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POLYNUCLEAR AROMATIC HYDROCARBONS IN ESTONIAN COASTAL WATERS

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Abstract. Benzo(*a*)pyrene (BaP) and other polycyclic aromatic hydrocarbons (PAH) were determined (1975—1987) in water, bottom sediments, and water organisms of several bays of Estonian coastal waters of the Baltic Sea. Bottom sediments and the biota were found to accumulate PAH. In the muscular tissue and various organs of different fish species BaP was present in average concentrations from 10 ng to 3 $\mu g \cdot kg^{-1}$ wet weight. Estimations indicate that an inhabitant of Estonia ingests yearly about 70 μg and during the lifetime over 4.9 mg BaP. A previously elaborated and proposed monitoring system for the PAH surveillance should be implemented.

Key words: benzo(*a*)pyrene, PAH, water, sediments, water organisms.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAH) are widespread environmental pollutants, many of them are carcinogenic, some are known as promoters, others as initiators (IARC..., 1983). Numerous data on the levels of benzo(*a*)pyrene (BaP) and other PAH in various bodies of water have been published (Borneff & Kunte, 1963; Andelmann & Suess, 1970; Шабад, 1973; Suess, 1976; et al.). The main sources of PAH in water are industrial sewage and other emissions as well as automobile exhaust gases. The content of BaP in waste waters of the Estonian oil shale industry fluctuates from 1.5—5 near the Kiviõli plant and up to 15—160 $\mu g \cdot l^{-1}$ at Kohtla-Järve (Veldre et al., 1979).

The Institute of Experimental and Clinical Medicine has in cooperation with the Institute of Chemistry of the Estonian Academy of Sciences studied the pollution of various inland bodies of water in Estonia and Estonian coastal waters of the Baltic Sea with carcinogenic PAH and especially BaP for about twenty years to recommend measures to prevent or reduce the pollution of water bodies in Estonia.

This article presents data on the concentrations of BaP and other four- to six-ring PAH in water, bottom sediments, and various water organisms, such as aquatic plants, zooplankton, and fish, in some bays of the Baltic Sea, among them in those used for recreation, i. e. Kloogarand (Lahepere Bay), Vääna-Jõesuu, Pirita, Narva-Jõesuu, Pärnu, Matsalu, and others.

MATERIAL AND METHODS

About 2000 samples of seawater, 400 of bottom sediments, and 2100 of various biota, among them 1200 fish from 15 locations of the Baltic Sea have been analysed. Most of the sampling was made at least once per season in the following years: 1975, 1976, 1979, 1980, 1981, 1982, 1984, 1987. The methods used for taking samples of water, sediments, plants, and fish are described in our previous papers (Bogovski et al., 1982; Veldre et al., 1982). The samples were analysed using spectroluminescence measurement of quasilinear spectra at 70 K (Khesina, 1979). The HPLC analysis of PAH has been described by Kirso et al. (1981).

RESULTS

Data on the BaP concentrations in water from the most frequented recreation areas of the Estonian coast of the Gulf of Finland are presented in Table 1.

Table 1

BaP in the water of some recreation areas of the Baltic Sea

Station	No of samples	Concentration of BaP, $ng \cdot l^{-1}$
Vääna-Jõesuu	44	5.1±2.32
Lahepere I	43	4.2±1.49
Lahepere II	89	2.3±0.61
Pirita I	42	3.6±1.44
Pirita II	82	2.7±1.12
Pärnu	163	4.9±0.61

As can be seen the mean values for BaP are below the threshold value adopted by the Chief Sanitary Inspectorate of the USSR on October 24, 1983, for water ($5\ ng \cdot l^{-1}$), the only exception being Vääna-Jõesuu Bay, where the BaP content reaches the limit. This fact is difficult to explain as in the area no industry is situated whereas in Pirita Bay, which is in the vicinity of Tallinn, the highly industrialized capital of Estonia, the BaP concentrations are about the same.

The concentrations of BaP in different years do not demonstrate any consistent trends, in some bays (Pirita and Lahepere) a decrease can be observed, in others (Vääna-Jõesuu and Matsalu) the concentrations have increased (Table 2).

