

## DEPOSITION FLUXES OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE BOTTOM SEDIMENTS OF LAKE PIHKVA

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**Abstract.** Traditionally the elevated concentrations of PAHs in the bottom sediments of Lake Peipsi are explained by the influence of oil shale industry. To estimate the role of Narva Power Plants (Narva PP) in the deposition of PAHs, we investigated the  $^{210}\text{Pb}$  dated sediment core from Lake Pihkva, where the influence of oil shale industry should be minimal. The distribution of 15 individual PAHs was established, the observed levels of  $\Sigma\text{PAHs}$  ranged between 75 and 345 ng/g. PAHs with 4–5 rings implying petrogenic activity accounted for 74 to 87% of  $\Sigma\text{PAHs}$ , which is higher than in a similar investigated profile in Lake Peipsi sensu stricto. It means that the role of oil shale industry in PAHs accumulation is strongly overestimated and there should be many other sources whose role needs further investigation.

**Keywords:** Lake Peipsi, Lake Pihkva, polycyclic aromatic hydrocarbons (PAHs), lake sediments, power plant pollution.

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants derived from the incomplete combustion of organic materials, e.g. any kind of fossil fuels including oil shale. PAHs are important to study because some of those compounds are of carcinogenic and/or mutagenic potential. If the temporal generation of PAHs is known, then the record of input stored in different deposits allows us to date sediment layers or follow changes in the processes affecting sediment deposition over certain periods of time [1–6]. It enables monitoring the surface water and air quality trends in the longer time span than it comes from the use of instrumental data. PAHs concentration and distribution studies in the atmosphere, water and surface sediment samples have made it possible to identify their common patterns and possible sources. Taking into account the chemical composition

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and stability of PAHs, there is evidence that two- and three-ring compounds indicate relatively stronger petrogenic origin and four- to six-ring compounds pyrogenic origin [7].

It is traditionally assumed that the high concentrations of PAHs in the bottom deposits of Lake Peipsi (L. Peipsi) have originated from the oil shale industry and are mainly transported by the wind from Narva Power Plants (Narva PP). Our studies in L. Peipsi *sensu stricto* (*s.s.*) [6] did not support an earlier hypothesis about the highly dominating impact of the oil shale fired power plant near the lake, because the respective emissions decreased significantly in the 1990s and the dominating winds are not blowing towards the lake. To our mind, PAHs find their way to the lake not only through air transport, but also via surface runoff and wastewater disposal, from inland waterway transport and motor boats movement on the lake. To confirm previous findings we studied bottom sediments of Lake Pihkva (L. Pihkva), where the direct atmospheric influence by PAHs from Narva PP is practically absent.

In Estonia more than 90% of energy production is based on oil shale combustion. Due to the high concentration of mineral matter in oil shale, more than 45% of burned oil shale generates oil shale ash. Semi-coke (i.e. solid residues), oil residues with high-ash fractions of oil shale which contain PAHs, phenols and other hazardous substances [8], and ash (called black ash) generated in the process of shale oil production are classified as hazardous wastes [9, 10]. The organic part of oil shale ash (< 1.5%) contains several PAHs: phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b+k*]fluoranthene, benzo[*a*]pyrene, etc. [11]. Total fly ash emission to the atmosphere from the power plant reached more than 300 kilotonnes per year by the end of the 1970s [12], among this more than 100 kg PAHs. Therefore, in the 1970s–1980s, much attention was paid to the study of the power plant emissions as a potential source of pollution to L. Peipsi and its catchment, because the lake water was used as drinking water by the city of Narva and there were plans to start to supply also the city of Tallinn with it. Since that time serious measures to decrease emissions have been implemented and by 2002 fly ash emissions from the power plant had decreased more than 10-fold compared with maximum rates during the late 1970s. The airborne emissions of PAHs (2003) have been shown to be comparable to PAHs concentrations in the urban air, and the dioxine emissions (2007) have been close to the detection limit, 4 pg/m<sup>3</sup> [13, 14]. However, there is a possible risk for accumulation of contaminants in soil and sediments [15], which may lead to bioconcentration.

The studies on the PAHs content in the bottom deposits of L. Peipsi conducted in 1979–1987 indicated that the atmospheric load can significantly contribute to the total pollution in L. Peipsi [16–19]. It was concluded that the benzo[*a*]pyrene (BAP) content in the bottom deposits of the lake was 10<sup>2</sup> to 10<sup>5</sup> times higher than in the water and its concentration in the lake mud much higher than in coarser sediments.

