

# Occurrence and Sources of Polycyclic Aromatic Hydrocarbons in the Tisza River and its Romanian Tributaries

Mihail Simion Beldean-Galea  · Radu Mihăiescu · Viorel Arghiuş · Adina Croitoru · Csaba Horvath · Virginia Coman

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**Abstract** The aim of this work is to assess the occurrence of Polycyclic aromatic hydrocarbons (PAHs) in the Tisza River and its main Romanian tributaries (Vişeu River and Iza River) and to establish the origin (pyrogenic/petrogenic) of pollution sources. Fifteen PAHs were investigated in surface water and sediment samples collected from three selected sampling point. The target compounds were isolated from the matrices by solid phase extraction for water samples and by ultrasound-assisted extraction for the sediment samples, respectively. The quantification of the target compounds was performed by HPLC coupled with a fluorescence detector. PAH diagnostic ratios, as the abundance ratio of 2–3 ring hydrocarbons to 4–6 ring hydrocarbons (LMW/HMW), ANT/(ANT + PHE), FLT/(FLT + PYR), B[a]A/(B[a]A + CHR), and IND/(IND+ B[g,h,i]P) were used as a tool for identification and assessment of the pollution emission sources. The results of the study showed that in the studied area, the total concentrations of PAHs detected in water samples ranged from 1.22 to

260.26 ng L<sup>-1</sup>, while those in sediment samples varied from 4.94 to 10.62 µg kg<sup>-1</sup>. Regarding the PAH pattern, mixed sources of pollution (pyrogenic and petrogenic) occur in both water and sediment samples. Thus, leaks of petroleum products and biomass, coal, and petroleum combustion are the main sources of pollution identified into the studied area.

**Keywords** Polycyclic aromatic hydrocarbons · River water · Sediment · PAH diagnostic ratios · Petrogenic · Pyrogenic

## 1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds included in the list of priority pollutants of/by US EPA and EEA (European Environmental Agency) due to their toxic, mutagenic, and carcinogenic potentials (Oliva et al. 2010). These compounds are widespread into environmental compartments and are present in atmosphere, surface water, soil, sediment, and organism (Guo et al. 2007) and are the most concerning contaminants at regional and global scales (Li et al. 2012).

PAHs can originate from natural processes such as biomass burning, volcanic eruptions and diagenesis (Wang et al. 2007), as well as from anthropogenic processes via two mechanisms: pyrolytic (fuel-combustion) and petrogenic (discharge of petroleum products) (Yunker et al. 2015).

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M. S. Beldean-Galea (✉) · R. Mihăiescu · V. Arghiuş  
Faculty of Environmental Science and Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania  
e-mail: simion.beldean@yahoo.com

A. Croitoru · C. Horvath  
Faculty of Geography, Babeş-Bolyai University, Cluj-Napoca, Romania

V. Coman  
Raluca Ripan Institute for Research in Chemistry, Babeş-Bolyai University, Cluj-Napoca, Romania

Usually, PAHs are emitted into the atmosphere where they are present as vapors phase or adsorbed to particles (Wang et al. 2013), but they also can enter into the hydrosphere and pedosphere by/through dry and wet depositions and runoff, industrial wastes, domestic wastewater or leaks of petroleum products (Zhu et al. 2008).

In the last decade, many studies were conducted for the assessment of concentration and distribution of PAHs in different environments as atmosphere (Ravindra et al. 2008; Wang et al. 2013), inland rivers and lakes (Guo et al. 2007; Zhu et al. 2008; Ding et al. 2014), estuary and marine waters and sediments (Wang et al. 2011; Bouloubassi et al. 2012; Yunker et al. 2015), soil (Maliszewska-Kordybach et al. 2009; Yuan et al. 2014), etc. Some other research papers focused on understanding the impact of particular emission sources, such as the impact of combustion sources and fossil fuels (Zhang et al. 2008; Yunker et al. 2015).

In general, combustion products are dominated by relatively high molecular weight (HMW) compounds, with four to six condensed rings, while fossil fuels by light molecular weight (LMW) compounds with two and three condensed rings (Wang et al. 2011). Due to the fact that PAHs are always emitted as a mixture, the relative molecular concentration ratios are considered to be characteristic of a given emission source (Tobiszewski and Namieśnik 2012).

Recently, PAH diagnostic ratios become a commonly used tool to identify and assess the pollution emission sources. Different ratios of selected PAH compounds could be used to detect the possible/potential origins of PAHs. Thus, one can distinguish between the PAHs coming from combustion (pyrolytic origin) and the discharge of petroleum products (petrogenic origin) (Yunker et al. 2002; Tobiszewski and Namieśnik 2012).

