Перед проведением работ по устройству выносных желобов необходимо произвести проверочные расчеты конструкций с учетом изменяющейся внешней нагрузки на парапет.

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DETECTION OF POLYNUCLEAR AROMATIC HYDROCARBON (PAH) COMPOUNDS IN RIVER WATERS USING HPLC-UV/VIS

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Abstract

This paper reports studies of six polynuclear aromatic hydrocarbons in river waters and wastewater samples. Acenaphthene was the most dominant PAHs found in studied samples while in most samples naphthalene is not observed. A maximum of 778,326 μ g l⁻¹ of the six PAHs was recorded in water collected from confluence of the Ciemięga River at December 2008. Probably it was result of episodic contamination which can be connected weather conditions in that period with atmospheric conditions. The sample collected after over two months from the same point contained comparable amount of PAHs as other samples.

Introduction

Polynuclear aromatic hydrocarbons, PAH, have widespread occurrence in the environment. They are a group of aromatic compounds containing two or more fused benzenoid rings in linear, angular or cluster structure and formed by pyrosynthesis during the combustion of organic matter. PAHs are found as trace pollutants in soil, air particulate matter, water, tobacco tar, coal tar, used engine oil and foodstuffs such as barbequed meat. Polycyclic aromatic hydrocarbons also occur in soot, vehicle exhausts and in hydrocarbon fuels. They are generally not very soluble in water but are readily adsorbed into particulate matter resulting in high concentrations where suspended solids are present in water. Nearly all PAHs are carcinogenous, although their potency varies, the most hazardous by far being benzo(a)pirene [1,2,3]. Fluoroantene, which is the most soluble but least hazardous of the PAHs compounds, is occasionally found in high concentrations in drinking water samples collected at consumers taps. PAHs in drinking water are thought to cause gastointenstinal tumours, however, drinking water contributes only small proportion (0.5%) of the total adult PAH intake. PAHs are rarely present in the environment on their own and the cancinogenic nature of individual compounds is through to increase in the presence of other PAH compounds.

While there are over 100 PAH compounds the Word Health Organization have listed six reference compounds that should be routinely analysed [1]. These represent the most widely occurring compounds of this group found in drinking water. Total concentration of polycyclic aromatic hydrocarbons in drinking water is calculated from concentration of mix reference compounds. The U.S.EPA has designed 16 PAH compound as priority pollutants [4]. They are naphthalene, acenaphtylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz[a,h]anthracene, benzo(g,h,i)perylene and indeno[1,2,3-cd]pyrene. This list of the 16 EPA priority PAHs is often target for measurement in environmental samples [4].

The EC has set a MAC for the sum of the six reference PAH compounds in drinking water as 200 ng 1⁻¹. The MAC value for PAHs compounds has been adopted in the UK although a separate maximum limit value has been set for benzo(a)pyrene of 10 ng Γ^{-1} , which is also the level set by the WHO and is equivalent to just 0.00001 mg Γ^{-1} [1].

Ground water sources and upland reservoirs in UK contain low levels of PAHs, less than 50 ng 1^{-1} , while lowland rivers used for supply contain between 40 and 300 ng 1^{-1} during normal flows, rising to in excess of 1000 ng 1^{-1} at high flows. According to data of Provincial Environment Protection Agency in Lublin, the sum of the six reference PAH compounds in row rivers is between 80 and 5000 ng 1^{-1} [5].

Even when PAH levels in raw water are high, due to localized industrial pollution, the water treatment can adequately remove PAH compounds to conform to EC limits [1].Conventional water treatment effectively removes the bulk of the PAH compound adsorbed onto particulate matter, although the majority of PAH remaining is fluoranthene due to its high solubility. Between 65 and 76% of the PAH in surface water is bound to particulate matter and so can effectively be removed by physical water treatment processes such as sedimentation, flocculation and filtration. The remainder can be either chemically oxidized [6,7] or removed by activated carbon. Granular activated carbon can remove 99.9% fluoranthene and any of the PAHs remaining in the water. Owing its relatively high solubility, fluoranthene is the major PAH to accumulate in ground water .

The best analytical techniques for determination of PAHs are HPLC and GC methods. Advantages of HPLC are the ability to resolve isomeric PAHs and the selective and sensitive quantitation by UV or fluorescence detection.

Experimental

Samples were collected from:

- the Bystrzyca River – it is left tributary of Wieprz Rivers, with a total length of 70.3 km. River is the disposal of treated domestic and industrial wastewater from the area of Lublin and Świdnik cities.

- the Kręzniczanka River - it is 20.3 km long, left tributary of the Bystrzyca River.

- the Ciemięga River - it is left tributary of the Bystrzyca River, with a length of 41 km.