Later research on the distribution of individual PAHs in the sediments of the northern part of L. Peipsi *s.s.* showed that the most stable are benzo[*b+k*]fluoranthene, indeno[*1,2,3-cd*]pyrene, benzo[*g,h,i*]perylene and fluoranthene [6]. The stability of these compounds might be caused, among other factors, by their tight link with settling particles and therefore quick emersion under oxidizing conditions. The influx of the most identified PAHs in the central part of L. Peipsi reached the first peak in the 1990s, and then, after some stabilization period, started to increase again, reaching maximum values in the surface layers [6].

A detailed map of bottom sediments of L. Peipsi has been drawn and its matter cycle analysis performed [6, 20]. This will open possibilities for understanding the matter exchange on the water-sediment interface in and for nutrients budgeting for L. Peipsi. Same should be done for L. Pihkva. The current study is one of the first of its kind in L. Pihkva and provides a better understanding of the different sources and pathways of hydrocarbons found in its sediments at present. Since the composition of PAHs from natural and anthropogenic sources is similar, the significance of anthropogenic PAHs in the environment must be evaluated against a dynamic background of natural PAHs. The levels of PAHs found in this study will serve as a natural baseline for future research.

## 2. Study area

Lake Peipsi is a transboundary water body on the border between the Republic of Estonia and the Russian Federation (Fig. 1). The lake consists of three distinct parts. There are two big lakes – Suurjärv, or Lake Peipsi *s.s.* (in Estonian Peipsi järv, in Russian Chudskoye ozero) in the north and Lake Pihkva (in Estonian Pihkva järv, in Russian Pskovskoye ozero) in the south, and a small strait-like Lake Lämmijärv (in Estonian also Soejärv, in Russian Teploye ozero) connecting them.

L. Pihkva is the shallowest part of L. Peipsi (Fig. 1) [21]. The lake catchment is a gently undulating glaciolacustrine or till-covered plain. The bottom of the lake is mainly covered with lake mud (organic content up to 35%). The sediment type by grain size is clayey silt whose dominant fraction (0.05–0.1 mm) accounts for 40–70%, in some places even up to 82% of the silt composition. The clay content can increase up to 25–35%. On coastal areas fine grained sand prevails [22]. Forests and semi-natural areas dominate in the lake drainage basin, next to agricultural areas.

The main source of inflow to L. Pihkva is the Velikaya River (catchment area 25 200 km<sup>2</sup>). L. Pihkva is almost entirely located in Pskov Oblast, Russian Federation. The city of Pskov (202 000 inhabitants) is situated in the immediate vicinity of the lake and is the largest point source of nutrients in the lake drainage area [23]. In Pskov Oblast the Pskov thermoelectric power station in Dedovichi and the Pskovskaya Poultry Farm are the largest con-