The most used diagnostic tools that can be applied/employed to detect the petrogenic and pyrolytic sources are the abundance ratio of 2–3 ring hydrocarbons to 4–6 ring hydrocarbons (LMW/HMW) (Zhang et al. 2008), isomeric ratios of anthracene/(anthracene + phenanthrene) (Yunker et al. 2002), fluoranthene/(fluoranthene + pyrene) (Zhu et al. 2008), benz(a)anthracene/(benz(a)anthracene + chrysen), indeno(1.2.3-cd)-pyrene/(indeno(1.2.3-cd)pyrene + benzo(g,h,i)perylene) (Tobiszewski and Namieśnik 2012).

The aim of this paper is to assess the occurrence of PAHs in the river waters and sediment samples collected from the Romanian Tisza River Watershed and to

establish the origin (pyrogenic/petrogenic) of pollution sources using the PAH diagnostic tools in order to provide useful information for a better environmental risk assessment and surface water quality management.

## 2 Experimental

### 2.1 Chemicals and Reagents

A mix standard containing 16 PAHs (naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FL), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLT), pyrene (PYR), benz(a)anthracene (B[a]A), chrysene (CHR), benzo(b)fluoranthene (B[b]F), benzo(k)fluoranthene (B[k]F), dibenz(a,h)anthracene (DB[a,h]A), benzo(a)pyrene (B[a]P), benzo(g,h,i)perylene (B[g,h,i]P), and indeno(1.2.3-cd)-pyrene (IND)) in concentration of  $10 \mu\text{g mL}^{-1}$  of each component in acetonitrile was purchased from Supelco.

Methylene chloride, hexane, toluene, methanol, and acetonitrile, all of them in HPLC grade purity were acquired from Merck (Darmstadt, Germany). Milli-Q water was prepared using a Milli-Q-Plus ultra-pure water system from Millipore (Milford, MA, USA).

### 2.2 Studied Area and Samples Collection

The present study research area covers the Romanian part of the Tisa River upstream watershed. The Tisa River is a natural border between Romania and Ukraine. It is the longest and has the largest watershed of all Danube's tributaries. In Romania, it has three main tributaries (Vișeu, Iza, and Săpânța), covering historical Maramureș Region in the northern Carpathians. Geographically, it overlaps the Maramureș Depression and the surrounding Eastern Carpathians. The hydrographic system is well developed due to high precipitation amounts; in the mountain region, precipitation reaches 1200–1400 mm/year and only in the lowest areas it falls under 700 mm. The hydrographic network is dense reaching  $0.8 \text{ km km}^{-2}$ . Its anthropogenic component is shared among five little towns (Sighetu Marmației, Vișeu de Sus, Borșa, Dragomirești, and Săliște de Sus) and a significant large rural area, so the average population density reaches 70 people  $\text{km}^{-2}$ . Presently, the industry is represented mainly by small wood and building material companies. But

in the past, prosperous mining areas were set up, which are in preservation nowadays.

Taking into account the trans-boundary characteristic of the Tisa River, the sampling points were chosen in order to have a better description of each main Romanian tributary contribution for the water quality of the Tisa River. Thus, the first sampling point was located in Vişeu Valley, near the confluence of Vişeu River with Tisza River, and the second one is located downstream from Sighetu Marmăţiei town, where Iza River flows into the Tisza River. The third sampling point was established downstream of Teceu Mic village; the place where Tisza River leaves the Romanian territory (Fig. 1).

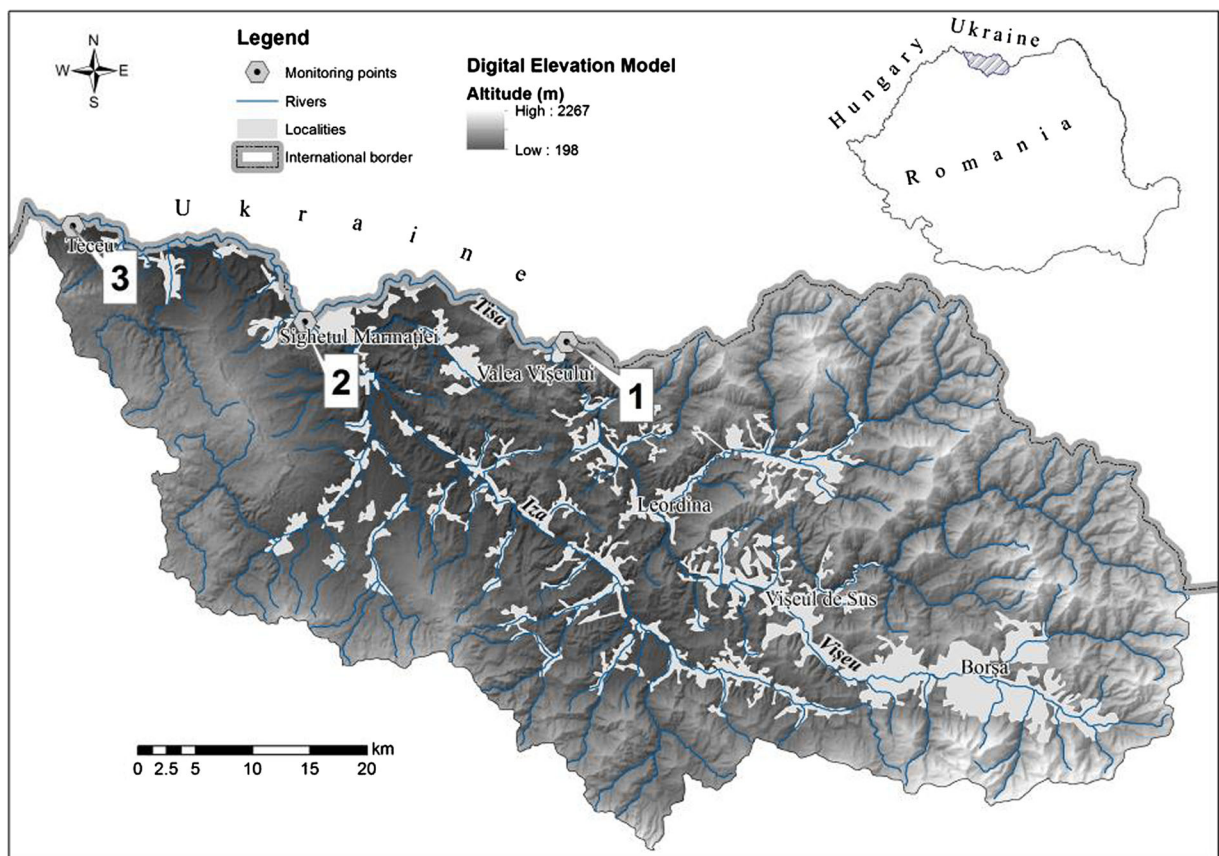
The river water samples were collected from the selected monitoring points using a manual water sample device from the layer at 30 cm depth. The water samples were kept in a brown glass bottle at 5.0 °C before analyses. For a better recovery of the tested compounds, 1 mL of hexane was added into the water samples after