- the Czerniejowka River - it is 32.4 km long and is right tributary of the Bystrzyca River.

- and wastewater treatment plant "Hajdow" – it is one of the largest wastewater treatment plants in Poland that pays special attention to environmental protection. The wastewater is being let directly into the Bystrzyca River.

The sampling points are present on Figure.

The samples required preconcentration before analysis due to the low levels of PAHs in water samples. The preconcentration study was carried out by passing 1000 ml of sample through Strate C18E syringe column. The PAHs were eluated with 2 ml methanol and volume of solution was reduced to 1 ml. PAHs were determined by HPLC-UV/VIS. Obtained results are listed in Table.

Results and discussion

The aim of our study was to determine the concentration of six chosen polynuclear aromatic hydrocarbons in rivers. Table 1 indicates that generally the total concentration of chosen PAHs in water of the investigated area ranged from 9.34 to 12.382 μ g L¹ (excluding one sampling site for Ciemięga River). This confluence point of the Ciemięga River contained very high level of PAHs, i.e. 778,326 μ g L⁻¹, where about 99.4% it is acenaphthene. Such high level of PAHs it was some episodic contamination probably caused by the intense rainfall. The sample collected after over two months from the same point contained comparable amount of PAHs as other samples. Acenaphthene was the most dominant PAHs in water samples. It may be associated with the fact that the Lublin Upland is an agricultural region and



acenaphthene is constituent of pesticides and wood preservatives, as well as it is products of coal combustion. In most cases, the naphthalene was not observed in collected water samples. Only water from source of the Czerniejówka River contained significant levels of this PAH, 0.437 μ g L⁻¹. The wastewater contained the similar concentrations of PAHs as remaining samples, only concentration of anthracene was higher than in river waters. It is indicated that wastewater treatment plant "Hajdow" is not important source of polynuclear aromatic hydrocarbons.

Fig. Map of the Bystrzyca River showing the location of sampling site.

Ratio values such as phenanthrene/anthracene (PHE/ANT) and fluoranthrene/pyrene (FLU/PYR) had been used to identify the origin of hydrocarbons. Phenanthrene and anthracene are both structural isomers. In particular, phenanthrene is more thermodynamically stable than anthracene; therefore, PHE/ANT ratio is observed to be very high (>10) in PAH petrogenic pollution, but low ratio (<10) in pyrolytic contamination cases. In addition, a FLU/PYR ratio of less than 1 suggested that the origin of PAH was attributed to petrogenic inputs, and values greater than 1 were related to a pyrolytic origin [8,9]. The isomer ratios PHE/ANT for almost of samples were below 2 and FLU/PYR were above 1, what indicated that the major PAH input

was from pyrolytic source (e.g. combustion of fossil fuel). Only for the Ciemięga River PHE/ANT ratios were high (17.39 in December 2008 and 7.92 in February 2009) what indicating that the sources of PAH contamination significant might depend on petrogenic sources.

s	Sampling points		Concentration ($\mu g L^{-1}$)					
Samping points		ACN	ANT	PHE	FLU	NAP	PYR	
Bystrzyca F	River							
13.02.09	Lublin, Piłsudskiego Av.	10.550	0.367	0.737	0.704	-	0.024	
Kręzniczan	ka River							
10.03.09	source	9.39	0.015	0.023	0.031	0.09	0.015	
	confluence	9.45	0.022	-	0.030	-	0.012	
28.04.09	source	9.166	0 083	0.037	0.04	-	0.108	
	confluence	9.005	0.125	0.217	0.232	-	0.175	
Ciemięga R	liver							
07.12.08	confluence	773.65	3.576	-	0.87	-	0.234	
28.02.09	confluence	9.545	0.152	-	0.512	-	0 074	
Czerniejow	ka River							
23.02.09	source	8.072	0.031	0.539	1.037	0.437	0.191	
	confluence	9.776	0.0096	0.076	-	-	0.033	
Sewage treatment Hajdow"		9.920	1.042	0.029	0.121	0.061	-	

Table Concentration of PAH's in collected samples.

PAH abbraviations: ACN - acenaphthene, ANT - anthracene, PHE - phenanthrene,

FLU - fluoranthene, NAP - naphthalene, PYR - pyrene.

Conclusion

In almost all sample the concentrations of six PAHs and individual PAH in river waters were similar. Only one sample had significant amount of PAHs what was connected with episodic contamination. The most dominant PAH in water samples was acenaphthene while naphthalene was not common contamination of studied rivers. Ratio values of PHE/ANT and FLU/PYR suggested that river waters were more dominated by pyrolytic input. In case of Ciemięga River was observed that petrogenic pollution also played significant role.

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