

Spatial and seasonal variation of PAHs concentration in the Spreča river

Mujić, E.^a, Pita Bahto, A.^a, Mahmutović, O.^b, Prazina, N.^b, Papić, S.^b

^aPublic Agency „Vodno područje rijeke Save“ Butile laboratory, Sarajevo, Bosnia and Herzegovina

^bUniversity of Sarajevo, Faculty of Educational Sciences, Skenderija 72, Sarajevo, Bosnia and Herzegovina

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*Corresponding author:

E-mail: omer3m@yahoo.com

Phone: +38762126818

Fax: +38733218828

Abstract: The largest part of the river Spreča flows through the heavily populated region of Tuzla canton, and it is also area of mining-industrial zone. This study monitors the PAHs content, in the part of Spreča's flow which is extremely exposed to these pollutants during the year of 2015. Content of PAHs in the river were analyzed on three locations: prior Modrac lake, in the lake and on the mouth of Spreča into river Bosna. Determination of PAHs in the water was performed by HPLC techniques - fluorescence detection, after liquid-liquid extraction. Eight PAHs, recommended by EU directive, have been analyzed: naphthalene, anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene. The highest concentration was found for naphthalene. Except naphthalene, concentration of all other PAHs was significantly higher on the mouth of Spreča than on the two previous locations. Concentration of all PAHs significantly varies during seasons and it was highest during the winter period. High level of naphthalene and fluoranthene comes from coal-mining area which is prior to Modrac lake and also from the soda drinks chemical industry further away from the lake. Other six PAHs mainly come from soda drinks -chemical industry.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are one of the most widely known pollutants in nature. They occur in all parts of the environment: air, soil, surface, underground, drinking and sea water, ice, food, sediment, plant, animal tissues etc. Depending on the chemical structure they can be poorly degradable with a long period of retention in the environment. They act toxically to the living world. Some of the PAHs show strong carcinogenic and mutagenic activity, leading to acute toxicity, developmental and reproductive toxicity, cytotoxicity and genotoxicity (Magi et al., 2002; WHO, 2000). PAHs, most commonly present in the environment, usually contain from two to seven benzene rings (Lundstedt, 2003). PAHs with the same number of condensed rings may be significantly different, depending on whether these rings have arranged linearly,

angular or clustered (Lundstedt, 2003). In order to determine the good ecological status of water, the EU legislations have listed the priority substances whose concentrations have to be determined in surface waters. Among those substances, eight PAHs have been listed: naphthalene, anthracene, fluoranthene, benzo(b)-fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene (EU Directive, 2013).

PAHs arise mainly due to the incomplete combustion of fossil fuels, wood masses, waste materials or on natural way such as volcanic eruptions and forest fires (Maliszewska-Kordybach, 1999). However, a number of these compounds emerge as a product of the industry, primarily of chemical and mining. PAHs in surface waters mostly have come from air during atmospheric

precipitation, then by discharging wastewater from settlements, waste water that comes from the area where coal has stored, wastewater after treatment of wood and wastewater of other types of industry (Achtana and Hofmann, 2009). The river Spreča, with its tributaries, is exposed to most of the mentioned PAHs emission sources, but the mining area and facilities of chemical industry in this region could be the main source of these pollutants. Coal from mining area is the important source of many PAHs, most naphthalene. These PAHs come in the river flows through the process of coal separation. The soda drinks chemical industry in Lukavac presents a potentially polluter of the river with many types of PAHs.

Purpose of this research was to monitor variation of PAHs content in the river Spreča, during different seasons of one calendar year. On the base of the results, it was done an assessment of the influence of industry, located in the river basin, on the content of PAHs in the aquatic environment. Seasonal monitoring of PAHs concentrations in the river can provide significant data on the impact of certain human activities on their content, which can be used to undertake the activity in order to reduce emissions or to prevent the harmful effects on the environment.