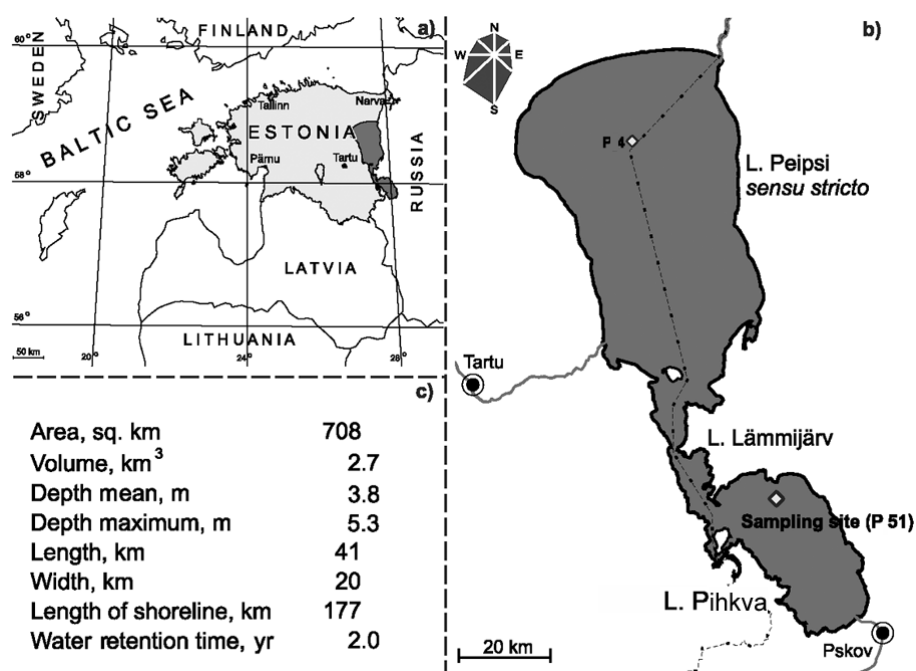


Fig. 1. a) Location of L. Peipsi, b) L. Pihkva with the sediment coring site and wind rose, c) morphometric data on L. Pihkva (at a mean water level of 30 m a.s.l.) [21].

tributors to the pollution coming from stationary sources [24]. In the city of Pskov the main sources of pollution are mechanical engineering enterprises, a cable factory, and the car factory “Pskovauto.” In Velikiye Luki town there are a locomotive repair plant, a furniture plant and other industrial enterprises. Motor transport is still the main source of air pollution in the region, accounting for 60% of total air pollution [24, 25]. No investigations of PAHs in Pskov Oblast have been conducted earlier.

Due to the large surface area and shallowness of L. Pihkva, its water temperature stratification is unstable and can be disturbed already by a moderate wind or undulation. Therefore, the water of the lake is usually rich in oxygen during the open water period. The lake’s ecosystem is under threat of eutrophication, which has led to an undesirable growth of algae, massive blooms of cyanobacteria accompanied by fish kills, low water transparency and silting of the lake bottom [26–28]. L. Pihkva receives pollution mainly through the river water and riverine transport is the major contributor to the input of nutrients from both point and nonpoint sources [29].

### 3. Study methods

To find out the concentrations of PAHs and their changes in time, we investigated in detail a 40 cm long sediment core from the northern part of L. Pihkva at the state monitoring station no. 51 (Fig. 1b). The coring was performed with a modified Livingstone-Vallentyne piston corer in early spring 2009 from the ice. The core was sub-sampled in the field at an interval of 2 cm, packed in plastic containers and stored at +5 °C in dark prior to analyses.

To determine the water content, the samples were dried to constant weight at 105 °C. The organic content (OM) was measured as loss-on-ignition (LOI) at 550 °C for 3.5 hours and expressed as percentage of dry matter and the carbonate content was calculated as the loss of weight after burning the LOI residue at 950 °C for 2.5 hours [30].

The radiometric dating of the core was determined by the  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{137}\text{Cs}$  methods at the Centre for Environmental Monitoring and Technology, Ukrainian Hydrometeorological Research Institute by direct gamma assay using an EG&G Ortec HPGe GWL series well-type coaxial low background germanium detector [31]. The CRS (constant rate of supply) dating model was used as a processing tool for sedimentation chronology reconstruction, taking into account the irregularity of  $^{210}\text{Pb}$  activity profile in the sediment core.

The PAHs analyses were performed at the Estonian Agricultural Research Centre. 15 individual PAHs were extracted from dried samples using hexane/acetone (1:1 v/v) in a Dionex ASE 300 accelerated solvent extraction system at a pressure of 2000 PSI at 100 °C in accordance with the EPA method 3545. The extracts were analyzed on a gas chromatograph coupled with an Agilent 6890/5973 mass spectrometric detector, the GC being fitted with a 30 cm × 250 mm × 0.25 μm HP-5MS capillary column. The detection limit of analyses for individual PAHs was 0.002 mg/kg.

Factor analysis (FA) and principal component analysis (PCA) were used to extract information from the most meaningful parameters (variables) which best described the overall data, affording data reduction with minimal loss of information with the XLSTAT (version 2010 3.06). Cluster analysis was used to identify groups with similar PAH composition and layers in the sediment core.

### 4. Results

The analyzed sediments sequence consisted of green-grey lake mud (gyttja). The water content in deeper sediment layers has permanent values (ca 85%) up to a depth of 12 cm, increasing then up to 97% in the surface layers. The concentration of organic matter expressed as LOI decreases from the layers at 40–34 cm from 24.7% to min 22.7% at a depth of 16 cm and then

increases up to 25% in the surface layers. According to the CRS model, the sedimentation rate in the upper 40 cm of the core L. Pihkva was steady below 0.05 g/m<sup>2</sup>/y until the early 1950s (Table 1). About 30 years ago a slight acceleration of sedimentation rate took place (0.065 g/m<sup>2</sup>/y), which then returned to historical normal range.