sampling. The period of sampling covers 11 months, from November 2014 to September 2015. Usually, the samples were collected in the last decade of each month.

Sediment samples were collected in June 2015 using a stainless steel grab sampler and were kept in a glass jars at 5.0 °C before analyses. All water and sediment samples were analyzed in a range time of 48 h after sampling in order to avoid the damage of the samples' integrity.

### 2.3 Instrumentation

The analyses of the selected PAHs were carried out using a HPLC system; model Agilent 1100, equipped with a quaternary pump, a fluorescence detector for multi-signal detection and on-line UV spectra, and a standard auto-sampler. The separation of the compounds was performed on a reverse phase column type Luna C18 10A (250 × 4.6 mm, 5-µm particle size) acquired from Phenomenex



**Fig. 1** Map of studied area and the sampling point location (1—Vişeu River, 2—Iza River, 3—Tisza River)

(USA) at 25.0 °C. A gradient elution mode using a mobile phase containing a mixture of acetonitrile and Milli-Q water at a flow rate of 1 mL min<sup>-1</sup> was used for the HPLC analysis.

In order to obtain the maximum sensitivity for the target compounds, the detection of the compounds was carried out at different emission/excitation wavelength: 270/330 nm (NAP, ACE, FL), 250/370 nm (PHE), 250/400 nm (ANT), 270/440 nm (FLT), 270/400 nm (PYR), 270/390 nm (B[a]A, CHR), 290/430 nm (B[b]F, B[k]F, B[a]P, DB[a,h]A, B[g,h,i]P), and 305/466 nm (INP) (Liaud et al. 2015).

## 2.4 Samples Extraction

Water samples (1 L) were extracted using a SPE device provided by Supelco, using a solid phase extraction procedure developed by Beldean-Galea et al. (Beldean-Galea et al. 2014). The target

compounds were extracted using Strata X cartridge (300 mg, 6 mL) acquired from Phenomenex. In order to remove the particulate matter, the water samples were filtered through a PVDF sample filter with pore size of 0.45 µm (Merck Milipore) before extraction. After extraction, the retained compounds were eluted with 5 mL methylene chloride. The resulted extracts were evaporated to dryness under nitrogen, and the residue was dissolved in 1.0 mL mixture of MilliQ water:acetonitrile 1:1 (v/v) and analyzed by HPLC under described conditions.

The sediment samples were extracted by ultrasound-assisted extraction method under protocol of Bouloubassi et al. (Bouloubassi et al. 2012), using an ultrasonic bath, model Elmasonic acquired from Elma Schmidbauer GmbH, Germany. Before extraction, the sediment samples were filtered through a PVDF sample filter, 0.45-µm pore size, in order to remove the water. Ten grams of wet sludge were extracted three times with

**Table 1** Individual, total PAHs, average concentrations, ratios LMW/HMW against months and ratios ANT/(ANT + PHE) and FLT/(FLT + PYR) in Vişeu River water samples