Methods of analysis, from sample preparation to instrumental analysis, must be highly specific and sensitive since that PAHs amounts in the samples are usually very low. The most widely used techniques in analysis of PAHs are high-performance liquid chromatography (HPLC) and gas chromatography (Khan *et al.*, 2005). The most commonly used method for testing river water samples is HPLC technique with fluorescent detection, after liquid-liquid extraction. This method is also specified by ISO standard for the determination of 15 selected PAHs in surface waters, where a mass concentration above 0,010 µg/L has been expected for each individual component (ISO, 2002).

Liquid-liquid extraction of PAHs is quite complicated. However, this is one of the most reliable methods, especially due to the efficiency. Beside water, this method includes extraction of PAHs that absorbed on the suspended matter, which finally gives a better assessment of water pollution.

MATERIALS AND METHODS

Samples

In the middle flow, the river Spreča flows into Modrac lake and also flows out from the other side of the lake. A mining area is placed in part of flow prior the lake, while the chemical industry is situated near the Spreča, after lake. Related to this, the content of PAHs in the river has been analyzed on the three locations: prior the Modrac lake, in the lake and at the mouth of the Spreča into the river Bosna. Samples from locations prior the lake and at the mouth of the Spreča, have been collected and analyzed monthly, during the year of 2015. Samples from lake have been collected and analyzed four time in mentioned year.

Water was collected in dark-glass bottles, previously weighed. The bottles were filled to the top (approx. 1000 mL), stored at about + 4 °C and protected from light until extraction was made. Extraction was performed within 24 h of the sampling, to avoid adsorption losses. If the complete analysis cannot be done within 24 h, the part of

sample from the sampling bottle has to be removed until the volume of 1000 ± 10 mL. Volume of sample is determined by weighing of bottle. Then 25 mL of hexane is added and well-stirred. Sample treated on this way, protected from light, can be stored 72 h at + 4 °C (ISO, 2014).

Selected PAHs

The analyses included 8 PAHs recommended by EU directive: naphthalene, anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene.

Chemicals and equipment

The following chemicals and equipment were used for analysis. Chemicals: deionized water; hexane (HPLC grade, Fisher Scientific); N,N-dimethylformamid (>99,9 %, Roth), acetonitrile (HPLC grade, Baker); acetone (HPLC grade, Fisher Scientific); sodium sulfate (p.a.); nitrogen (99,999 %); PAH standards: naphthalene (99,7 %, Supelco), anthracene (99,0 %, Supelco), fluoranthene (99,5 %, Supelco), benzo(b)fluoranthene (97,3 %, Supelco), benzo(k)fluoranthene (99,5 %, Supelco), benzo(a)pyrene (95 %, Supelco), indeno(1,2,3-cd)pyrene (99,7 %, Supelco) and benzo(ghi)perylene (99,4 %, Supelco). Equipment: magnetic stirrer (Agimatic-E, Selecta); rotavapor (Laborota 4011 digital, Heidolph); coulumn C18 (Zorbax Eclipse PAH, Analytical 4,6 x 250 mm; 5-Micron, Agilent); HPLC system with fluorescence detector (Solvent delivery module LC-20AT Prominence; On-line Degasser DGU-20A5; Auto sampler SIL-20A Prominence; Column oven CTO-20AC Prominence; Spectrofluorometric detector RF-10Axl; System controller CBM-20A Prominence, SHIMADZU).

The extraction of PAHs

Volume of the water sample in the bottle was adjusted on the 1000 ± 10 mL, by removing a part of sample. Exact volume of sample has been determined by weighing the bottle (difference between full and empty bottle).

Then, 25 mL of hexane was added and well-stirred. The sample was extracted by mixing it on a magnetic stirrer, set at 1000 rpm, about 60 min. After extraction, sample was transferred to a separating funnel and left until phase separation, for at least 5 minutes.

The hexane layer was transferred to a 100 mL conical bottle and the extract was dried with sodium sulfate for at least 30 min. The dried extract was decanted in the solvent evaporator flask. The conical bottle was washed with 5 mL of hexane, two times, and all added to the same bottle for solvent evaporation.

