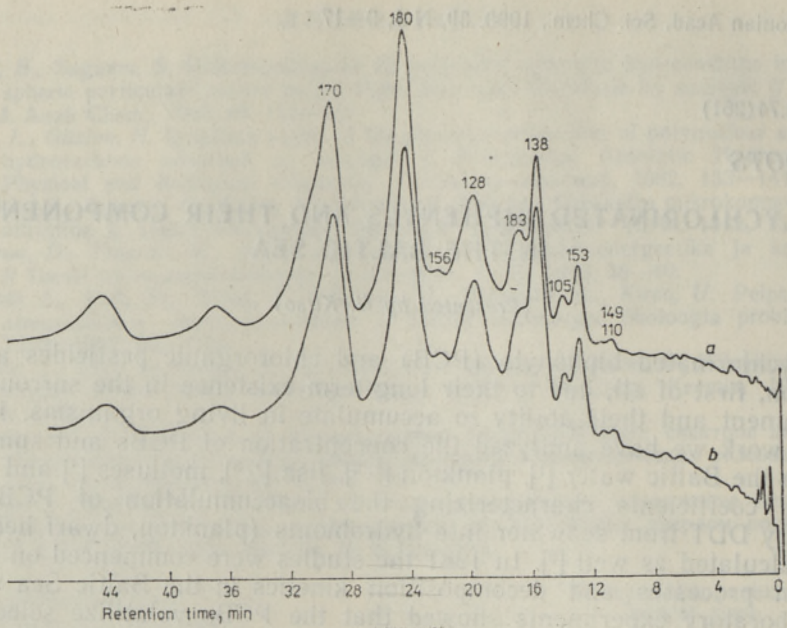

Fig. 1. PCB chromatograms of the sea water sample (*a*) and of the part adsorbed on glassware (*b*) after a 1095-days storage at 20—22 °C.

Systematic enumeration of PCB compounds [15]

N	Structure	N	Structure
	Dichlorobiphenyls		**Hexachlorobiphenyls**
15	4, 4′	128	2, 2′, 3, 3′, 4, 4′
	Trichlorobiphenyls	132	2, 2′, 3, 3′, 4, 6′
18	2, 2′, 5	138	2, 2′, 3, 4, 4′, 5′
26	2, 3′, 5	141	2, 2′, 3, 4, 5, 5′
28	2, 4, 4′	149	2, 2′, 3, 4′, 5′, 6
	Tetrachlorobiphenyls	151	2, 2′, 3, 5, 5′, 6
44	2, 2′, 3, 5′	153	2, 2′, 4, 4′, 5, 5′
49	2, 2′, 4, 5′	156	2, 3, 3′, 4, 4′, 5
52	2, 2′, 5, 5′	163	2, 3, 3′, 4′, 5, 6
	Pentachlorobiphenyls		**Heptachlorobiphenyls**
95	2, 2′, 3, 5′, 6	170	2, 2′, 3, 3′, 4, 4′, 5
101	2, 2′, 4, 5, 5′	179	2, 2′, 3, 3′, 5, 6, 6′
105	2, 3, 3′, 4, 4′	180	2, 2′, 3, 4, 4′, 5, 5′
110	2, 3, 3′, 4′, 6	183	2, 2′, 3, 4, 4′, 5′, 6
118	2, 3′, 4, 4′, 5	187	2, 2′, 3, 4′, 5, 5′, 6.

Further the author was interested in whether the so-called selection of PCBs components takes place in nature, i. e. in the Baltic Sea.

The atmosphere is an important contributor of anthropogenic matter to the marine ecosystem. Only a few authors [9] have analyzed the concentration of PCB simultaneously in the atmosphere above the Baltic Sea and in dry particle and wet deposition. Above the Baltic Sea the concentration of PCB proved higher with the southwesters (this endangers the islands of Hiiumaa and Saaremaa since these winds are the prevailing ones on the Baltic Sea [9]). The concentration of PCBs in particulate matter depends on air temperature, the concentrations in winter are considerably higher [9].