Table 2

Average BaP concentration ($ng \cdot l^{-1}$) in the water of some bays in different years

Bays	Years							
	1975	1976	1979	1980	1981	1982	1983	1987
Pirita	3.1	0.9	0.5	—	0.3	—	—	—
Vääna-Jõesuu	5.4	0.5	—	—	7.5	20.1	—	—
Lahepere	4.1	4.3	0.2	—	1.5	0.6	0.7	—
Matsalu	—	—	—	0.7	0.2	—	—	1.0

— no samples taken.

The comparison of the BaP levels in various seasons shows that it is lower in summer and higher in winter (Table 3). This can be explained by the fact that the natural purification processes are slow at low temperatures under ice. The content of BaP in Pirita, Tallinn, and Pärnu bays was higher in summer apparently due to supplementary pollution by motorboats and ships.

Table 3

Seasonal variations of BaP in the water of some bays of the Baltic sea (average BaP content, ng · l^{-1})

Bays	Spring	Summer	Autumn	Winter
Pirita	9.1±2.6	11.0±3.7	0.2±0.08	2.3±0.45
Lahepere	9.2±0.35	3.5±0.41	0.04±0.02	8.1±0.26
Vääna-Jõesuu	1.6±0.41	1.1±0.36	0.04±0.01	23.5±8.1
Pärnu	0.7±0.12	2.3±0.70	1.2±0.41	1.0±0.33
Tallinn	2.7±0.5	8.3±1.23	0.1±0.012	2.3±0.09
Narva-Jõesuu	1.3±0.14	0.2±0.03	0.4±0.02	0.5±0.14
Matsalu	1.3±0.32	0.7±0.1	0.4±0.12	—

— no samples taken

Though the BaP levels in water are relatively low the compound accumulates in bottom sediments and marine organisms. The sediments contain up to 10^4—10^6 times more BaP than the water samples of the bay taken simultaneously (Table 4). We studied eight species of algae and took about 200 samples from May till October. The question whether algae contain BaP was raised in connection with the use of some species for producing Estagar, a product used as agar in marmalade, jellies, and ice-cream. At present *Furcellaria* spp. are used, but apparently it will be necessary to use other species of algae in the future as the yields of *Furcellaria* are decreasing.

Table 4

BaP in the water and bottom sediments of some bays

Bay	Average BaP concentration in	
	water, ng·l^{-1}	sediments, ng · kg^{-1}
Lahepere	4.2	1400±330
Vääna-Jõesuu	5.1	980±330
Pirita I	3.6	4720±2160
Pärnu	4.9	23580±1800

Table 5

PAH (ng · l^{-1}) in water and bottom sediments (Lahepere Bay)

PAH	In water	In sediments
Pyrene	35	16000
Benz(*a*)anthracene	0	13000
Chrysene	13	28000
Benzo(*e*)pyrene	15	7900
Benz(*b*)fluoranthene	0	16500
Benz(*k*)fluoranthene	1	4300
Benzo(*a*)pyrene	22	16500
Benz(*ghi*)perylene	0	9300
Dibenz(*a,h*)anthracene	0	2500

Figs. 1 and 2 present data on the content of BaP in four common species of algae from coastal waters of Estonia. Because of low water salinity the red alga *Furcellaria lumbricalis* (Huds.) Lamour. is not observed east of Kunda, while *Fucus vesiculosus* L. is found as far as at Mahu (western part of Narva Bay). Green algae of the species *Cladophora glomerata* (L.) Kütz. and *Enteromorpha intestinalis* L. occur also in the eastern part of the Gulf of Finland. As shown in Fig. 1, the lowest levels of BaP were found in *Furcellaria*, while in *Fucus* they were higher. This is likely due to the fact that *Fucus* grows in shallow waters (about 0.5—8 m) and hence closer to the polluted surface water than *Furcellaria* (5—15 m) (Veldre et al., 1984). The BaP concentration is considerably higher in *Cladophora glomerata* and *Enteromorpha intestinalis* because these algae grow in shallow coastal waters that are usually more heavily polluted by oil. The concentration of BaP in algae depends on the pollution of the water of the corresponding bay but apparently also on the intensity at which diverse species accumulate BaP. Fig. 1 demonstrates the difference of BaP accumulation by *Fucus* and *Furcellaria* collected at the same stations.