Compound name	Concentration (ng L <sup>-1</sup> )											
	November	December	January	February	March	April	May	June	July	August	September	Average
NAP	188.5	6.4	9.8	101.4	11.4	0.76	10.3	nd	nd	nd	0.98	29.89
ACE	3.0	nd	nd	2.4	nd	nd	nd	nd	nd	nd	nd	0.49
FL	0.4	1.1	2.1	7.7	1.7	nd	nd	nd	5.8	nd	nd	1.71
ANT	2.1	nd	nd	1.4	0.03	nd	nd	nd	0.13	4.22	nd	0.72
PHE	30	1.1	nd	21	22	0.46	2.8	4.5	13.88	4.22	0.33	9.05
FLT	16	4.3	22.2	nd	nd	nd	nd	2.3	nd	nd	nd	4.07
PYR	19	4.5	1.4	nd	nd	nd	nd	nd	nd	nd	nd	2.26
B[a]A	nd	nd	nd	0.49	nd	nd	nd	nd	nd	nd	nd	0.04
CHR	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00
B[b]F	1.26	nd	nd	0.8	0.7	nd	1.8	nd	nd	nd	nd	0.41
B[k]F	nd	nd	nd	nd	nd	nd	2.6	nd	nd	nd	nd	0.24
B[g,h,i]P	nd	2.9	nd	nd	nd	nd	2.42	nd	nd	nd	nd	0.48
B[a]P	nd	nd	nd	0.23	nd	nd	nd	nd	nd	nd	nd	0.02
DB[a,h]A	nd	nd	nd	1.2	nd	nd	nd	nd	nd	nd	nd	0.11
INP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00
Total PAH	260.26	20.3	35.5	136.62	35.83	1.22	19.92	6.8	19.81	8.44	1.31	49.73
∑LMW	224	8.6	11.9	133.9	35.13	1.22	13.1	4.5	19.81	8.44	1.31	42.08
∑HMW	36.26	11.7	23.6	2.72	0.7	0	6.82	2.3	0	0	0	7.65
∑LMW/∑HMW	6.18	0.74	0.50	49.23	50.19	–	1.92	1.96	–	–	–	5.50
ANT/(ANT + PHE)	–	–	–	–	–	–	–	–	–	–	–	0.073
FLT/(FLT + PYR)	–	–	–	–	–	–	–	–	–	–	–	0.64

nd not detected, “–” not calculated

15 mL mixture of methylene chloride:methanol 3:1 (v/v). Subsequently, the extracts were unified and the resulting extract was purified on SPE-SiOH cartridge. The retained compounds were eluted with 2 mL mixture of hexane:toluene 85:15 (v:v), and then the obtained extract was evaporated to dryness under nitrogen, re-dissolved in 1 mL mixture of MilliQ water:acetonitrile 1:1 (v/v) and analyzed by HPLC.

### 3 Results and Discussion

#### 3.1 PAH Concentrations in Water and Sediment Samples

For the analyzed water samples, the concentration range of individual PAHs in each river is shown in Tables 1, 2, and 3.

The results show that the PAH concentrations have monthly variation, depending on the rivers discharge; the concentrations are lower for bigger rivers and in those periods with high discharge flows. The total PAHs in Vişeu River ranged from 1.22 to 260.26 ng L<sup>-1</sup> with a mean value of 49.73 ng L<sup>-1</sup>, in Iza River ranged from 11.34 to 197.02 ng L<sup>-1</sup> with a mean value of 64.71 ng L<sup>-1</sup>, while in Tisza River varied between 2.23 and 71.4 ng L<sup>-1</sup> with a mean value of 31.59 ng L<sup>-1</sup>. The lowest concentration of total PAH (1.22 ng L<sup>-1</sup>) was registered in Vişeu River in April, when the discharge flow is usually high due to water release from snow layer in the mountain areas. The highest concentration (260.26 ng L<sup>-1</sup>) was detected for Vişeu River in November, when the low discharge flow is generated mainly by two factors: small amount of precipitation and its conservation as snow layer. The main PAHs were NAP ranging from 5.54 to 29.89 ng L<sup>-1</sup>, PHE ranging from 9.05 to

**Table 2** Individual, total PAHs, average concentrations, ratios LMW/HMW against months and ratios ANT/(ANT + PHE) and FLT/(FLT + PYR) in Iza River water samples

