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CONTENT OF BENZO(*a*)PYRENE IN ESTONIAN SMALL LAKES

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Abstract. The content of benzo(*a*)pyrene (BaP) in 62 small lakes was studied. It was found that the pollution with BaP was not high, although there was a wide variation in its concentrations. The mean value of BaP fluctuated from 0.11 to 9.30 ng L^{-1}. The situation and economic use of the lakes played a certain part in the BaP content in their water. The study of seasonal variations of BaP in the small lakes did not establish distinct differences between the seasons. Only the urban and suburban lakes showed about an order of magnitude higher concentration of BaP in water in winter than in other seasons. The hydrobiological type (trophicity) of a lake did not influence the content of BaP in the lake water. The concentration of BaP in fish tissues depended on its amount in the lake water and on the fat content of the fish tissue.

Key words: lakes, water pollution, polycyclic aromatic hydrocarbons, benzo(*a*)pyrene, fish tissue.

Estonian small lakes have been thoroughly studied for many years. The results of a long-term study of a large group of scientists were concentrated in the book by Ott & Kõiv (1999). Changes in the trophic state of the lakes that had taken place during the study are described in the book. However, there is only one comment about the anthropogenic pollution of these lakes with carcinogenic substances. Various polycyclic aromatic hydrocarbons (PAHs) form a large group of environmental pollutants. Among them there are substances that are classified as probable and possible carcinogens (WHO…, 1987; Menzie et al., 1992). One of the most thoroughly investigated PAHs is benzo(*a*)pyrene (BaP) as a probable carcinogen and because of its wide-spread distribution in the environment and high activity and stability.

The contamination of various Estonian water bodies with PAHs has been studied since 1972 by the staff of the Institute of Experimental and Clinical Medicine in cooperation with the Institute of Chemistry at Tallinn Technical University. Estonian small lakes were investigated with scientists of the Võrtsjärv Limnological Station since 1970. Environmental pollution with PAHs is one of the main problems in environmental protection. Epidemiological studies have shown a correlation between increased mortality in humans from lung cancer and exposure to coke-oven emissions, roof-tar emissions, and cigarette smoke (Dabestani & Ivanov, 1999). Studying environmental pollution and human exposure to PAHs in Estonia Hemminki & Veidebaum (1999) found that where lung cancer incidence is higher than elsewhere the deoxyribonucleic acid (DNA) adduct levels in white blood cells are increased in groups of residents with apparently only environmental exposure.

We possess a large amount of data on the pollution of Estonian lakes with PAH that may represent a supplementary material for characterizing the lakes. Therefore, the aim of this paper is to complete the hydrobiological description of small lakes of different economic use and different trophic types with data on their pollution with carcinogenic compounds, especially with BaP.

MATERIAL AND METHODS

We investigated 62 small lakes in Estonia, 52 of them only in summer. Two to three samples, seldom up to six, were taken from one lake. Ten lakes were studied in all seasons of a two-year period. These lakes were selected to characterize lakes of different economic use and of various regions. In our work we used the trophic characteristics of lakes by Mäemets (1974). The following lakes were studied during the two-year period: Viitna Pikk- and Linajärv in Lahemaa National Park, used for recreation; lakes Saadjärv, Kaarepere Pikkjärv, Kaiavere, and Kuremaa, which belong to the Vooremaa Landscape Reserve; Lake Ülemiste, which with its tributaries and water reservoirs is the drinking water supply for about 3/4 of the inhabitants of the capital Tallinn; Lake Harku in the western part of Tallinn, used for recreation and water-sports; Lake Maardu in the suburbs of Tallinn; and Lake Kahala, a small lake in a rural area about 50 km from Tallinn. In Lake Võrtsjärv we carried out a long-term study at 12 permanent sampling sites to investigate the seasonal variations of the BaP content in water and the accumulation of BaP in different components of the ecosystem – bottom sediments, water plants, plankton, and fish (Veldre et al., 1980). The great number of small lakes did not permit us to carry out all these investigations, therefore we compared our data with those of Lake Võrtsjärv.

Water samples were taken from the surface layer of about 0.2–0.5 m and were extracted with *n*-hexane: 4 L of water was shaked twice with 80 mL of hexane. When immediate extraction was not possible, samples were conserved with 30 mL *n*-hexane per 1 L water.