The determination of other PAH showed that they accumulate in the sediments in a similar proportion as BaP (Tables 4 and 5).

Fig. 3 demonstrates the percentage share of the analysed PAH in seawater, Fig. 4 in sediments, and Fig. 5 in algae. BaP was determined in zooplankton, which is an important fish food. The average concentration was 2.41 $\mu g \cdot kg^{-1}$ (min.—0.26, max.—21.00 $\mu g \cdot kg^{-1}$).

One of our goals was to study the BaP content in fish to find out how much BaP can be ingested by an average fish-consuming Estonian. BaP was determined in various organs and tissues of diverse species of fish belonging to five different groups (Table 6). As the salinity of our seawater is low, there are many fish species, especially in estuaries, which live practically in freshwater.

The average BaP content is very close in three groups, but the migratory fish contain notably more BaP. We are inclined to explain this by the fact that the analysed migratory fish contained more fat than the fish of the other groups.

Our previous investigations have established (Велдре et al., 1985) that the BaP concentration in water organisms corresponds to its content in water.

It has been also observed that in more heavily polluted waters more lymphosarcomas are found in pikes (Bogovski, 1988). A source of water pollution with PAH are wrecks of oil tankers. After such an accident in 1981 near the west coast of the Estonian islands numerous dead fish were found and the muscular tissue of these fish contained considerably more BaP than the fish caught from this area earlier. A long-time study of the BaP content in the fillets of the Baltic herring (Велдре et al., 1985) caught in the Gulf of Finland revealed a decreasing trend of BaP concentrations from 1976—1977 to 1983 (Fig. 6). The results of our analyses of various fish organs do not show significant differences in the BaP levels in the liver, kidneys, gills, roe, milt, intestinal fat, and muscular tissue and no correlation was revealed between the age (weight) of the fish and the contents of BaP (Veldre et al., 1979, 1982). According to our findings the average BaP concentration in various species of fish was 10 ng to 3 $\mu g \cdot kg^{-1}$ (wet weight); it does not depend, as shown in our earlier studies (Велдре et al., 1985, 1986), on the weight, i. e. age of fish. The population of Estonia consumes per person about 25 kg of fish per year over 80% of which is caught in the Baltic Sea. So an inhabitant of Estonia ingests about 70 μg BaP yearly and during lifetime (70 years) up to 4900 μg or about 4.9 mg.