The graph (Fig 2, 3a) shows that penta- (101, 118), hexa- (138, 153) and hepta- (170, 180) PCBs prevail in rain, with the hexachlorobiphenyls N 138 and 153 (see the table) accounting for one third of the concentration of the analyzed components (17 altogether). Let us consider which PCBs prevail in the atmosphere and particulate matter: in the atmosphere these were N 18, 44, 49, 52 and 149, supplemented by N 101, 138, 128, 149, 170, 180 in particulate matter (Fig. 3b). Unfortunately, the concentration of N 153 was measured neither in the atmosphere nor in particulate matter. Consequently, selection occurs in nature as well, and the rain contributes to the input of the same penta-, hexa- and heptaPCBs to the Baltic Sea which were detected in our water samples after their long-time storage.

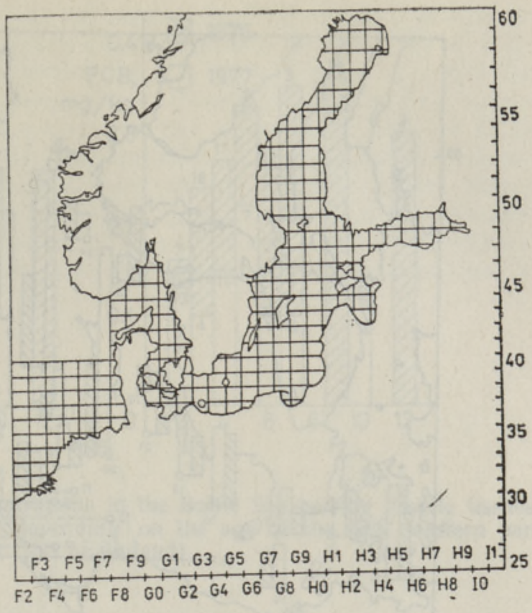

Fig. 2. Map of sampling sites [16].

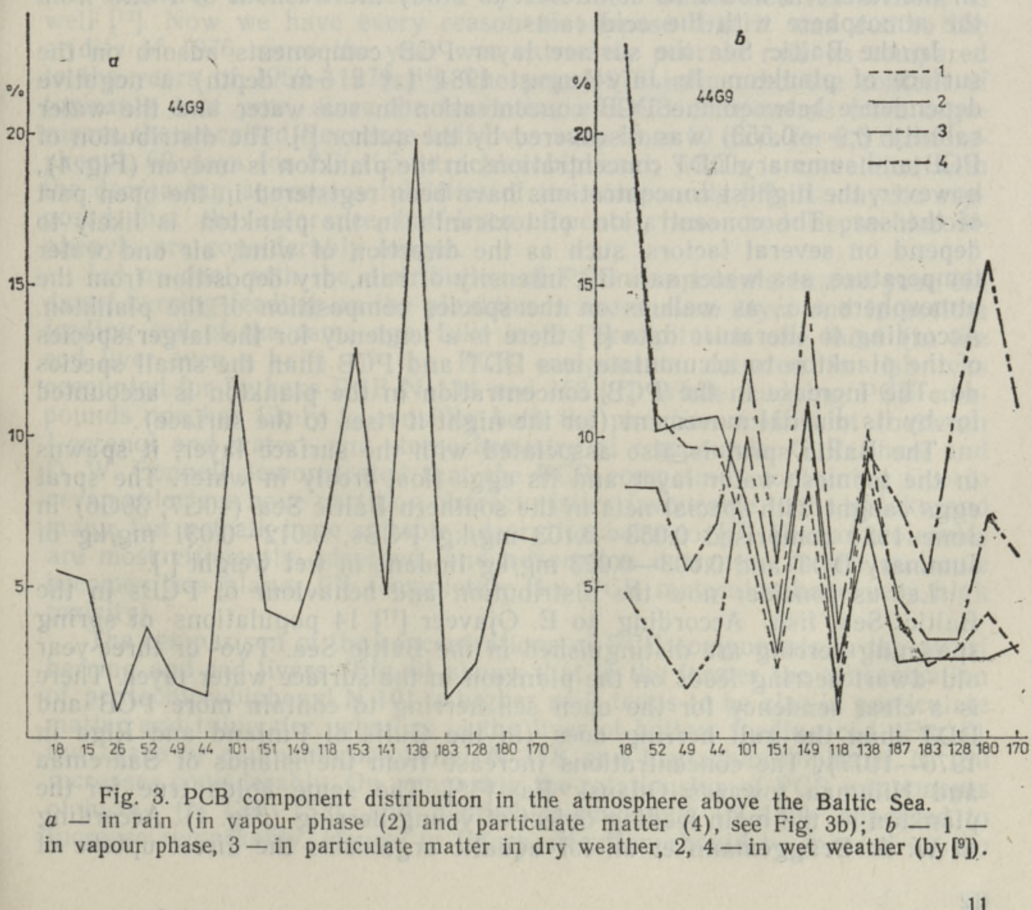

Fig. 3. PCB component distribution in the atmosphere above the Baltic Sea. *a* — in rain (in vapour phase (2) and particulate matter (4), see Fig. 3b); *b* — 1 — in vapour phase, 3 — in particulate matter in dry weather, 2, 4 — in wet weather (by [9]).

