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# THE ASSESSMENT OF CONTAMINATION AND SOURCE OF POLYCYCLIC AROMATIC HYDROCARBONS FROM THE SEDIMENTS OF THE SOMEȘ RIVER

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**ABSTRACT.** Polycyclic aromatic hydrocarbons (PAHs) represent an important class of environmental pollutants that are derived from both natural and anthropogenic sources. Due to their toxic, mutagenic, carcinogenic and bioaccumulation potential there are continuous concerns over the PAHs contents in the aquatic media. The aim of this work was to evaluate the distribution of PAHs in the sediments of Someș River, to assess their occurrence and to establish the origin (pyrogenic/petrogenic) of pollution sources. 13 sampling points were selected covering the distance from Cluj-Napoca to Satu Mare in order to assess the contribution of urban agglomeration over the concentration of PAHs in sediments. For the determination of the compounds GC-MS analyses were performed. PAH diagnostic ratios have been used as a tool for identifying and assessing the pollution emission sources. The obtained results showed that, the concentration of PAHs measured varied between 33.3 and 251.6 μg $kg^{-1}$. Benzo[a]pyrene was found in most of the samples. A general tendency of higher concentration values on the exit point of the river from cities than from the entering point was found. The isomeric ratios indicated that most of the sources were of pyrogenic origin, rather than petrogenic. As expected, the concentrations of ΣPAHs were below the maximum accepted limit of 1 mg $kg^{-1}$ regulated in Romania.

**Key words:** *Someș River, PAHs, GC-MS, sediments.*

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds containing two or more condensed aromatic rings (Souza et al., 2018).

PAHs are ubiquitous organic pollutants all over the world, semi-volatile, lipophilic, photosensitive, persistent, having a high capacity of transport in the environment and have low solubility in water. With a wide environmental presence and multitude, only 16 congeners were classified as Prior Pollutants by the United States Environmental Protection Agency (USEPA) (Riaz et al., 2019; He et al., 2014; Zeng et al., 2018), some of them being considered carcinogens, mutagens and tend to bioaccumulate in the organisms (Tu et al., 2018; Zeng et al., 2018).

Rivers are the main way of transporting pollutants from the terrestrial environment into the aquatic environment. Polluted river beds and suspended particles can have a significant impact on riverine ecosystems (Schwientek et al., 2017).

The advantage of using sediments is that the fraction of organic matter influences the PAHs content, so once adsorbed, PAHs are no longer released into the water (Belles et al., 2016). For this reason, unlike other chemical compounds, such as trace elements, dioxins, chlorinated pesticides etc. the concentration of PAHs in sediments does not decrease with the passage of time (Sanctorum et al., 2011). Thus, analysing the content of PAHs in water or in suspended particles gives a picture of the degree of contamination of PAHs at that moment. In the meantime, the sediment provides a historical picture.

From this reason, in the last time, the use of sediments for the evaluation of the PAHs level rivers contamination is a topical subject for many researches (He et al., 2014; Grung et al., 2016; Beldean-Galea et al., 2016; Liu et al., 2017; Dubovina et al., 2018; dos Santos Rodrigues et al., 2018; Zeng et al., 2018; Davis et al., 2018).

Moreover, the normative regarding the classification of surface water quality in order to establish the ecological state of the water bodies stipulate that, the maximum allowable amount of PAHs (benzo[a]pyrene, naphthalene, anthracene, phenanthrene, fluoranthene, benzo[a]anthracene, crysene, indeno(1,2,3-cd)pyrene and benz[k]fluoranthene) in sediments is 1 mg kg$^{-1}$ (Rowater).

PAHs appear in the environment from different sources and can be characterized as natural (resulting from chemical and biological transformations of organic matter, volcanic eruption, forest fires, oil seeps) (Rocha and Palma, 2019; Riaz et al., 2019) and anthropogenic which can be classified in pyrogenic (incomplete combustion of organic matter, fossil fuels and biomass such coal and wood, or industrial waste) and petrogenic originating from crude and refined petroleum like kerosene, gasoline, lubricating oils, diesel, asphalt etc. (Davis et al., 2018; He et al., 2014).