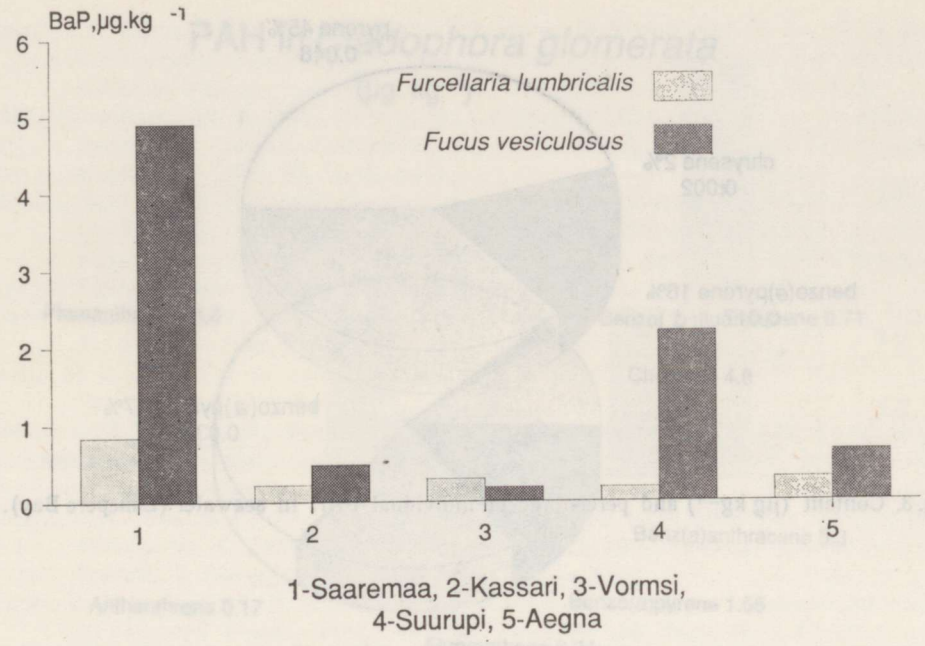


Fig. 1. Average BaP concentrations in algae (*Fucus* and *Furcellaria*) of some bays of Estonian coastal waters.

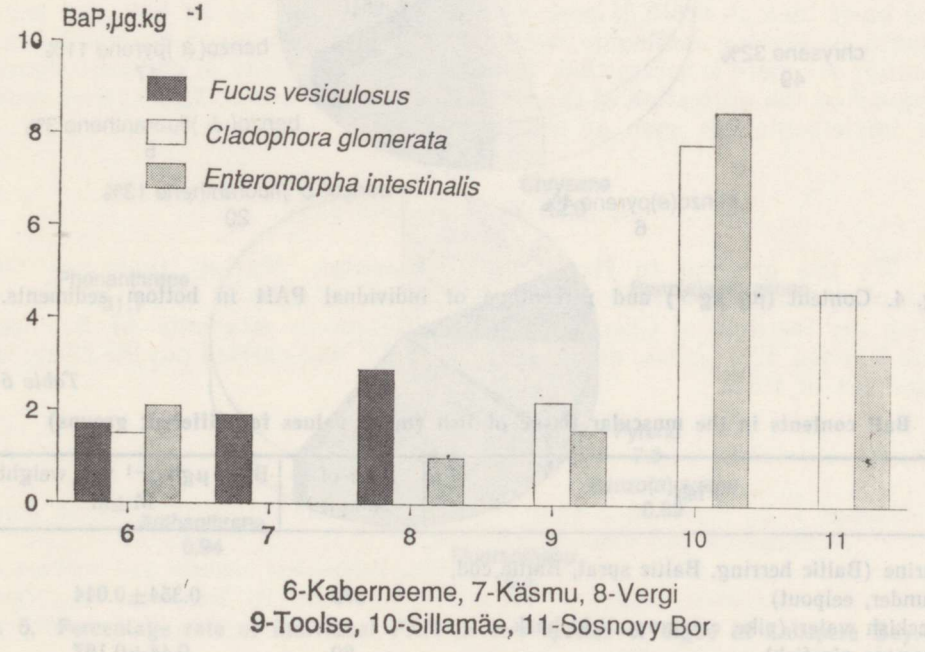


Fig. 2. Average BaP concentrations in algae (*Fucus*, *Enteromorpha*, and *Cladophora*) of some Estonian bays.

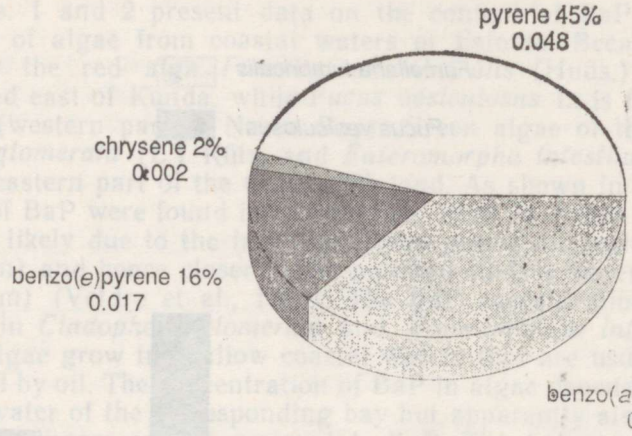


Fig. 3. Content (μg kg^{-1}) and percentage of individual PAH in seawater (Lahepere Bay).