Hexane extraction of dry samples of bottom sediments (5–20 g) and water plants was conducted in Soxhlet during 8–10 h. Fish tissues were analysed for BaP as follows: fish fillet was homogenized, 100 g homogenized tissues was immersed in 100 mL ethyl alcohol, and 15 to 25 g KOH was added. Then the mixture was boiled for 2 h. The resultant mass was immersed in water and extracted five times with ethyl ether. The extract was washed initially with acidic water (5% H_2SO_4) and finally with distilled water. Na_2SO_4 was added to the extract, and the ether was removed by steam distillation. The residue was dissolved in *n*-octane.

Two different kinds of analytical techniques were applied. The method based on the Shpol'skij effect (specific fluorescence emission spectra in frozen hexane at 77 K) was applied for the determination of BaP (Fedoseeva & Khesina, 1968; Khesina et al., 1983). The sensitivity of this method is 0.01 ng per sample.

High performance liquid chromatography (model 1311, Minsk, Belarus) was applied for the separation and quantitative determination of PAH. For the chromatographic determination of PAH hexane was vaporized from the aliquots of hexane extracts in air and the residue was dissolved in 0.2 mL ethanol. As an eluting solvent the mixture of acetonitril and water 93 : 7 by volume with a flow rate of 8 μL min^{-1} was used. Detection was fluorimetric (initiation wavelengths 254 and 298 nm, the range of registration 330–600 nm). PAHs were identified by their retention times and quantified by comparing the response from the sample with the fluorescence response of a pure compound (purchased from Aldrich Co, USA). The chromatographic column (0.5×300 mm) was filled with Silosorb C18 (Chemapol, Czechoslovakia). The sensitivity of this method varied slightly for different PAH under study and was approximately 2 ng per sample.

RESULTS

Our investigations showed that the pollution of Estonian small lakes with BaP was not high. Table 1 presents a summary of the results of our study for various trophic types of lakes. The concentration of BaP in lakes of different trophic types fluctuated on a wide scale as demonstrated also by Table 2. The concentrations of BaP in the repeatedly investigated ten lakes showed a rather substantial variability in the mean values, which fluctuated from 0.34 to 2.27 ng L^{-1} The situation and the economic use of the lakes played a certain role in the BaP content of their water. The trophic type had no essential effect on the levels of BaP. This finding was confirmed by the results on the Viitna lakes. Lake Pikkjärv, which belonged in the period of our study to the oligotrophic type, contained as much BaP as eutrophic Lake Linajärv. The latter had a muddy bottom whereas Pikkjärv sediments were mostly sandy.

On ground of analyses of BaP in water it is very difficult to find distinct differences in the BaP content in various seasons. In our earlier study (Veldre & Itra, 1991) we showed that the concentrations of BaP in water fluctuate depending on hydrological and meteorological factors as well as on accidental short-term pollution of water. Therefore, we recommended for PAH monitoring in the water bodies to analyse the content of BaP in bottom sediments. Bottom sediments accumulate BaP and other PAHs to a high degree, the concentration coefficient being about 10^4–10^6.

Table 1. Comparison of the BaP content in lakes of various trophic state in 1970–77

Trophic type*	Number of studied lakes	BaP concentration, ng L^{-1}		
		Min	Max	Mean
Eutrophic	35	0.00	20.3	9.30
Dystrophic	2	0.01	0.27	0.14
Dyseutrophic (mixotrophic)	18	0.00	8.54	1.89
Semvidystrophic	2	0.00	0.39	0.19
Oligotrophic	2	0.03	0.19	0.11
Halotrophic	3	0.00	3.33	1.10

* Classification of lakes according to Mäemets (1974).

Table 2. Concentrations of BaP (mean ± SD) in lake water in 1970–78

Lake	Trophic type*	Number of water samples	Concentration of BaP, ng L^{-1}
Viitna Pikkjärv	O	63	2.05 ± 0.66
Viitna Linajärv	E	32	2.27 ± 0.86
Saadjärv	E	30	0.41 ± 0.11
Kaiavere	E	28	0.49 ± 0.25
Kaarepere Pikkjärv	E	36	1.41 ± 0.46
Kuremaa	E	39	0.49 ± 0.17
Harku	E	46	1.58 ± 0.48
Maardu	DE	43	2.27 ± 0.49
Ülemiste	E	54	1.22 ± 0.35
Kahala	DE	9	0.34 ± 0.13
Võrtsjärv	E	155	0.57 ± 0.15

* Classification of lakes (Mäemets, 1974): O, oligotrophic; E, eutrophic; DE, dyseutrophic (mixotrophic).