Identification of PAH sources in sediments is necessary, not only because of their persistence and effects on organisms, but also because sediments behave as a secondary source of PAH pollution, being a reservoir of these compounds. Locating the origins of PAHs in ecosystems allows reducing pollution from the sources of emissions. A challenge in identifying sources of pollution is the presence of a large number of sources of emissions (Rocha and Palma, 2019).

In the last time, different researches were carried out on this subject. The conclusion is that the isomeric ratio of PAHs seems to be the most convenient methodology for the identification of the sources of PAHs in the environment because it allows the differentiation of PAHs from petrogenic and pyrogenic sources (Tobiszewski and Namieśnik, 2012; Yunker et al., 2002).

The aim of this work was to investigate the occurrence of PAHs in sediments from the Someș River, in 13 points, before and after the entrance of the river in major urban agglomerations in its river basin area and to establish the pollution emission sources, applying different diagnostic ratios.

## MATERIAL AND METHODS

### *Chemicals and reagents*

For qualitative and quantitative analysis, a PAH standard mixture was used and it contained 16 priority congeners listed by the United States Environmental Protection Agency (US EPA): naphthalene (Nap), acenaphthylene (Acy), acenaphtene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP) in concentration of 1.0 µg mL$^{-1}$ of each compound was obtained from Sigma Aldrich (Germany).

Silica, alumina and granular anhydrous sodium sulphate used for the extract clean-up were purchase from Merck (Germany). All solvents used for sample processing (dichloromethane, n-hexane, acetone) were HPLC grade. Highly purified deionized water used in the chemical analysis was prepared using a Direct-Q UV 3 system (18.2 MΩ/cm) from Millipore (Molsheim, France).

### *Sample collection and geographical coordinates*

A total of thirteen surface sediment samples were collected in May 2017 from different location of the Someș River watershed. The name of the sampling point, assigned number and the geographical coordinates are given in table 1, and in the map of the studied watershed (figure 1).

**Table 1.** Sampling points, abbreviation and the geographical coordinates

| Sampling point | Number | Geographical coordinates | |
|---|---|---|---|
| | | Latitude (N) | Longitude (E) |
| Entrance in Cluj-Napoca city, Someșul Mic River | P1 | 46°75´9.47” | 23°53´5.04” |
| Exit of Cluj-Napoca city, Someșul Mic River | P2 | 46°78´7.51” | 23°70´8.68” |
| Entrance in Gherla city, Someșul Mic River | P3 | 47°01´6.78” | 23°88´5.65” |
| Exit of Gherla city, Someșul Mic River | P4 | 47°06´1.15” | 23°91´6.32” |
| Entrance in Dej city, Someșul Mic River | P5 | 47°14´4.32” | 23°91´6.78” |
| Entrance in Dej city, Someșul Mare River | P6 | 47°14´6.24” | 23°91´2.87” |
| Exit of Dej city, Someș River | P7 | 47°17´0.98” | 23°84´7.62” |
| Entrance in Jibou town, Someș River | P8 | 47°24´4.66” | 23°28´4.52” |
| Exit of Jibou town, Someș River | P9 | 47°30´5.92” | 23°27´5.26” |
| Before confluence with Lăpuș River, Someș River | P10 | 47°65´5.12” | 23°40´1.74” |
| After confluence with Lăpuș River, Someș River | P11 | 47°65´9.25” | 23°39´9.25” |
| Entrance in Satu Mare city, Someș River | P12 | 47°78´2.58” | 22°92´1.68” |
| Exit of Satu Mare city, Someș River | P13 | 47°79´8.17” | 22°83´7.43” |