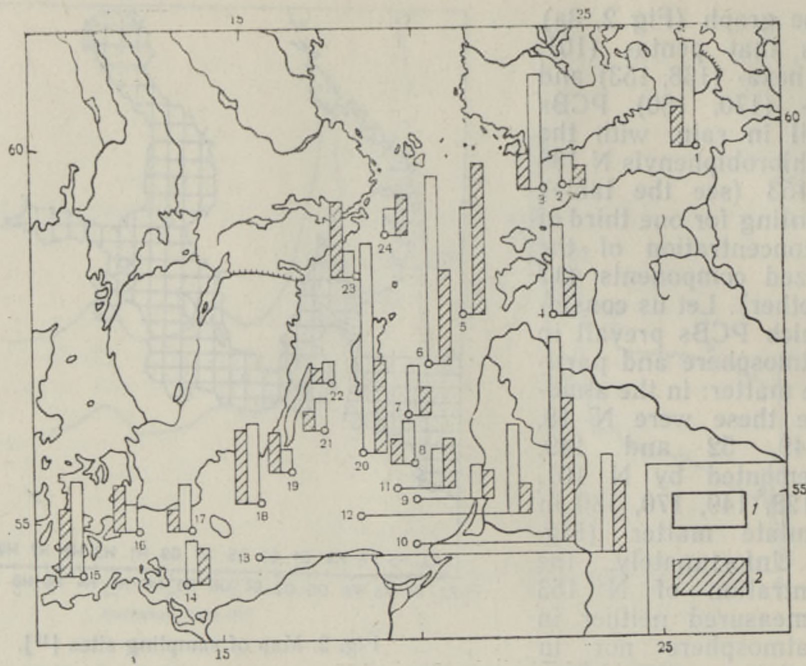

Fig. 4. PCB (*1*) and summary DDT (*2*) concentrations in the Baltic Sea plankton in September-October 1978 (1 cm corresponds to 0.1 mg/kg, wet weight) [1, 2].

In the future it would be of interest to study the washout of PCBs from the atmosphere with the acid rains.

In the Baltic Sea the surface layer PCB components adsorb on the surface of plankton. In July-August 1981 (at a 5 m depth) a negative dependence between the PCB concentration in sea water and the water salinity ($r = -0.553$) was discovered by the author [1]. The distribution of PCB and summary DDT concentrations in the plankton is uneven (Fig. 4), however, the highest concentrations have been registered in the open part of the sea. The concentration of toxicants in the plankton is likely to depend on several factors, such as the direction of wind, air and water temperature, sea water salinity, intensity of rain, dry deposition from the atmosphere etc., as well as on the species composition of the plankton. According to literature data [10] there is a tendency for the larger species of the plankton to accumulate less DDT and PCB than the small species do. The increase in the PCB concentration in the plankton is accounted for by its diurnal movement (for the night it rises to the surface).

The Baltic sprat is also associated with the surface layer, it spawns in the topmost water layer and its eggs float freely in water. The sprat eggs caught with special nets in the southern Baltic Sea (40G7; 39G6) in June 1984 comprised 0.053—0.103 mg/kg PCBs, 0.012—0.031 mg/kg of summary DDT and 0.003—0.023 mg/kg lindane in wet weight [1].