As it was not possible to study BaP in the sediments of small lakes we had to compare the BaP content in different seasons in the lake water. Our results showed that in the urban and suburban lakes Harku and Maardu the BaP concentrations in winter under ice cover were about an order of magnitude higher than in other seasons and higher than in other lakes (Table 3).

In Lake Võrtsjärv the difference between BaP levels in winter and the other seasons was very distinct, although the concentrations were much lower than in lakes Harku and Maardu. In Lake Võrtsjärv the concentration of BaP had decreased in 1977 in comparison to the previous year; nevertheless the highest concentrations of BaP were in both years in winter. The seasonal fluctuation of BaP in the water of Lake Võrtsjärv in 1977 is shown in Fig. 1.

Table 3. Seasonal variations of BaP (ng L^{-1}) in the water of some lakes in 1970–78

Lake	Winter[a]	Spring[b]	Summer[c]	Autumn[d]
Viitna Pikkjärv	0.215	0.221	0.465	1.979
Viitna Linajärv	0.167	1.235	0.304	0.223
Saadjärv	0.326	0.063	0.839	0.524
Kaiavere	0.400	0.106	2.119	1.226
Kaarepere Pikkjärv	0.556	0.699	0.578	3.504
Kuremaa	0.401	0.163	0.360	1.246
Harku	7.177	0.954	0.369	0.831
Maardu	7.065	1.203	1.089	1.496

[a] under ice cover, [b] the period of spring high water, [c] summer dry period, [d] the period of autumn rains.

Comparison of our data on the BaP concentration in small lakes with those in Lake Peipsi (Trapido & Veldre, 1996) showed that, as a rule, there was no significant difference in them; only in summer the BaP concentrations in Lake Peipsi were higher due to oil spillage and fuel exhausts from boats and ships, since Lake Peipsi is largely used for recreation and fishing, especially in summer. The PAH analyses in Lake Peipsi showed that BaP formed 3–5% of the total content of PAHs in water, which fluctuated from 0.0073 to 0.017 μg L^{-1}, while the Estonian threshold limit for PAHs is 0.2 μg L^{-1} (Eesti Standard EVS 663, 1995). The BaP content in small lakes did not exceed 9.30 ng L^{-1} or 0.0093 μg L^{-1}.

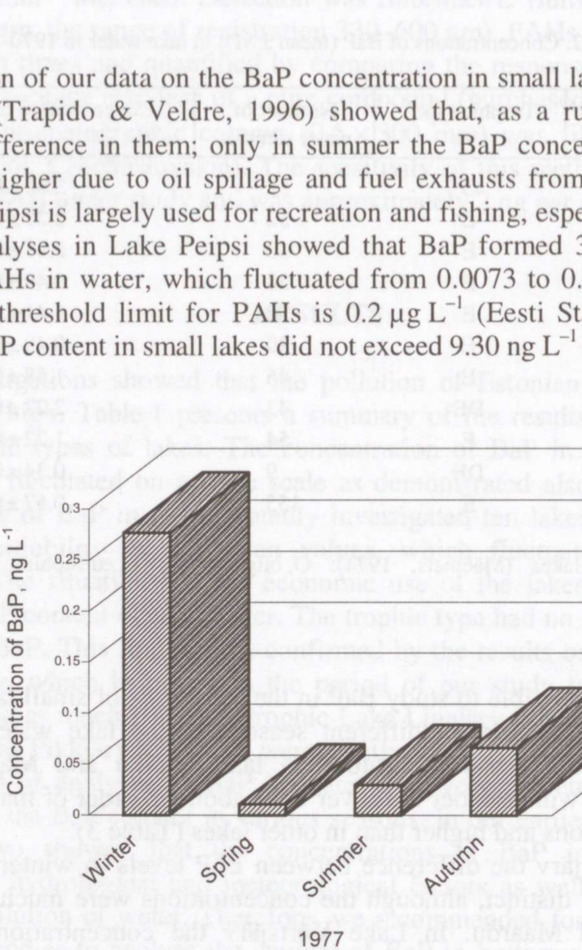

Fig. 1. Seasonal variation of BaP in the water of Lake Võrtsjärv at the Limnological Station. For definition of seasons see Table 3.