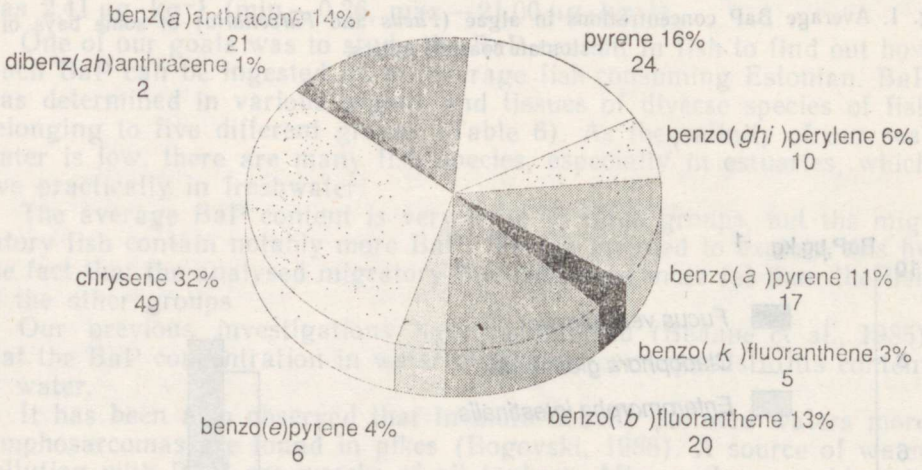
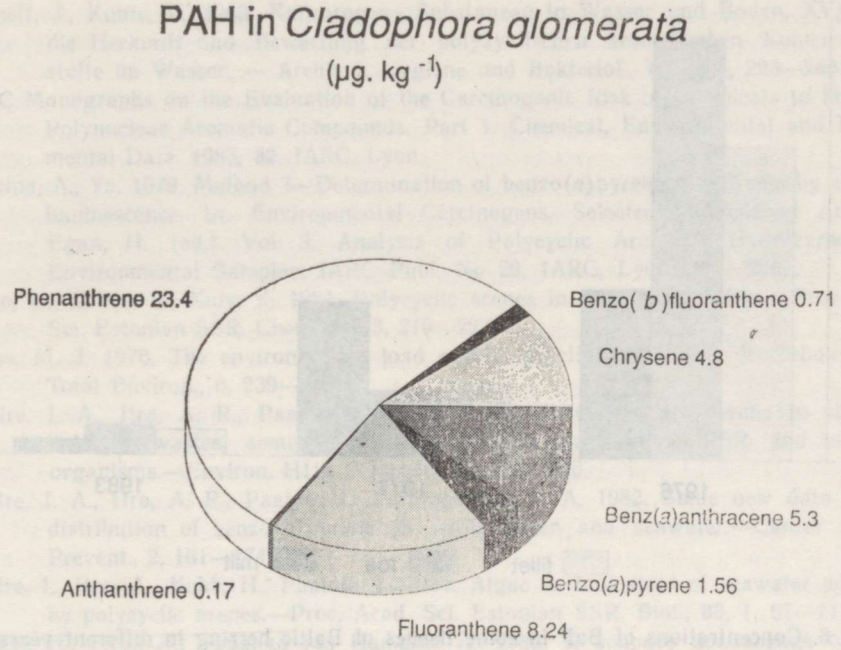


Fig. 4. Content (μg kg^{-1}) and percentage of individual PAH in bottom sediments.

Table 6

BaP contents in the muscular tissue of fish (mean values for different groups)

Fish	No of samples	BaP, μg·kg^{-1} wet weight M±m
Marine (Baltic herring, Baltic sprat, Baltic cod, flounder, eelpout)	379	0.354±0.044
Brackish water (pike, common stickleback, deepnose pipefish)	60	0.44±0.167
Migratory (eel, salmon, sea trout, European smelt)	37	1.34±0.717
Half-migratory (vimba, ide, asp)	33	0.29±0.092
Freshwater (burbot, carp, perch, bream, tench, pike)	255	0.77±0.150