Let us consider now the distribution and behaviour of PCBs in the Baltic Sea fish. According to E. Ojaveer [11] 14 populations of spring spawning herring are distinguished in the Baltic Sea. Two- or three-year old dwarf herring feeds on the plankton in the surface water layer. There is a clear tendency for the open sea herring to contain more PCB and DDT than the gulf herring does (in the Gulfs of Finland and Riga in 1976—1977). The concentrations increase from the islands of Saaremaa and Hiiumaa towards Gdansk Bay [3, 6]. The same holds true for the plankton — the main feeding object of young herring (Fig. 4). According to W. A. Brüggemann et al. for aquatic organisms the direct uptake of

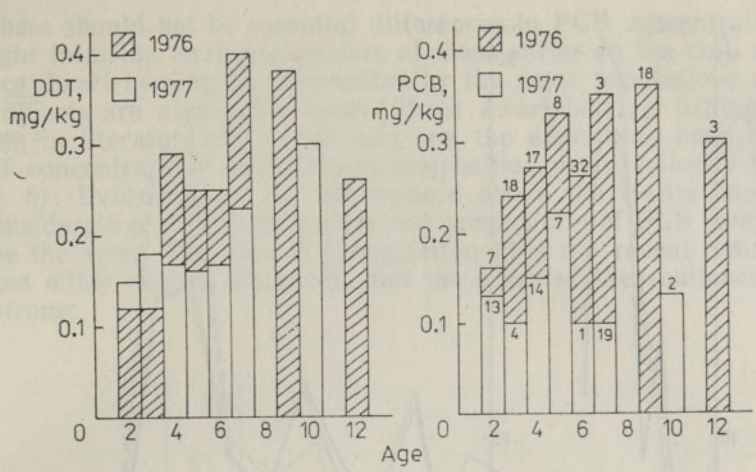

Fig. 5. PCB and summary DDT concentrations in the Baltic Sea herring muscle tissues, wet weight in spring 1976 and 1977 depending on the age of the fish (eastern part of the Gulf of Finland).

PCB from water is much more important than the bioaccumulation from food. Adsorption efficiencies from water and food are higher than 40% [12].

Rains seem to contribute to the increase in the PCB concentration in fish in autumn (the fat content increases in fish as well). So far it has proved difficult to explain why in 1977 the concentrations of PCB abruptly decreased in comparison with the year of 1976. Beside the author (Fig. 5) this tendency has been observed by the other Baltic Sea researchers as well [13]. Now we have every reason to suppose that it was due to the aridity of 1976, since the year was extremely poor in rain as compared to the years of 1969—1979 [14]. The year 1976 influenced the content of toxicants next year, since the transition of PCB components from organisms, the so-called clearance half-lives vary from 10 days for 2,5 dichlorophenyl, 60 days for 2,3′,4′,5-tetrachlorobiphenyl, which is correlated with the decreasing aqueous solubilities of the compounds [12]. It may be supposed that the clearance half-lives of penta-, hexa- and heptachlorobiphenyls are considerably longer.

Let us deal with the distribution of PCB components in two-year old dwarf herring feeding on the plankton in the surface layer and in bottom feeding cod of the same age. Like in the precipitation one third (in the cod liver even a half) of the PCB components detected in fish was accounted for by hexa-PCB N 138 and 153 [16]. While studying PCB compounds one has likely to consider both the partition coefficient (between 1-octanol and water) and stereochemistry of compounds. G. R. Shaw and D. W. Connell demonstrated that the PCB compounds containing five to seven chlorines have partition characteristics favourable to the uptake, and many, but not all, have suitable adsorption behavior [17]. Planar molecules are most efficiently adsorbed, and adsorption decreases as the molecule becomes less planar [17] (completely flat PCB molecules have very high toxicity).

The comparison of the concentrations of PCB components in the dwarf herring and cod livers (Fig. 6) shows that in the former the concentration of pentachlorobiphenyl N 101 is higher as it tends to be also in particulate matter and rainwater, whereas in the liver of bottom feeding cod (Fig. 7) the share of pentachlorobiphenyl N 118 and heptachlorobiphenyl N 180 increases considerably. On comparing the relationship of PCB components of hexa- (N 138, 153) and heptachlorobiphenyls (N 180) appeared to increase remarkably. Hence, in future attention should be focused on the

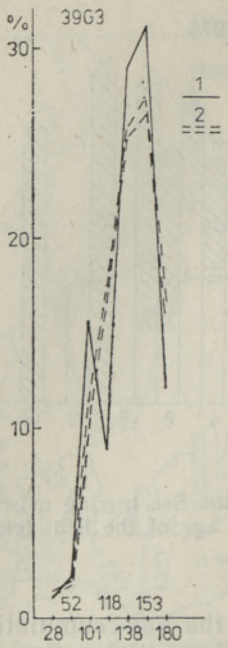

Fig. 6.