Compound name	Concentration (ng L <sup>-1</sup> )											
	November	December	January	February	March	April	May	June	July	August	September	Average
NAP	160.1	24.9	48.12	58.39	31.31	nd	nd	nd	nd	nd	3.79	29.69
ACE	1.5	nd	1.7	1.4	nd	nd	nd	nd	nd	nd	nd	0.42
FL	8.1	2.8	nd	7.2	1.9	nd	nd	nd	3.45	2.78	nd	2.38
ANT	1.3	nd	nd	1.69	nd	0.17	nd	nd	nd	nd	nd	0.29
PHE	21	14	nd	33	12	8.0	4.8	13	24.59	9.36	8.28	13.46
FLT	nd	nd	24.2	75.9	nd	nd	8.63	19.61	19.88	nd	11.43	14.51
PYR	nd	3.8	nd	4.4	nd	3.0	nd	4.3	nd	nd	nd	1.41
B[a]A	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHR	nd	nd	nd	2.3	nd	nd	nd	nd	nd	nd	nd	0.21
B[b]F	nd	nd	nd	12.5	nd	0.17	1.2	nd	nd	nd	nd	1.26
B[k]F	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
B[g,h,i]P	nd	nd	8.0	nd	nd	nd	nd	3.65	nd	nd	nd	1.06
B[a]P	nd	nd	nd	0.24	nd	nd	nd	nd	nd	nd	nd	0.02
DB[a,h]A	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
INP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Total PAH	191.9	45.5	82	197.02	45.21	11.34	14.63	40.56	47.92	12.14	23.5	64.71
∑LMW	191.9	41.7	49.8	101.68	45.21	8.17	4.8	13	28.04	12.14	12.07	46.23
∑HMW	0	3.8	32.2	95.34	0	3.17	9.83	27.56	19.88	0	11.43	18.36
∑LMW/∑HMW	–	10.97	1.55	1.07	–	2.58	0.49	0.47	1.41	–	1.06	2.52
ANT/(ANT + PHE)	–	–	–	–	–	–	–	–	–	–	–	0.021
FLT/(FLT + PYR)	–	–	–	–	–	–	–	–	–	–	–	0.91

nd not detected, “–” not calculated

**Table 3** Individual, total PAHs, average concentrations, ratios LMW/HMW against months and ratios ANT/(ANT + PHE) and FLT/(FLT + PYR) in Tisza River water samples

Compound name	Concentration (ng L <sup>-1</sup> )											
	November	December	January	February	March	April	May	June	July	August	September	Average
NAP	16	22	8.0	nd	13	nd	1.9	nd	nd	nd	nd	5.54
ACE	2.78	nd	nd	3.3	nd	nd	nd	nd	nd	1.45	nd	0.68
FL	1.0	14	nd	11	1.5	nd	nd	nd	2.22	2.61	nd	2.94
ANT	1.3	nd	nd	2.3	0.2	0.03	nd	nd	nd	nd	nd	0.35
PHE	12	14	nd	38	13	nd	3.7	4.8	15.29	3.89	3.51	9.84
FLT	1.0	1.9	9.1	nd	nd	nd	nd	3.38	24.35	nd	14.9	4.97
PYR	nd	7.0	2.1	6.0	nd	2.0	nd	nd	nd	nd	nd	1.55
B[a]A	nd	nd	nd	3.1	nd	nd	nd	nd	nd	nd	nd	0.28
CHR	nd	nd	1.9	nd	nd	nd	nd	nd	nd	nd	nd	0.17
B[b]F	nd	nd	nd	4.1	2.4	0.2	4.3	0.9	nd	nd	nd	1.08
B[k]F	1.2	nd	8.4	nd	nd	nd	2.6	nd	nd	nd	nd	1.11
B[g,h,i]P	nd	nd	7.3	nd	nd	nd	nd	4.4	nd	nd	nd	1.06
B[a]P	nd	nd	8.7	2.9	1.6	nd	nd	0.32	nd	nd	nd	1.23
DB[a,h]A	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
INP	nd	3.5	2.3	0.7	2.2	nd	nd	nd	nd	nd	nd	0.79
Total PAH	35.28	62.4	47.8	71.4	33.9	2.23	12.5	13.8	41.86	7.95	18.41	31.59
∑LMW	33.08	50	8.0	54.6	27.7	0.03	5.6	4.8	17.51	7.95	3.51	19.35
∑HMW	2.2	12.4	39.8	16.8	6.2	2.2	6.9	9.0	24.35	0	14.9	12.24
∑LMW/∑HMW	15.04	4.03	0.20	3.25	4.47	0.01	0.81	0.53	0.72	–	0.24	1.58
ANT/(ANT + PHE)	–	–	–	–	–	–	–	–	–	–	–	0.034
FLT/(FLT + PYR)	–	–	–	–	–	–	–	–	–	–	–	0.76

nd not detected, “–” not calculated

13.46 ng L<sup>-1</sup>, and FLT with a variation from 4.07 to 14.51 ng L<sup>-1</sup>, respectively.

The concentration of B[a]P in Vişeu and Iza Rivers was in the range of below the LOQ to 0.24 ng L<sup>-1</sup> with an average value of 0.02 ng/L, which is less than 0.17 ng L<sup>-1</sup>, the annual average established by Directive 2013/39/EU of the European Parliament and of the Council (Directive 2013/39/EU). For Tisza River, the concentration of B[a]P ranges below the LOQ to 8.7 ng L<sup>-1</sup>, with the average value of 1.20 ng L<sup>-1</sup>, which exceeds 0.17 ng L<sup>-1</sup> suggesting that important sources of pollution other than in Vişeu and Iza Rivers are present in the studied area.

In sediment samples, the concentrations of total PAH varied from 4.94 µg kg<sup>-1</sup> in Vişeu River to 10.62 µg kg<sup>-1</sup> in Tisza River. The main PAHs found were NAP, PHE, FLT, and PYR (Table 4).