The hexane extract was lightly evaporated to volume of 2 mL approximately. It was done by rotary-evaporator, under pressure of 210 mbar and in the thermostatic bath at 30 °C. It has been performed carefully to avoid evaporation to the dryness, because it can produce losses of PAHs with 2 and 3 benzene rings.

The concentrated 2 mL extract was transferred to the test tube. To this extract it was added 250 µL of N,N-dimethylformamide and 500 µL of acetone and mixed. Hexane and acetone were removed with a gentle stream of

nitrogen, so that the volume of the extract was reduced to a volume between 200 μL and 250 μL , the remain was N,N-dimethylformamide with the analyte. The extract was diluted to 2 mL with acetonitrile (ISO, 2002).

Analysis

HPLC separation was performed with acetonitrile/water combination on the polymerically bonded C18 column optimized for the separation of PAHs. Elution was carried out with a solvent mixture in a gradient mode. Time and percentages of acetonitrile: 0-2 min. 60-60 %; 2-15 min. 60-100 %; 15-20 min. 100 %; 20-22 min. 100-60 %; 22-26 min. 60-60 %. Separation was carried out at constant temperature of 30 $^{\circ}\text{C}$. The injection volume was 10 μL . Fluorescence detector was used for detection. The appropriate wavelength for excitation and emission for respective individual PAHs has been adjusted with respect to their sensitivity and selectivity. The calibration curve was made from five different concentration standards, diluted in acetonitrile (ISO, 2002).

RESULTS AND DISCUSSION

The basin of the river Spreča is exposed by two major industrial sources of PAHs. The first are coal mines Đurđevik and Banovići, where inevitably comes the emission of PAHs into water during the coal separation process. The mines are bound to the river Spreča by the left tributary, prior to the Modrac lake. Another important source of PAH is a coke-chemical industry, which is potentially the most dangerous emitter of these substances. It is located in Lukavac, in the part of Spreča's flow down

the lake. The habitants of heavily populated region surrounding the lake, commonly use coal and wood for the heating of their households. With rainfall and poor air circulation during the winter months, emission of PAHs from households may significantly increase of PAH concentration in the river, depending on weather conditions.

Concentration of all tested PAHs has been higher on the mouth of the river Spreča than on two previously locations, and for most of PAHs this difference in concentration was extremely high (Figure 1). This result was expected, with regard to the accumulation of PAHs from both significant sources during the flowing of the river, and the inability that PAHs to be degraded within a relatively short time of flow. The exception is naphthalene, which was on annual-average in the highest concentration at the mouth of Spreča, but in certain months naphthalene was in highest concentration on the location prior the lake. The reason for reduction of naphthalene at the mouth, in some months, could be relatively rapid degradation of naphthalene (Oleszczuk and Baran, 2003; ATSDR, 1995). Indication for degradation of naphthalene was also its content during the winter prior the lake and March's concentration in the lake (Figure 1b, Figure 1c). The concentration of naphthalene during the March in the lake was much lower than in the Spreča prior the lake during the previous months, that indicates the relatively rapid decomposition of naphthalene. It is true that lake also has been filled from several smaller streams, but it is not so significant for this decrease.