The concentrations of acenaphthene, acenaphthylene, anthracene, fluorene and naphthalene were near or beyond the detection limit. The observed levels of PAHs concentrations ranged between 0 and 73 ng/g (Table 2, Fig. 2) and of the sum PAHs ( $\Sigma$ PAHs) between 75 and 345 ng/g.

**Table 1. Radiometric dates and sedimentation accumulation rates of L. Pihkva sediment core according to the CRS model <sup>210</sup>Pb**

Depth, cm	Cum dry mass, g/cm <sup>2</sup>	<sup>210</sup> Pb inventory, Bq/m <sup>2</sup>	Radiometric date, y	Std error, y	Sedimentation rate		
					g/cm <sup>2</sup> /y	cm/y	% error
0	0	3188.2	2009				
5	0.3518	2643.7	2003	2	0.0573	0.729	6.9
7	0.5507	2339	1999	2	0.0446	0.368	10.6
11	1.0796	1712.6	1989	2	0.0645	0.451	17.1
15	1.6939	1168.2	1977	3	0.0384	0.246	19.7
17	2.0168	890.3	1968	4	0.0356	0.219	23.4
19	2.3444	692.1	1960	6	0.0468	0.281	28.7
23	3.0166	433.8	1945	7	0.0426	0.249	44.2
29	4.0523	196.2	1919	11	0.0383	0.227	51.8
35	5.0438	69	1886	20	0.0212	0.127	66

**Table 2. Characteristics of analysed PAHs in L. Pihkva sediment core**

PAH	Code	Molecular weight	Group by vertical distribution (Fig. 2)	Benzene (and total) rings
Naphthalene (LMW)	NAP	128	–	2
Acenaphthylene (LMW)	ACPy	152	–	2
Acenaphthene (LMW)	ACP	154	–	2
Fluorene (LMW)	FLU	166	–	2 (3)
Anthracene (LMW)	ANT	178	–	3
Phenanthrene (LMW)	PHE	178	II	3
Fluoranthene (LMW)	FLT	202	III	3 (4)
Pyrene (HMW)	PYR	202	III	4
Chrysene (HMW)	CHR	228	III	4
Benzo[ <i>a</i> ]anthracene (HMW)	BAA	228	II	4
Benzo[ <i>b+k</i> ]fluoranthene (HMW)	BBF	252	III	4 (5)
Benzo[ <i>a</i> ]pyrene (HMW)	BAP	252	II	5
Indeno[ <i>1,2,3-cd</i> ]pyrene (HMW)	INP	276	III	5 (6)
Benzo[ <i>g,h,i</i> ]perylene (HMW)	BGP	276	III	6
Dibenzo[ <i>a,h</i> ]anthracene (HMW)	DBA	278	I	6

LMW – low molecular weight, HMW – higher molecular weight.

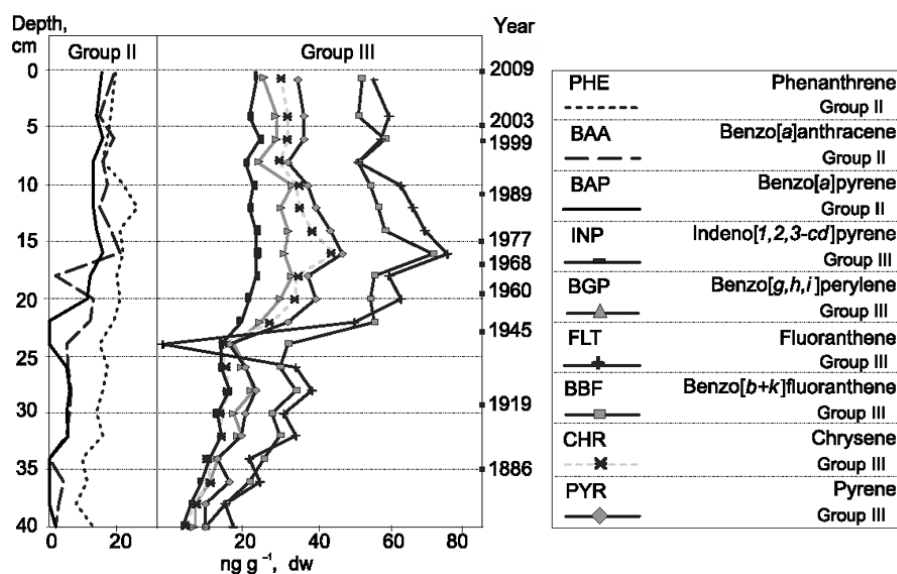


Fig. 2. PAHs and groups by vertical distribution in L. Pihkva sediment core.