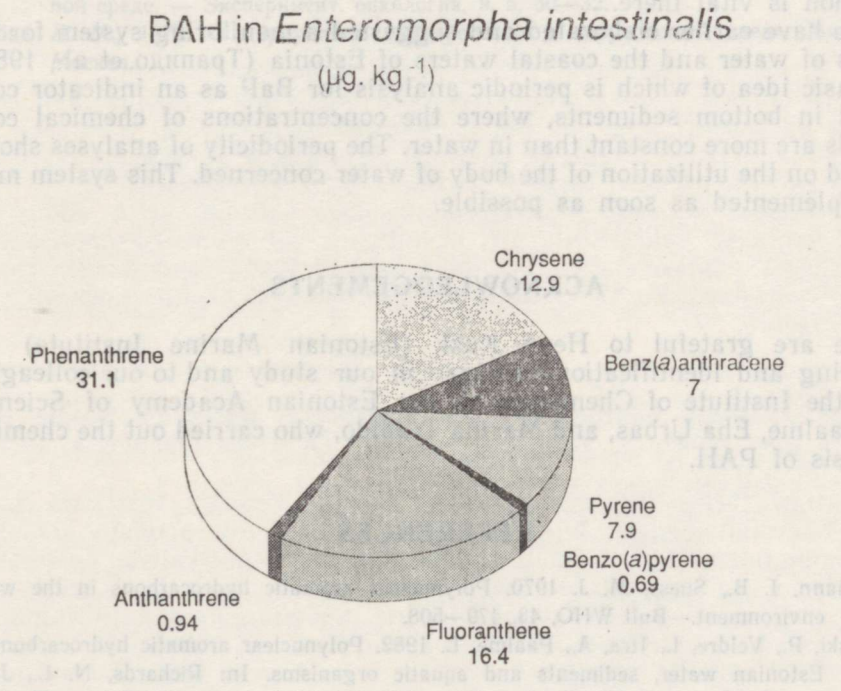


Fig. 5. Percentage rate of individual PAH in two species of algae in Lahepere Bay.

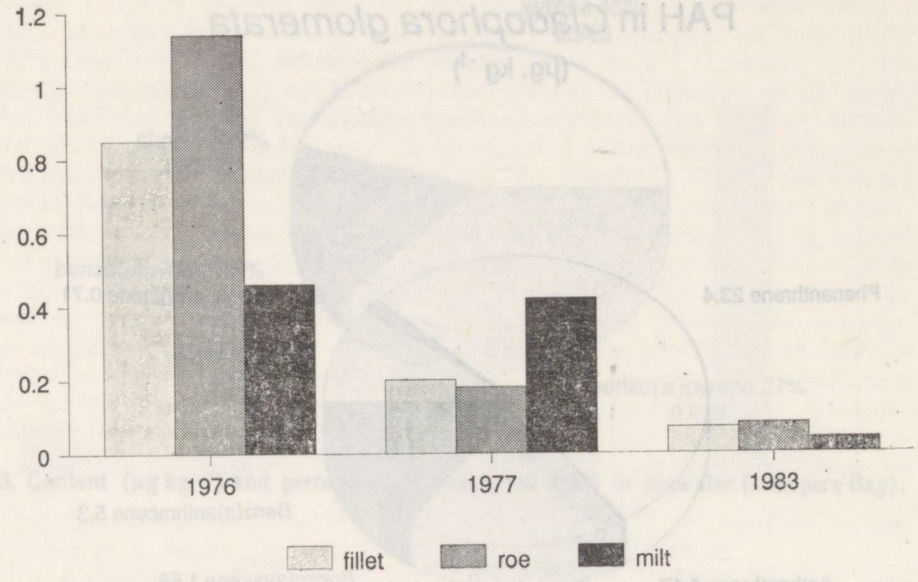


Fig. 6. Concentrations of BaP in some tissues of Baltic herring in different years.

Since many bays of the Baltic Sea have important fishing grounds and are widely used for recreation and water sports, surveillance of PAH pollution is vital there.

We have earlier elaborated and suggested a monitoring system for the bodies of water and the coastal waters of Estonia (Трапидо et al., 1987), the basic idea of which is periodic analysis for BaP as an indicator compound in bottom sediments, where the concentrations of chemical compounds are more constant than in water. The periodicity of analyses should depend on the utilization of the body of water concerned. This system must be implemented as soon as possible.

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