In order to assess the sediment quality, the PAH levels in sediment were compared against effect-based

guideline values such as the effects range low (ERL) and effects range median (ERM) concentrations (Liu et al. 2009; Guo et al. 2007). The results showed that the concentrations of the individual PAH and total PAH values were below their respective ERL and ERM values in all samples, which indicated that PAHs cause no adverse ecological effects in studied area (Table 4).

### 3.2 Analysis of PAH Sources

In order to assess the sources of PAH discharged in the Tisza River and in its main Romanian tributaries, ratios of ∑LMW/∑HMW, ANT/(ANT + PHE), FLT/(FLT + PYR), B[a]A/(B[a]A + CHR), and IND/(IND + B[g,h,i]P) were considered. The scientific literature suggests that in the most cases, a ∑LMW/∑HMW ratio less than or equal to 1 indicates pyrogenic contribution while a value greater than 1 is an indicator for the petrogenic contribution (Zhang et al. 2008). A ratio of ANT/

**Table 4** Individual and total PAH concentrations, ERL, ERM and ratios ANT/(ANT + PHE), FLT/(FLT + PYR), B[a]A/(B[a]A + CHR), and INP/(INP + B[g,h,i]P) in analyzed sediment samples

Compound name	Sediment ( $\mu\text{g kg}^{-1}$ )				
	Vişeu	Iza	Tisza	ERL <sup>a</sup>	ERM <sup>a</sup>
NAP	1.36	2.23	3.13	160	2100
ACE	nd	0.15	0.23	16	500
FL	0.29	0.49	0.49	19	540
ANT	0.087	0.05	0.10	853	1100
PHE	0.81	0.49	1.80	240	1500
FLT	1.22	0.67	1.36	600	5100
PYR	1.03	0.18	1.11	665	2600
B[a]A	0.016	0.022	0.21	261	1600
CHR	0.018	0.047	0.33	384	2800
B[b]F	0.068	0.35	0.43	320	880
B[k]F	nd	nd	0.25	280	1620
B[g,h,i]P	0.02	0.16	0.50	430	1600
B[a]P	nd	0.052	0.28	430	1600
DB[a,h]A	0.002	0.17	0.05	63.4	260
INP	0.016	0.019	0.36	NA	NA
Total PAH	4.94	5.03	10.62	4022	44,792
$\Sigma$ LMW	2.55	3.41	5.75	–	–
$\Sigma$ HMW	2.39	1.67	4.88	–	–
$\Sigma$ LMW/ $\Sigma$ HMW	1.07	2.04	1.18	–	–
ANT/(ANT + PHE)	0.097	0.093	0.053	–	–
FLT/(FLT + PYR)	0.54	0.79	0.55	–	–
B[a]A/(B[a]A + CHR)	0.47	0.32	0.39	–	–
INP/(INP + B[g,h,i]P)	0.44	0.11	0.42	–	–

nd not detected, NA not applied, “–” not calculated

<sup>a</sup>Concentration under (Liu et al. 2009)

(ANT + PHE) less than or equal to 0.1 indicates petrogenic input, and a ratio greater than 0.1 points indicates pyrogenic input (Zhu et al. 2008); ratios of FLT/(FLT + PYR) less than 0.4 indicates petroleum input; the ratio between 0.4 and 0.5 suggests fossil fuel combustion, and the ratio greater than 0.5 involves natural sources such as biomass and coal combustion. A ratio of B[a]A/(B[a]A + CHR) less than 0.2 indicates petrogenic input; 0.2–0.35 indicates petroleum combustion (liquid fossil fuel, vehicle, and crude oil), and >0.35 indicates natural sources such as combustion of biomass and coal. A ratio of INP/(INP + B[g,h,i]P) less than 0.2 indicates petrogenic input, 0.2–0.5 petroleum combustion, and above 0.5 indicates combustion of coal, grass, and wood (Yunker et al. 2002).

For the water samples, due to the lack of results, only the ratios  $\Sigma$ LMW/ $\Sigma$ HMW and ANT/(ANT + PHE) against FLT/(FLT + PYR) was used.

For the ratio  $\Sigma$ LMW/ $\Sigma$ HMW, the results suggest that in studied area, mixed sources of pollution are present and dependent by the period of sampling. Generally, it can be concluded that, in Vişeu and Iza Rivers, the petrogenic input sources are dominant, while in Tisza River pyrogenic sources are more frequent (Tables 1, 2, and 3).

From the cross plot of the isomeric ratios of ANT/(ANT + PHE) against FLT/(FLT + PYR) taking into account the average value of 11 months of monitoring, the results suggest that the main sources of pollution in all studied rivers mixed petroleum leaks and biomass and coal combustion (Fig. 2).