According to the k-means clustering of their concentrations measured, PAHs may be divided into three groups (Table 2; Fig. 2, except group I): group I contains PAHs that are present in very low concentrations; group II contains PAHs that are present in all samples and their concentrations in the upper layers increase insignificantly; group III contains PAHs that are present in small concentrations in the lower layers but these concentrations increase significantly from a depth of 25 cm upward (accumulated since 1930). Group I contains only dibenzo[*a,h*]anthracene (DBA) in low concentration (6 ng/g, dry weight) in 4 and 12 cm cores only. The most significant increases can be observed for fluoranthene (FLT), benzo[*b+k*]fluoranthene (BBF), pyrene (PYR), chrysene (CHR) and benzo[*g,h,i*]perylene (BGP).

In the vertical distribution of PAHs concentrations in the core there may be observed three distinct zones, according to cluster analysis and PCA. At the lowermost depth, from 40 to 32 cm, the concentrations of all analyzed PAHs, which according to  $^{210}\text{Pb}$  data accumulated from around the 18th century until the first decade of the 20th century, are low and fairly uniform. From 31 cm upward the concentrations of most PAHs begin slowly to increase, followed by increases from 21 cm (since approximately 1956) towards the surface with maximum concentrations at the end of the 1970s–beginning of the 1980s.

## 5. Discussion

According to monitoring data, in 1987, three- and four-ring PAHs (FLT, PHE) prevailed in the lake water and five- and six-ring PAHs (BBF, INP, BGP) were predominant in sediments. This means that while PAHs with lower molecular weights (FLT, PHE) might be transported in the gaseous phase and are in soluble form in water, then those with more than five rings are almost completely associated with solid particles. It is well known that the stability of individual PAHs in various environmental processes is different and that photo-oxidation is the major decomposition process beside the biodegradation by microorganisms [32]. The influence of these processes on low molecular weight two- and three-ring PAHs is much higher than on four- and six-ring compounds. This is to be taken into account in air transport. The distribution of individual PAHs in L. Pihkva sediments shows that the most stable are FLT, BBF and PYR, which accounted for approximately 20%, 20% and 13% of  $\Sigma$ PAHs, respectively. The stability of these compounds might be mainly caused by their tight link with settling particles and therefore quick emersion under the oxidizing conditions.

The sediment core data shows that the influx of most of the analyzed PAHs increased continuously in the layers accumulated since the 1930s to the present (Fig. 3). The influx values are the highest for FLT and BBF. This means that while FLT might be transported in the gaseous phase, then BBF are almost completely associated with solid particles emissions from diesel fuelled vehicles, which have been rapidly increasing during recent decades.

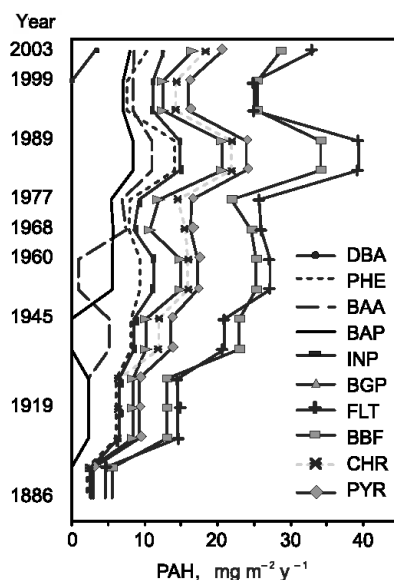


Fig. 3. Values of PAHs influx into L. Pihkva since 1886 to the present.



The obtained data allow us to distinguish PAHs of different origins by using the correlation factors between the sediment concentrations of all individual PAHs [33]. No correlation was observed only between DBA and other PAHs, showing that DBA has another origin. However, the content of DBA is sporadic with low concentration (Fig. 3).