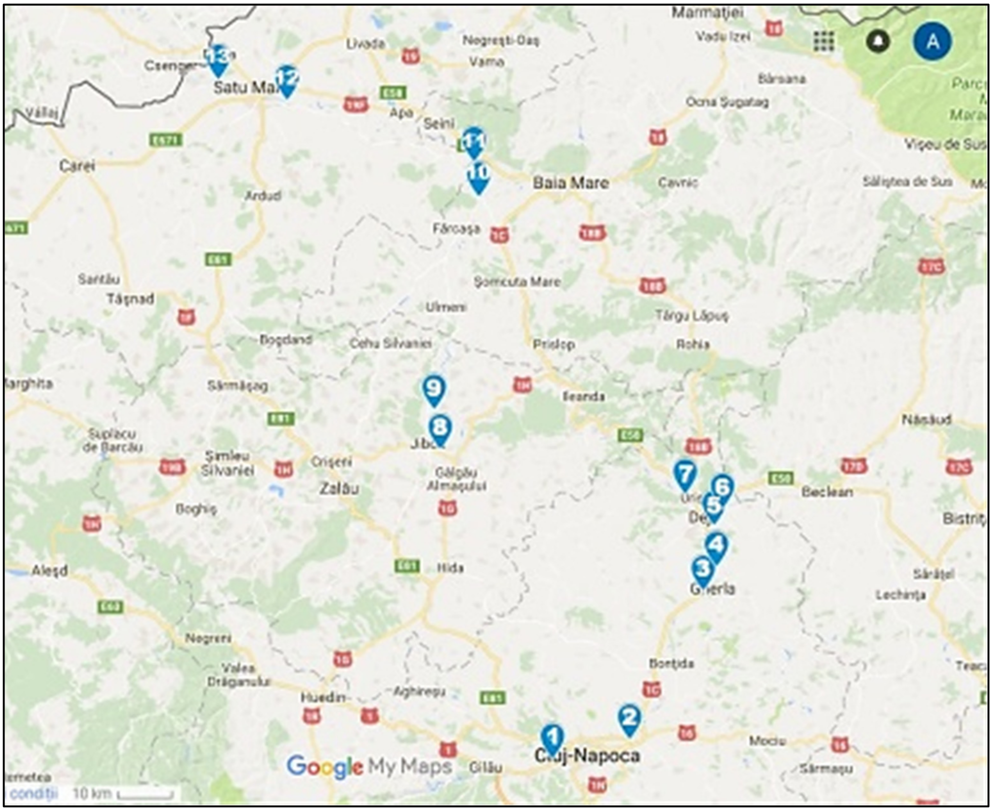

Fig. 1. Map of the studied watershed and the location of sampling point

Samples were collected using a stainless steel shovel at about 0.5 – 2.5 m water depth, sealed in clean polyethylene bags and stored at 4℃ until analysis. Before extraction, samples were oven-dried at 40°C, ground up in a gear mortar, and then sieved through a 2 mm-mesh sieve to remove the large stones, roots or other coarse particles.

### *Instrumentation*

PAHs compounds were analysed by gas chromatography coupled with mass spectrometry (GC–MS) using a Focus GC-DSQII, (ThermoElectron) equipped with a DB-5 MS column (25 m × 0.25 mm × 0.25 μm) and operating in electron impact (EI) ionization mode (70 eV). Helium of high purity at a constant flow rate of 1.2 mL min$^{-1}$ was used as carrier gas. A volume of 1.0 µL sample was injected in the splitless mode using a TriPlus autosampler. The injector, detector, ion source, and transfer line temperatures were 280, 310, 200 and 300ºC, respectively. The separation of the compounds was performed with a gradient temperature program of 10ºC min$^{-1}$ from 120 to 220ºC, and of 3ºC min$^{-1}$ from 220 to 300 ºC, with a holding time of 1 min. Identification of individual PAH compounds was based on the selected ion monitoring (SIM) mode by the comparison of retention times between sample and the standard mixture. Quantification was carried out using external standard method. All data acquisition was performed using the Xcalibur™ software.