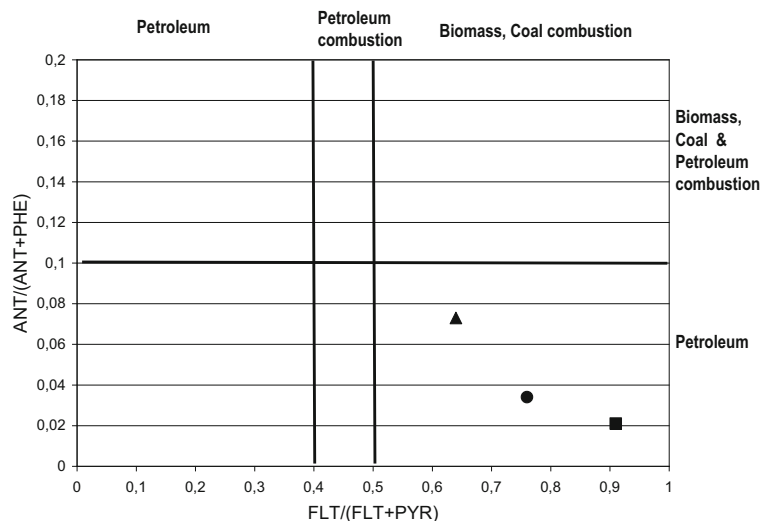
In the analyzed water samples, the ANT/(ANT + PHE) ratios varied from 0.021 to 0.073 suggesting a main petroleum origin of PAH. The lower value was obtained in Iza River while the highest value in Vişeu River. These values could be a consequence of fossil fuel spill from different gravel mining activities and also to an inefficient removal during the wastewater treatment. The FLT/(FLT + PYR) ratio varied from 0.64 to 0.91 suggesting that natural sources such as biomass and coal combustion are an important sources of PAH in studied area. The lowest value was obtained in Vişeu River and the highest in Iza River. The results are quite logical taking into account that burning of biomass and coal are the main process used for residential heating.

For sediment samples, ratios ANT/(ANT + PHE) against FLT/(FLT + PYR) and B[a]A/(B[a]A + CHR) against IND/(IND + B[g,h,i]P) were plotted (Figs. 3 and 4).

The results suggest that mixed sources of petrogenic and pyrogenic are present in sediment samples. Thus, from the cross plot of the isomeric ratios of ANT/(ANT + PHE) against FLT/(FLT + PYR) (Fig. 3), it can be concluded that the sources of pollution in all studied river sediment samples are similar with those obtained for water samples and combine petroleum leaks with biomass and coal combustion.

In the analyzed sediment samples, the ANT/(ANT + PHE) ratios varied from 0.053 to 0.097 suggesting like in the case of water samples a petrogenic input of PAH. The value of FLT/(FLT + PYR) ratios ranged from 0.54 to 0.79 indicating that biomass and coal combustion have an important contribution to the PAH content in sediment. The values are similar with those obtained for

**Fig. 2** The Cross plot for the isomeric ratios of ANT/(ANT + PHE) versus FLT/(FLT + PYR) in water samples (mean values) (*triangle*—Vişeu River, *square*—Iza River, *circle*—Tisza River)



water samples; the lowest value being obtained in Vişeu River and highest value in Iza River, respectively.

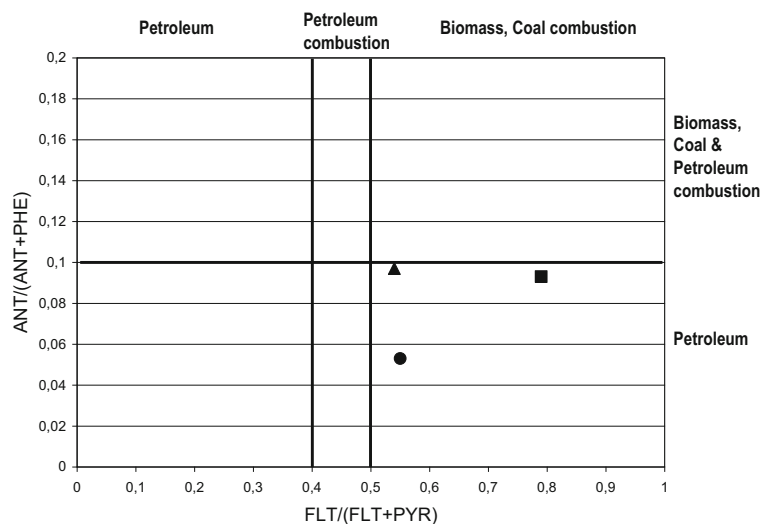
From the cross plot of the isomeric ratios of B[a]A/(B[a]A + CHR) against IND/(IND + B[g,h,i]P) (Fig. 4), it can be concluded that in Iza River the origin of PAHs has a petroleum and petroleum-combustion fingerprint, while in Vişeu and Tisza Rivers petroleum combustion as well as biomass and coal combustion is dominant.