Several molecular ratios have been developed for interpreting PAHs compositions and inferring possible sources. In our study the assessments are made using FLT/PYR and CHR/BAA parental PAH ratios. FLT and PYR were often associated during natural matrices analyses and were considered as typical pyrogenic products derived from the high-temperature condensation of lower molecular weight aromatic compounds. The excellent coefficient of correlation (0.95) observed between these two PAHs indicates probably their similar behavior. According to Laflamme and Hite [34] the FLT/PYR ratios higher than 1.0 indicate pyrolytic contamination. In our case FLT/PYR ratios are very stable, around 1.50, which indicates pyrolytic sources of PAHs (with one exception at a depth of 24 cm). According to Yunker et al. [1] the FLT/FLT+PYR ratio below 0.50 is observed for most petroleum samples and above 0.50, like in our core in the range from 0.58 to 0.63, suggests probably sources from kerosene, grass, coal and wood combustion.

Furthermore, BAA and CHR derive from pyrolytic sources (from processes of organic matter combustion at high temperature) in a ratio that should be lower than 1 [33]. It has been shown that CHR derivatives are more stable than BAA ones, because of the convertibility of the latter to CHR compounds. The CHR is a compound found in the sediment and is believed to be an aromatic compound of natural origin formed mainly during combustion processes and only at low concentration during biosynthesis. Our values of CHR/BAA range mostly from 1.68 to 3.00 (with one exception at a depth of 18 cm at a ratio of 17), indicating some influence of petrogenic contamination or degradation of the less stable BAA.

While PAHs with  $LMW_{PAH}$  (sum of low molecular weight PAHs, two–three rings) came mainly from petrogenic sources, those with  $HMW_{PAH}$  (sum of higher molecular weight PAHs, four–five–six rings) originate mostly from pyrolytic sources (Table 2). The values of the ratio  $LMW_{PAH}/HMW_{PAH}$  lower than 1 suggest pyrolytic origin pollution in general. In L. Pihkva inputs of PAHs with four–five rings averaged  $0.15 \pm 0.08$  ng/g, implying petrogenic activity and ranged from 74 to 87% of  $\Sigma$  PAHs (Fig. 2). It is higher than a similar profile for L. Peipsi *s.s.*, in whose sediments the four- and five-ring PAHs accounted for 57–62% [6]. Similarly to the northern part of L. Peipsi, the BAP and PHE in the sediments of L. Pihkva come mainly from natural sources, their concentrations having increased rather modestly in sediments accumulated since the beginning of the 20<sup>th</sup> century.

## 6. Conclusions

Based on earlier studies, we hypothesized that there must be a certain accordance between the distribution of PAHs in the sediment sequence in L. Peipsi *s.s.* due to atmospheric emissions from oil shale combustion. As the bottom deposits of L. Pihkva have been investigated poorly, we assumed the plurality of pollution sources. On the basis of earlier and present data we may conclude that while in the 1970s mostly the oil shale operated power plants were responsible for PAHs emissions to L. Peipsi and its catchments, then since the 1980s the role of other sources has increased.

The top 20 cm is the most important layer that contributes to PAHs fluxes. PAHs in deeper layers are relatively inactive and stable. Therefore, one may assume PAHs fluxes from: a) deposits of sediment acting as PAHs sources to the sediment layer, b) desorbed PAHs from sediment particles behaving like a sink as they are spread by turbulence-driven diffusion and bioturbation. The atmospheric transformation and high stability of five- and six-ring PAHs in sediments suggest that their elevated concentration in the sediments may be used as a time marker of intensive anthropogenic impact since the 1920s–30s.

Located rather far L. Pihkva is not directly influenced by emissions from Narva Power Plants. So, one should consider PAHs pollution from other sources, like the city of Pskov via the Velikaya River and Pskov Oblast's enterprises. Major contributors are the Pskov thermoelectric power station, other thermoelectric power stations, a big poultry farm, mechanical engineering enterprises, a cable factory, etc., but also inland waterway transport and motor boats movement on the lake. As the PAHs content in the investigated profile in L. Pihkva is higher than in the similar investigated profile in Lake Peipsi *s.s.*, we can conclude that the role of Narva Power Plants in PAHs accumulation in Lake Peipsi *s.s.* is also strongly overestimated. Due to incomplete information on sources, pathways and behavior of pollutants in the whole Lake Peipsi basin, further investigations will be needed to fill in the gaps in data.

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