### *Sample extraction and clean-up*

The extraction of PAH from sediment samples were performed by ultrasound extraction procedure (Beldean-Galea et al., 2016) using the follow protocol: 5 g of dry sediment samples were placed into a 50-mL conical vial and after the addition of 20 mL acetone:hexane mixture (1:1, *v/v*), the vial were capped and sonicated for 20 min using an ultrasonic bath, model Elmasonic acquired from Elma Schmidbauer GmbH, Germany. After sonication, the sample was centrifuged and the upper layer (solvent extract) was transferred in a round flask. The extraction procedure was repeated two more times with fresh solvent and finally the all three extracts were reunified together. The resulted extract was, concentrated to approximately 2 mL using a rotary evaporator.

For the purification of the extract, silica-alumina column (10 mm i.d., made of glass) was prepared by filling from bottom to top with 4 g activated silica, 4 g activated alumina and 1 g dehydrated sodium sulphate. The column was then conditioned with 20 mL of n-hexane and used for extract purification. For purification, the concentrated extract was loaded to the column and the target compounds (PAH) were eluted with a mixture of 40 mL n-hexane/ dichloromethane (80:20 *v/v*). The collected fraction was concentrated by rotary evaporation to approximately 2 mL and then reduced down to 1 mL under nitrogen stream.

The obtained extract was then subjected to GC-MS analysis.

## RESULTS AND DISCUSSIONS

### *PAH concentrations in sediment samples*

The concentration of the PAHs in the analysed sediment samples were situated between 33.25 and 251.6 μg kg$^{-1}$ (table 2). The highest value was obtained in the sampling point P2 (Exit from Cluj-Napoca city, Someșul Mic River), while the lowest value in the sampling point P1 (Entrance in Cluj-Napoca city, Someșul Mic River).

**Table 2.** PAH concentrations in the analysed samples

| **Compound Abreviation** | **Sampling point/concentration (μg kg$^{-1}$)** | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **P1** | **P2** | **P3** | **P4** | **P5** | **P6** | **P7** | **P8** | **P9** | **P10** | **P11** | **P12** | **P13** |
| Nap | 2.57 | 39.4 | 10.7 | 13.3 | 6.27 | 4.16 | 6.07 | 10.6 | 4.34 | 4.90 | 13.4 | 3.00 | 2.20 |
| Acy | 0.24 | nd[*] | nd | 1.78 | nd | nd | 0.53 | nd | nd | nd | nd | nd | nd |
| Ace | 0.76 | nd | nd | 0.62 | nd | nd | 1.66 | 3.20 | 4.74 | 1.03 | 0.46 | 2.71 | 0.49 |
| Fl | 1.01 | 7.76 | 1.59 | 2.26 | 3.41 | 1.80 | 9.64 | 1.68 | 3.17 | 5.13 | 2.11 | 1.23 | 2.52 |
| Ant | 5.93 | 21.2 | 19.1 | 15.3 | 22.2 | 10.0 | 25.4 | 14.5 | 25.7 | 15.5 | 26.8 | 13.9 | 11.9 |
| Phe | 0.98 | 9.28 | 7.43 | 7.76 | 7.00 | 3.69 | 12.6 | 5.69 | 13.4 | 5.07 | 7.77 | 4.51 | 4.07 |
| Flu | 6.42 | 43.8 | 18.0 | 20.2 | 17.6 | 3.91 | 20.4 | 11.8 | 36.2 | 8.71 | 8.04 | 8.51 | 10.8 |
| Pyr | 6.31 | 42.8 | 17.8 | 18.9 | 17.8 | 4.47 | 25.7 | 13.7 | 37.2 | 8.62 | 8.34 | 7.91 | 11.3 |
| BaA | 0.74 | 15.5 | 3.95 | 1.53 | 1.16 | 0.11 | 1.44 | 2.93 | 1.78 | 0.44 | 1.46 | 1.68 | 1.12 |
| Chr | 3.26 | 24.3 | 6.53 | 4.52 | 4.96 | 0.88 | 3.55 | 6.13 | 5.65 | 1.81 | 6.48 | 3.21 | 3.95 |
| BbF + BkF | 2.00 | 13.4 | 4.38 | 7.48 | 2.94 | 0.15 | 11.0 | 2.33 | 7.02 | 2.71 | 0.11 | 1.20 | 2.07 |
| **BaP** | **1.56** | **10.4** | **2.33** | **7.36** | **2.11** | **0.56** | **4.52** | **1.59** | **5.93** | **1.37** | **8.31** | **0.54** | **25.1** |
| IcdP | 0.80 | 4.42 | 1.33 | 2.81 | 1.06 | 0.42 | 3.20 | 0.71 | 2.44 | 0.97 | 0.57 | 2.48 | 8.12 |
| DahA | 1.06 | 8.82 | 2.78 | 4.81 | 1.69 | 1.47 | 8.68 | 1.06 | 2.25 | 1.45 | 0.74 | 0.75 | 0.83 |
| BghiP | 0.61 | 10.6 | 1.92 | 4.85 | 2.13 | 2.20 | 7.68 | 1.12 | 1.63 | 2.03 | 0.76 | 2.05 | 2.51 |
| Total PAH | 33.3 | 251.6 | 97.8 | 113.6 | 89.3 | 33.8 | 142.1 | 77.1 | 151.7 | 59.8 | 85.3 | 53.7 | 87.1 |
| $\sum_{LMW}/\sum_{HMW}$ | 0.53 | 0.45 | 0.66 | 0.57 | 0.77 | 1.39 | 0.65 | 0.86 | 0.51 | 1.13 | 1.45 | 0.89 | 0.32 |
| Ant/(Ant+Phe) | 0.86 | 0.70 | 0.72 | 0.66 | 0.76 | 0.73 | 0.67 | 0.72 | 0.66 | 0.75 | 0.78 | 0.75 | 0.75 |
| Flu/(Flu+Pyr) | 0.50 | 0.51 | 0.50 | 0.52 | 0.50 | 0.47 | 0.44 | 0.46 | 0.49 | 0.50 | 0.49 | 0.52 | 0.49 |
| IcdP/(IcdP+BghiP) | 0.57 | 0.29 | 0.41 | 0.37 | 0.33 | 0.16 | 0.29 | 0.39 | 0.60 | 0.32 | 0.43 | 0.55 | 0.76 |
| BaA/(BaA+Chr) | 0.25 | 0.39 | 0.38 | 0.25 | 0.23 | 0.11 | 0.29 | 0.32 | 0.24 | 0.20 | 0.18 | 0.34 | 0.22 |