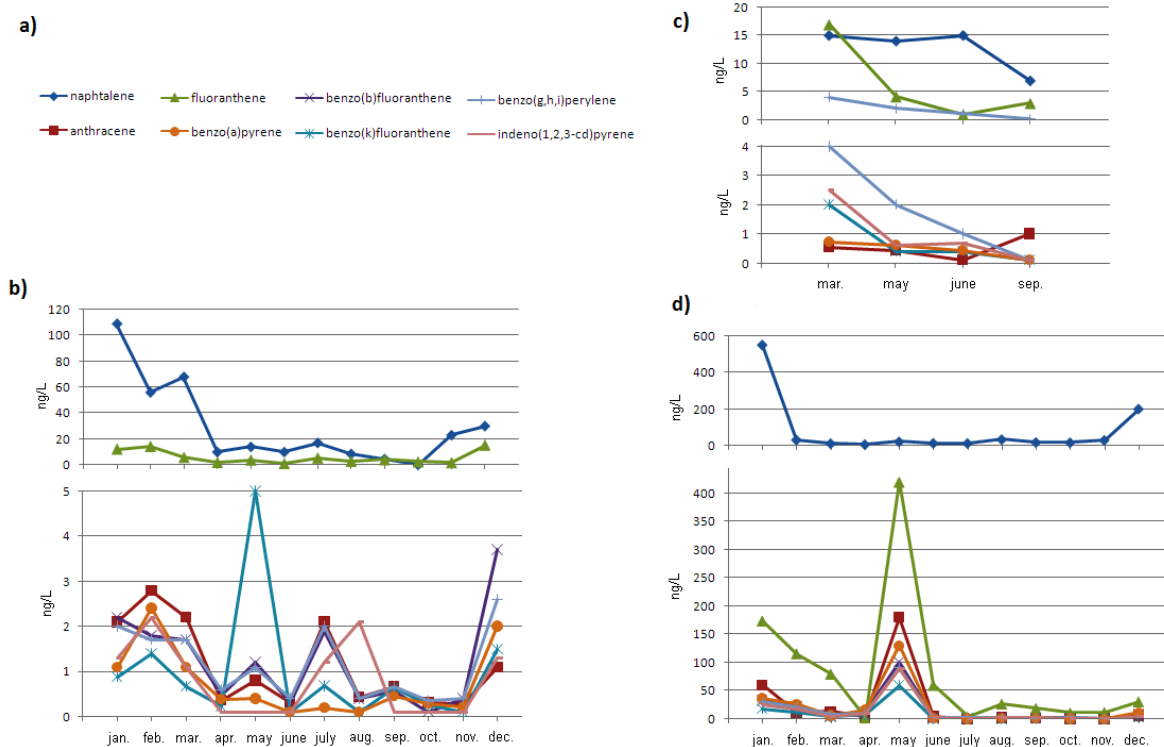


Figure 1: Concentration of PAHs: a) legend; b) in the Spreča river, prior the Modrac lake; c) in the Modrac lake; d) on the mouth of Spreča into Bosna river

The results, especially Figure 1d, indicate different sources of pollution for naphthalene compared to other PAHs, because concentration of naphthalene was not following variation in the content of other PAHs. Certainly, a great source of naphthalene in the river Spreča lies in the mining zone prior to the lake, but its increased concentration during winter months means that there is a significant emission during the heating season (Figure 1b). It means that naphthalene in the river comes from several sources, including non-industrial (coal and wood burning during the heating season), and not only from the coal separation process and the coke-chemical industry. Otherwise, among all tested PAHs, the greatest concentration was found for naphthalene. On the other side, that fact doesn't present a problem because allowed concentration for naphthalene is high, so all values for this PAH were in the scope of acceptable ecological standards

Excluding naphthalene, other seven PAHs were in extremely higher concentration on the mouth of river than on the previous locations (Figure 1). It assumes that the main source of these PAHs is in the part of the river flow after the lake. Cause of this probably comes from soda drinks chemical industry located near the river, after the lake. Among these PAHs the highest concentration was found for fluoranthene. The reason could be in its emission from other sources - fluoranthene has been significantly contained in the river on the measure points prior to the lake and in the lake (Figure 1b, Figure 1c). Fluoranthene is contained in many types of coal and surely came into river by the process of coal separation (Chen *et al.*, 2004; Willsch and Radke, 1995). As natural components of coal, from the group of analyzed PAHs, naphthalene is most common followed by fluoranthene, while other PAHs are significantly less presented (Achtana and Hofmann, 2009). Emission from process of coal separation, slow degradation in environment and emission from soda drinks chemical industry contributed to high content fluoranthene on the mouth of Spreča. However, obtained values of fluoranthene rarely exceed values that are environmentally hazardous, while the annual average level has been acceptable to the environment (EU Directive, 2013).