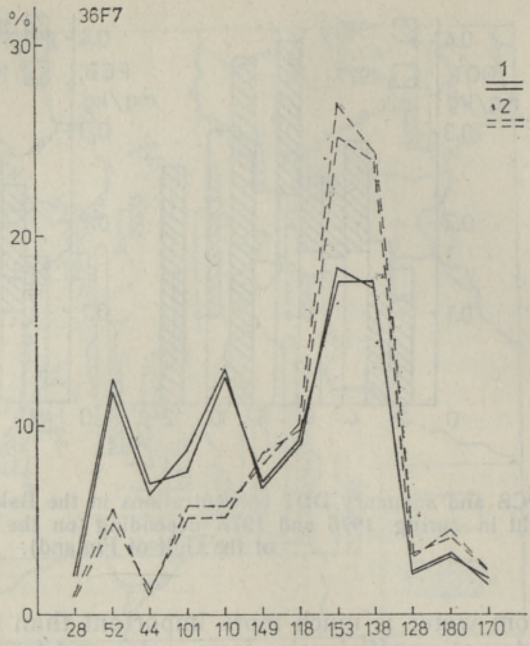

Fig. 7.

Fig. 6. PCB components distribution in the herring (*1*) and cod (*2*) liver (with the results of the parallel analyses) [16].

Fig. 7. PCB components distribution in the cod muscle tissue (*1*) and liver (*2*) (with the results of the parallel analyses) [16].

concentrations of PCB and DDT in the fish liver, where e. g. in the case of cod, the concentrations of chlororganic compounds are 80—100 times higher [16]. Clearance half-lives of PCB components with the greater number of chlorine atoms should be also studied. Of urgent necessity is the elucidation of the PCB components, most dangerous for man. In one of his earlier works the author has stated that fish serve as the main link through which PCB and DDT enter human organism in the Baltic Sea countries [18]. The PCB and DDT concentrations detected in the organisms of women in Finland and Estonia did not reveal remarkable differences.

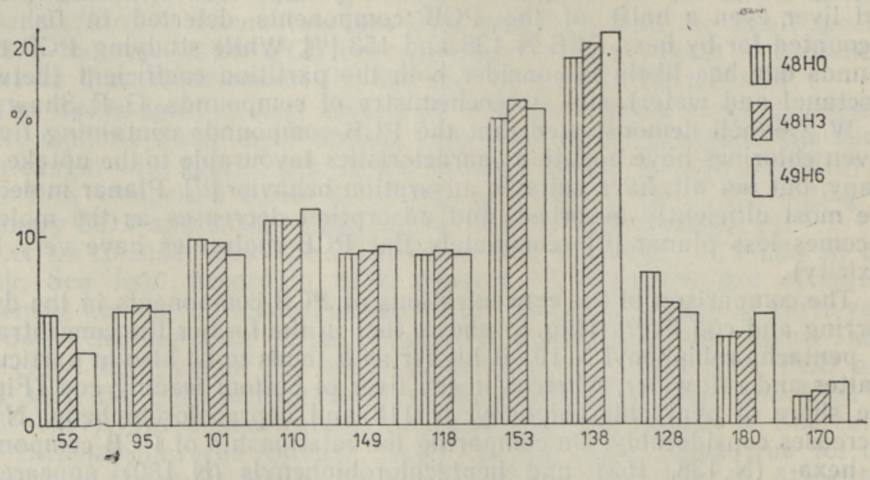

Fig. 8. PCB components distribution in the dwarf herring muscle tissue in three regions[16].

Hence, there should not be essential differences in PCB concentrations in fish caught from the territorial waters of these states on the Gulf of Finland since dwarf herring is represented by the same populations and its feeding objects are almost the same. Three dwarf herring fishing areas are shown in literature [19]. As we can see, the differences both in PCB and DDT concentrations and isomers composition are practically lacking [19] (Fig. 8). Evidently, in the atmosphere above the Baltic Sea areas under consideration the concentration and composition of PCB compounds should be the same. The annual precipitation does not reveal remarkable differences either (small distance), and the effect of the southwesters is not so strong.