[*] *nd* - not detected

It can also be observed that the compounds mentioned in the Romanian legislation referred to PAHs in sediment (benzo[a]pyrene, naphthalene, anthracene, phenanthrene, fluoranthene, benzo[a]anthracene, crysene, indeno(1,2,3-cd)pyrene and benz[k]fluoranthene) are presented in all analysed samples but, their concentrations do not exceed the maximum allowable concentration (1 mg kg$^{-1}$). This fact indicates that, PAHs cause no adverse ecological effects in studied area.

Anyway, the analysis of the PAH concentration in water or sediment samples provide information about the level of contamination and do not give information about the sources of pollution. In this way other research are necessary for the identification of the PAHs pollution sources and implicitly to establish ways to reduce PAH pollution of water courses.

### *Identification of PAH sources*

In order to assess the sources of PAH discharged in the Someș River, ratios of $\Sigma_{LMW}/\Sigma_{HMW}$ (sum of PAH with low molecular weight (2-3 aromatic rings) (LMW) and PAH with high molecular weight (more than 3 aromatic rings), (HMW)), Ant/(Ant+Phe), Flu/(Flu+Pyr), IcdP/(IcdP+BghiP) and BaA/(BaA+Chr), were considered. According to the values obtained from these ratios, estimates of the sources of PAHs pollution can be made. (table 3).