The winter-summer variations were the most expressed for the naphthalene and fluoranthene concentrations. Higher concentrations of naphthalene are usual in the environment during the heating season, what is also mentioned for fluoranthene in some studies (Bari *et al.*, 2010). Other six PAHs: anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, showed some variations of content during summer and winter season (Figure 1b, Figure 1c). For these six PAHs emission during coal separation was excluded because they didn't show monthly extreme values. During the winter period they could be emitted in air by combusting biomass and coal, as they shown high content in that period.

The densely populated region, with precipitation and poor air circulation contributes to this. Also, these six PAHs were in significantly higher concentration at the mouth of the river Spreča than on the two previous mentioned points. The reason for this is their very low presence in coal (Achtana and Hofmann, 2009). In the river, significant levels were detected in the river, down the lake presumably as a result of emission from the soda drinks chemical industry. In all measurements and calculations, monthly and yearly, the anthracene has been within the environmentally safe level. The other five PAHs, at the river mouth, often had value that a risky for the environment, as well as at the annual average, according to the environmental standards of EU.

The PAHs content in the lake showed the lower seasonal oscillations than in the river (Figure 1c). Of course, it is caused by long period of accumulation of water, mixing and homogenization of different monthly values for river. The concentration in March is a good indicator of the average value of the PAHs during the later winter period, and in September for the summer period. Ratio of PAHs concentration for March/September in the lake shows a clear seasonal variation, evident for most PAHs. There are several reasons for decreasing of PAHs content in the lake during the summer such as significant reduction of PAH emission in the air usually caused by coal using households, as well as stronger air circulation during that period. Also, more intense sunlight during the summer leads to faster degradation of PAHs (ATSDR, 1995).

The results from Figure 1d are the most important, because they are from the mouth of the river and sum up all the pollutants and consequences for the wider region. Regarding that, river Spreča has no good ecological status with regard to PAH concentration, which has been assumed.

CONCLUSIONS

Concentrations of PAHs often exceeded the maximum of allowed monthly value that specified in EU standards, related to good ecological status of the river (EU Directive, 2013). The highest detected concentration was for naphthalene, but since is relatively quickly degradable, it is not serious threat for the environment. All PAHs showed seasonal variations and increased concentration during the winter. During the coal separation in mining area, the most emitted PAH is naphthalene, and slightly less fluoranthene. Among all tested PAHs, fluoranthene with its content and environmental impact presents the most serious ecological threat to the river Spreča. Naphthalene and fluoranthene come from multiple sources while the other PAHs mainly have the origin from the soda drinks chemical industrial zone, located in the part of the flow after the lake. Finally, it could be concluded that the river Spreča is contaminated with PAHs on the level that could be threat to living organisms in the river.

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Summary/Sažetak

Najvećim dijelom rijeka Spreča protiče kroz gusto naseljenu regiju Tuzlanskog kantona, a to je ujedno i područje rudarsko-industrijske zone. Ovaj rad prati sadržaj policikličnih aromatskih ugljikovodika (PAH) tokom kalendarske godine, u dijelu Spreče koji je izrazito izložen ovim polutantima. Sadržaj PAH-ova u rijeci je analiziran na tri lokacije: prije jezera Modrac, u jezeru i na ušću Spreče u rijeku Bosnu. Analiza PAH-ova obavljena je tehnikom HPLC uz fluorescentni detector, a nakon ekstrakcije tečno-tečno. Analizirano je osam PAH-ova, u skladu s preporukom direktive Evropske unije. Generalno, među analiziranim PAH-ovima, najveću koncentraciju je imao naftalen. Na ušću Spreče u Bosnu je nađena najveća koncentracija svih PAH-ova, osobito fluorantena. Izuzev naftalena, sadržaj svih ostalih PAH-ova je osjetno veći na ušću Spreče nego na dvije lokacije prije. Koncentracija svih PAH-ova značajno varira tokom sezona i najveća je u zimskom periodu. Visok nivo naftalena i fluorantena potiče iz zone rudnika uglja smještene prije jezera Modrac i koksno-hemijske industrije koja se nalazi u dijelu toka nakon Jezera. Ostali PAH-ovi najviše potiču iz koksno-hemijske industrije.