PAHs are chemically quite stable and, due to their lipophilic nature, can easily penetrate biological membranes and accumulate in organisms. PAHs are exceedingly toxic to aquatic organisms at concentrations of about 0.2–10 ppm (Tuvikene, 1995). BaP, as well as other PAHs, accumulates in various biota.

From the point of view of human health fish are the most important component of the ecosystem of a water body. We studied the content of BaP in muscular tissues of eight fish species from various water bodies (Table 4). The average content of BaP in muscular tissues of various species of fish was in most cases less than 1 μg kg^{-1}. The concentration of BaP was in the first place dependent on the pollution level of the water bodies with BaP. For instance, the tissue of fish caught from the Gulf of Finland contained 0.633±0.085 μg kg^{-1} BaP (n = 110), from Matsalu Bay (n = 81) 0.273±0.041 μg kg^{-1}, and from Pärnu Bay (n = 101) 0.155±0.017 μg kg^{-1}. The water of the Gulf of Finland was much more polluted with BaP than that of the two bays (Veldre et al., 1985). The content of BaP in fish tissue of the same species corresponds to the level of BaP in the lake water. Comparison of the BaP content in the tissues of different fish species from the same lake showed that fat fish contained more BaP than lean fish, because fat accumulates PAHs as well as many other pollutants. The higher concentrations of BaP in the tissues of eel in comparison with other fishes confirmed that fact. The trophic state of the lakes seemed not to influence the content of BaP in fish tissues. The mass (age) of fish had no influence on the BaP content in fish tissues (Veldre et al., 1979).

Table 4. Content of BaP (μg kg^{-1} wet weight) in fish tissue

Lake	Tench	Pike	Eel	Perch	Roach	Bream	Pope	Pikeperch
Kuremaa	0.38	0.70	3.08	1.02	1.76	1.12	–	–
Kaiavere	1.05	0.38	1.54	–	0.18	0.37	–	–
Elistvere	0.66	0.24	4.64	1.16	0.25	0.28	–	–
Võrtsjärv	–	0.12	–	0.59	–	0.12	2.05	0.31
Peipsi	–	–	–	0.14	0.08	0.03	0.05	0.005

– No specimen of the species was caught.

CONCLUSION

The concentration of BaP in small lakes was not high, although there was quite a wide variation in its levels. The mean values of BaP fluctuated from 0.11 (oligotrophic lakes) to 9.30 ng L^{-1} (eutrophic lakes). The summarized data of all the studied lakes (Table 1) give the notion of a higher pollution in the water of eutrophic lakes in comparison to the others; however, the results of a two-year study of ten lakes, where the number of water samples from each lake was approximately 30–50, does not permit such a conclusion.

The situation and economic use of the lakes played a certain part in the BaP content in their water. The seasonal variations in the small lakes did not allow us to establish distinct differences. Only in the suburban and urban lakes Maardu and Harku the BaP content in water was about an order of magnitude higher in winter than in the other seasons and also higher than in other lakes. In Lake Võrtsjärv the BaP content was also higher in winter than in the other seasons.

Analysis of fish tissues from eight species of fish caught from different lakes showed that the BaP accumulation in fish depended on the pollution of the lake water with BaP and not on the trophic type of the lake. The fat content of the fish plays an important role in BaP pollution of fish, because fatty tissues accumulate more BaP than lean ones.

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EESTI VÄIKEJÄRVEDE SAASTUMISEST BENSO(*a*)PÜREENIGA

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On uuritud benso(*a*)püreeni (BaP) sisaldust 62 väikejärves ja võrreldud seda suuremate järvede omaga. BaP kontsentratsioon järvevees polnud kõrge, kuid kõikus võrdlemisi suures ulatuses. Selle keskmine väärtus oli vahemikus 0,11–9,30 ng l^{-1}. Aastaajati polnud BaP sisalduses tõepäraseid erinevusi. Mõnes järves, eriti linna piires (Harku ja Maardu), täheldati talvel kõrgemaid näitajaid. Järvede troofsuse iseloom ei mõjutanud BaP hulka. BaP kontsentratsioon kalakudedes sõltus selle kogusest järvevees, samuti kudede rasvasusest.