**Table 3.** Diagnostic ratios used to identify the origin of PAHs

| Diagnostic Ratio | Pyrolytic source | Petrogenic source | Fuel combustion | Grass/coal/ wood combustion | Reference |
|---|---|---|---|---|---|
| Ant/(Ant + Phe) | > 0.1 | ≤ 0.1 | ndef* | ndef | Zhu et al., 2008 |
| Flu/(Flu+Pyr) | > 0.5 | < 0.4 | 0.4–0.5 | > 0.5 | Yunker et al., 2002 |
| IcdP/(IcdP+BghiP) | > 0.5 | < 0.2 | 0.2–0.5 | > 0.5 | |
| BaA/(BaA+Chr) | > 0.2 | < 0.2 | > 0.35 | 0.2-0.35 | Tobiszewski & Namieśnik, 2012 |
| $\sum_{LMW}/\sum_{HMW}$ | < 1 | > 1 | ndef | ndef | |

**ndef – not defined*

The obtained results suggest that mixed sources of pollution with PAH occurs in the investigated samples (table 4).

**Table 4.** Values of the diagnostic ratios obtained for the analysed sediment samples

| | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 | P10 | P11 | P12 | P13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\sum_{LMW}/\sum_{HMW}$ | Pyr$^a$ | Pyr | Pyr | Pyr | Pyr | Petr$^b$ | Pyr | Pyr | Pyr | Petr | Petr | Pyr | Pyr |
| Ant/(Ant+Phe) | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr |
| Flu/(Flu+Pyr) | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr |
| IcdP/(IcdP+BghiP) | Pyr | Pyr | Pyr | Pyr | Pyr | Petr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr | Pyr |
| BaA/(BaA+Chr) | Pyr | Pyr | Pyr | Pyr | Pyr | Petr | Pyr | Pyr | Pyr | Petr | Petr | Pyr | Pyr |

where: Pyr$^a$ mean “Pyrolitic source” and Petr$^b$ means “Petrogenic source”

Thus, from the ratio of $\Sigma_{LMW}/\Sigma_{HMW}$ it can be observed that, excepting the sampling points P6, P10 and P11, the main source of pollution in the investigated sites is pyrogenic, and the obtained ratios exceed “1” in almost all sampling points. Similar results have been obtained for other used ratios which confirm that, the main sources of pollution in the investigated area are pyrogenic sources.

For a better estimation of the PAH sources the cross plot of the ratios of Ant/(Ant+Phe) against Flu/(Flu+Pyr) and IcdP/(IcdP+BghiP) against BaA/(BaA+Chr) were done (figures 3 and 4).