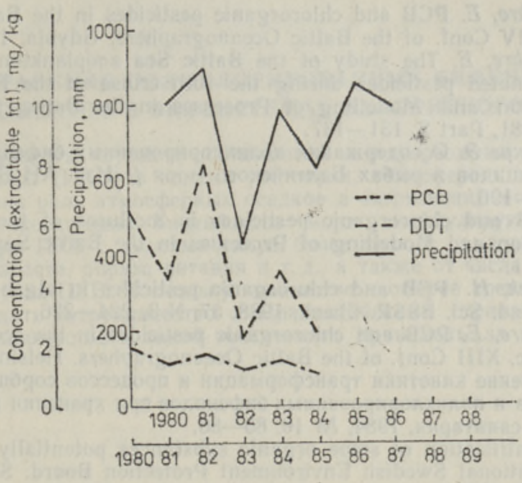

Fig. 9. Annual precipitation in the Baltic Sea (station 39HO) and the average PCB concentrations in the cod liver station (48H3) [19, 20].

The effect of precipitation on PCB concentration in the cod liver in the western Gulf of Finland is well observable in Fig. 9. The data on annual precipitation by years are based on long-term observations at the Preila station in the central part of the Baltic Sea [20]. The figure shows the potential dependence of PCB concentration in the cod liver upon the amount of the previous year precipitation.

Conclusions

1. More attention should be paid to the input of PCB components to the Baltic Sea from the atmosphere (both wet and dry deposition), especially at low temperatures and with southwestern winds. Studies should be performed on acid rains and their effect on the washout of compounds from the atmosphere. The usage of data on the relationship of PCB concentration together with meteorological parameters will contribute to the better knowledge of the direction and origin of the air masses above the Baltic Sea (this is of great importance in view of the protection of the islands of Hiiumaa and Saaremaa).

2. Since the PCB components used for determining the PCB concentrations differ with authors, it is of urgent necessity to agree which PCB components should serve as the standard to make the results comparable.

3. While studying fish, in addition to the muscle tissue livers should be analysed. Beside two-year-old dwarf herring feeding on the plankton

on the surface layer and bottom feeding cod of the same age observations should also be performed on older herring, over five years in age, which has passed to the feeding in the nearbottom layer. The author is of the opinion that the studies on the relationship of PCB components in fish may contribute to a new trend of investigation of fish feeding and migration. In the Baltic Sea countries dwarf herring (14 populations in all) should serve as the study object.

4. In future attention is to be focused on the open part of the sea in the area of Gdansk Bay.

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POLÜKLOREERITUD BIFENÜÜLIDE ISOMEERIDE OMAVAHELISTEST SUHETEST LÄÄNEMERES

On uuritud polüklooreeritud bifenüülide (PCB) omavahelisi suhteid vesilahustes, atmosfääris ja Läänemere ökosüsteemis ning näidatud, et peamiselt satub PCB Läänemerre atmosfääri kaudu. On välja toodud, missuguses seoses on PCB sisaldus tursas ning eelneva aasta sademete hulk. Kalade organismi kogunevad PCB isomeerid kloori aatomite arvuga üle viie. PCB isomeeride akumuleerumine bioloogilistesse objektidesse (kaladesse) oleneb viimaste toitumisviisist (kas pinna- või põhjatoiduline), vanusest ja muust.

Edaspidi oleks otstarbekohane valida PCB isomeeride hulgast need, mille peaksid kõik Läänemereriigid võtma määramise aluseks. Valik peaks toimuma isomeeride toksilisuse alusel.

Отт РООТС

РАСПРОСТРАНЕНИЕ ПОЛИХЛОРИРОВАННЫХ БИФЕНИЛОВ И ИХ КОМПОНЕНТОВ В ЭКОСИСТЕМАХ БАЛТИЙСКОГО МОРЯ

Приведены результаты изучения соотношений между разными изомерами полихлорированных бифенилов (ПХБ) в водных растворах, атмосфере и экосистемах Балтийского моря. Показана роль атмосферных осадков в загрязнении моря изомерами ПХБ. Установлено, что в экосистемах Балтийского моря аккумулируются и долгое время сохраняются изомеры ПХБ с атомами хлора более пяти, а сама аккумуляция зависит от вида рыб, их возраста, образа питания и т. д., а также от числа атомов хлора и их положения в молекулах ПХБ. Поскольку количество изомеров превышает 200, признано необходимым наладить сотрудничество с Прибалтийскими странами и решить, какие изомеры, в каком количестве и какой токсичности принимать за основу при анализе ПХБ.