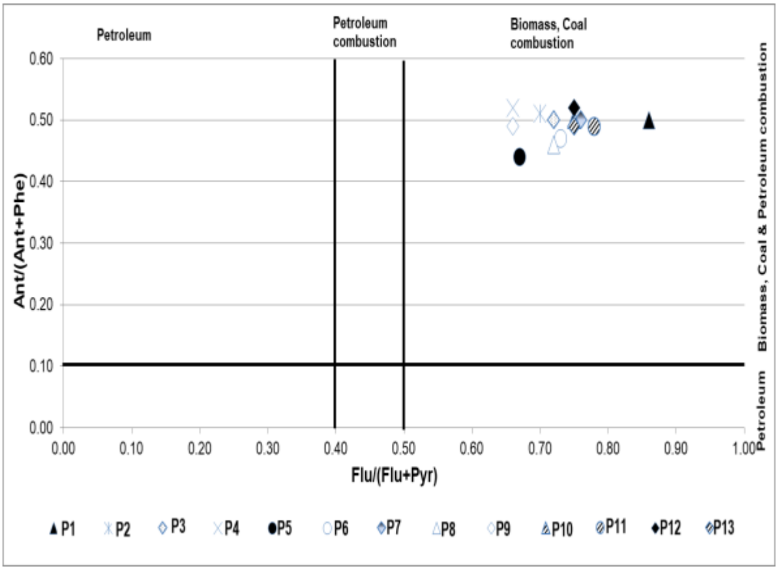

**Fig. 3.** The cross plot of the ratio of Ant/(Ant+Phe) against Flu/(Flu+Pyr)

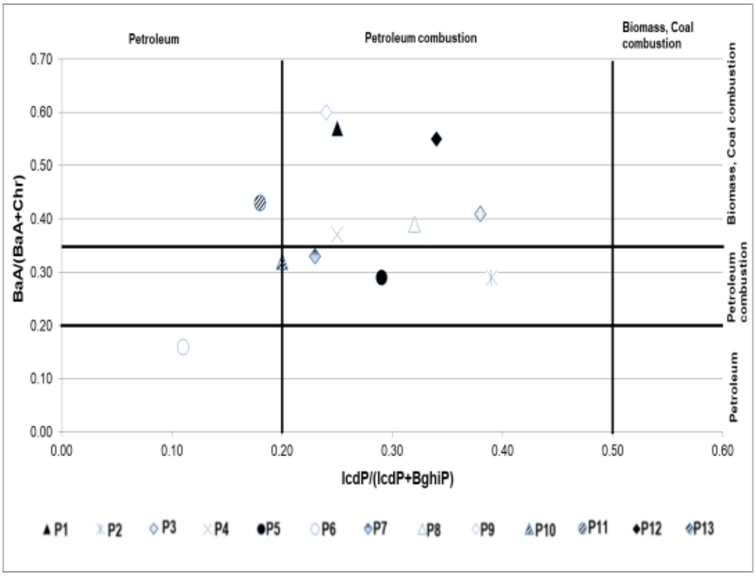

**Fig. 4.** The cross plot of the ratio of IcdP/(IcdP+BghiP) against BaA/(BaA+Chr)

Thus, from the cross plot of the ratio of Ant/(Ant+Phe) against Flu/(Flu+Pyr) it can be observed that the main source of PAH is the combustion of biomass, coal and petroleum products, while for the cross plot of the ratio of IcdP/(IcdP+BghiP) against BaA/(BaA+Chr) it can be observed that, in the sampling points P6, P10 and P11 the source of pollution has a petrogenic fingerprint while in other the petroleum combustion fingerprint.

Taking into consideration the obtained results, it can be concluded that the PAH pattern obtained for the analysed sediment are in connection with the anthropic activities, the petrogenic fingerprint being a result of the petroleum products leaks and to an inefficient removal during the wastewater treatment, while the pyrogenic fingerprint is given mainly by the burning of wood and coal necessary for houses heating and to the combustion of petroleum products generated by traffic or different industrial activities.

## CONCLUSIONS

The results of the study showed that, in the studied area, the concentration of the PAH in sediment samples ranged between 33.25 and 251.6 μg $kg^{-1}$ μg $kg^{-1}$. The lowest values were obtained at the entrance of the river into the urban agglomerations while the highest at the exit which indicate that the urban activities are the main reason for the PAHs contamination of the river.

The concentrations of the PAH in sediment samples do not exceed the maximum allowable concentration established by the Romanian legislation which indicated that PAH causes no adverse ecological effects in the area under study.

Regarding the PAH pattern, the obtained results indicate that mixed sources, petrogenic, and pyrogenic are present in the analysed sediment samples. The main sources of pollution are the leaks of petroleum products, the combustion of fossil fuels and biomass and coal combustions respectively.

## REFERENCES

Belles A., Alary C., Mamindy-Pajany Y., Abriak N.E., 2016, Relationship between the water-exchangeable fraction of PAH and the organic matter composition of sediments. *Environmental Pollution*, **219**, pp. 512-518.

Beldean-Galea M.S., Mihăiescu R., Arghiuş V., Croitoru A., Horvath C., Coman V., 2016, Occurrence and Sources of Polycyclic Aromatic Hydrocarbons in the Tisza River and its Romanian Tributaries. *Water Air and Soil Pollution*, **227**(10), 377 p.

Davis E., Walker T.R., Adams M., Willis R., 2018, Characterization of polycyclic aromatic hydrocarbons (PAHs) in small craft harbour (SCH) sediments in Nova Scotia, Canada. *Marine Pollution Bulletin*, **137**, pp. 285–294.

dos Santos Rodrigues C.C., Vieira Santos L.G.G., Santos E., Damasceno F.C., Martins Corrêa J.A., 2018, Polycyclic aromatic hydrocarbons in sediments of the Amazon River Estuary (Amapá, Northern Brazil): Distribution, sources and potential ecological risk. *Marine Pollution Bulletin*, **135**, pp. 769–775.

Dubovina M., Krcmar D., Grba N., Watson M. A., Radenovic D., Tomasevic-Pilipovic D., Dalmacija B., 2018, Distribution and ecological risk assessment of organic and inorganic pollutants in the sediments of the transnational Begej canal (Serbia-Romania). *Environmental Pollution*, **236**, pp. 773-784.

Grung M., Petersen K., Fjeld E., Allan I., Christensen J.H., Malmqvist L.M.V., Meland S., Ranneklev S., 2016, PAH related effects on fish in sedimentation ponds for road runoff and potential transfer of PAHs from sediment to biota. *Science of the Total Environment*, **566–567**, pp. 1309–1317.

He X., Pang Y., Song X., Chen B., Feng Z., Ma Y., 2014, Distribution, sources and ecological risk assessment of PAHs in surface sediments from Guan River Estuary, China. *Marine Pollution Bulletin*, **80**, pp.52–58.

Liu A., Duodu G.O., Mummullage S., Ayoko G.A., Goonetilleke A., 2017, Hierarchy of factors which influence polycyclic aromatic hydrocarbons (PAHs) distribution in river sediments. *Environmental Pollution*, **223**, pp. 81-89.

Riaz R., Ali U., Li J., Zhang G., Alam K., Sweetman A.J., Jones K.C., Malik R.N., 2019, Assessing the level and sources of Polycyclic Aromatic Hydrocarbons (PAHs) in soil and sediments along Jhelum riverine system of lesser Himalayan region of Pakistan. *Chemosphere*, **216**, pp. 640-652.

Rocha A.C., Palma C., 2019, Source identification of polycyclic aromatic hydrocarbons in soil sediments: Application of different methods, *Science of the Total Environment*, **652**, pp. 1077–1089.

Rowater, National Administration of Romanian Waters, No. 161/16 February 2006, http://www.rowater.ro/dacrisuri/Documente%20Repository/Legislatie/gospodarirea%20apelor/ORD.%20161_16.02.2006.pdf, Accessed on 14.12.2018.

Sanctorum H., Elskens M., Leermakers M., Gao Y., Charriau A., Billon G., Goscinny S., De Cooman W., Baeyens W., 2011, Sources of PCDD/Fs, non-ortho PCBs and PAHs in sediments of high and low impacted transboundary rivers (Belgium–France). *Chemosphere*, **85**, pp. 203–209.

Schwientek M., Rügner H., Scherer U., Rode M., Grathwohl P., 2017, A parsimonious approach to estimate PAH concentrations in river sediments of anthropogenically impacted watersheds. *Science of the Total Environment*, **601–602**, pp. 636–645.

Souza M. R.R., Santos E., Suzarte J. S., Carmo L. O., Frena M., Damasceno F. C., Alexandre M. R., 2018, Concentration, distribution and source apportionment of polycyclic aromatic hydrocarbons (PAH) in Poxim River sediments, Brazil. *Marine Pollution Bulletin*, **127**, pp. 478–483.

Tobiszewski M., Namieśnik J., 2012, PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution*, **162**, pp. 110-119.

Tu Y.T., Ou J.H., Tsang D.C.W., Dong C.D., Chen C.W., Kao C.M., 2018, Source identification and ecological impact evaluation of PAHs in urban river sediments: A case study in Taiwan. *Chemosphere*, **194**, pp. 666-674.

Yunker M.B., Macdonald R.W., Vingarzan R., Mitchell R.H., Goyette D., Sylvestre S., 2002, PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, **33**, pp, 489–515.

Zeng Q., Jeppesen E., Gu X., Mao Z., Chen H., 2018, Distribution, fate and risk assessment of PAHs in water and sediments from an aquaculture and shipping-impacted subtropical lake, China. *Chemosphere*, **201**, pp. 612-620.

Zhu L., Chen Y., Zhou R., 2008, Distribution of polycyclic aromatic hydrocarbons in water, sediment and soil in drinking water resource of Zhejiang Province, China. *Journal of Hazardous Materials*, **150**, pp. 308–316.