The B[a]A/(B[a]A + CHR) ratios at selected sampling sites ranged from 0.32 to 0.47 suggesting a pyrogenic origin of PAH generated mainly from natural sources such as biomass and coal combustion in Vişeu and Tisza River and a petroleum combustion fingerprint in Iza River. The value of IND/(IND + B[g,h,i]P) ratio varied from 0.11 to 0.44 with the lowest value registered

in Iza River and highest in Vişeu River, respectively. Thus, it means that in Iza River, PAHs has petroleum origin while in Vişeu and Tisza River the main source of pollution is petroleum combustion.

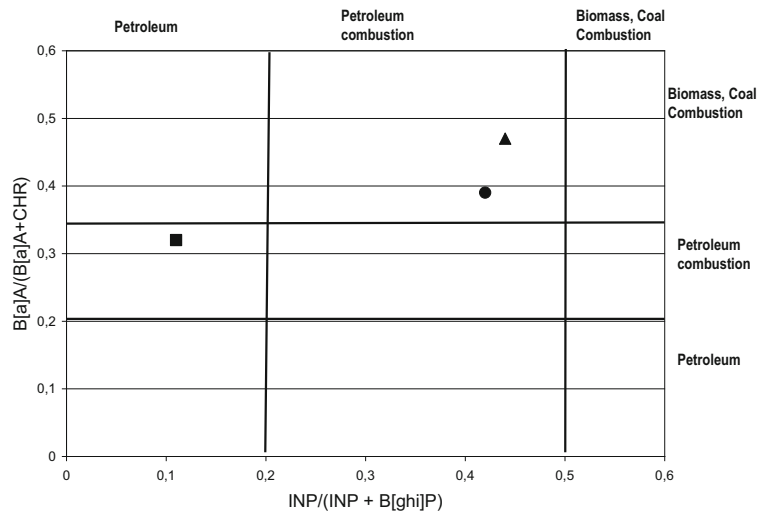
Another important aspect which should be taken into account in the establishment of the PAH pattern is the stability of different PAH isomers in the environmental compartments. It is well known that PAH degradation processes, similarities between the PAH sources, and the mixing of multiple sources can affect the PAH molecular ratio values making it more difficult for the identification of pattern sources. From this reason, at least for the identified petrogenic sources, the contribution of weathering should be taken into account. In this way, degradation/weathering PAH ratios of the more stable

**Fig. 3** The Cross plot for the isomeric ratios of ANT/(ANT + PHE) versus FLT/(FLT + PYR) in sediment samples (*triangle*—Vişeu River, *square*—Iza River, *circle*—Tisza River)





**Fig. 4** The Cross plot for the isomeric ratios of B[a]A/(B[a]A + CHR) versus INP/(INP + B[g,h,i]P) in sediment samples (*triangle*—Vişeu River, *square*—Iza River, *circle*—Tisza River)



PAHs to the less recalcitrant PAHs (LMW/HMW) of the EPA16 PAH both in water and sediment are often used for the assessments of petrogenic PAH contribution. Thus, if the weathering ratio value decreases, it means that extensive degradation of PAHs occur and the contribution of petrogenic sources is significant. Moreover, if LMW/HMW >2.3, then recent input of petrogenic products is implied (Stogiannidis and Laane 2015).

From the analyzed samples, it can be observed that the weathering has a significant contribution in Vişeu River, the obtained LMW/HMW ratio value for water samples being five times higher compared with sediment samples (5.50 for water samples and 1.07 for sediment sample, respectively) and Iza River where the obtained LMW/HMW ratio values are 2.52 for water sample and 2.04 for sediment sample. For Tisza River, the weathering contribution is small; the obtained LMW/HMW ratio values are almost similar (1.58 for water samples and 1.18 for sediment sample), and the values under 2.3 suggest that no recent input of petrogenic products is implied. These results can be explained by the fact that in Vişeu River, the intense gravel mining activities generate high spelling of fossil fuels, while in the Iza River the vicinity of Sighetu Marmatiei town has a significant contribution to the petrogenic input.

Taking into consideration the results discussed above, a reasonable conclusion for the performed study is that, in the studied area, the results of PAH pattern obtained for sediment and water samples are in connection with the anthropic activities. Thus, the petrogenic fingerprint is a result of gravel mining activity

performed in the studied area and to an inefficient removal during the wastewater treatment, while the pyrogenic fingerprint is given mainly from natural sources such as the burning of wood and coal necessary for houses heating.

#### 4 Conclusions

The results of the study showed that, in the studied area, the total concentrations of PAH in water samples ranged from 1.22 to 260.26 ng L<sup>-1</sup> and from 4.94 to 10.62 µg kg<sup>-1</sup> in sediment samples, respectively.

The average concentration of B[a]P in Vişeu and Iza Rivers is less than 0.17 ng L<sup>-1</sup>, while for Tisza River exceeds 0.17 ng L<sup>-1</sup> suggesting that, in Tisza River, important sources of pollution other than in Vişeu and Iza Rivers are present.

In sediment samples, the concentrations of the individual PAH and total PAH values were below their respective ERL and ERM values, in all samples, which indicated that PAH causes no adverse ecological effects in the area under study.

Regarding the PAH pattern, mixed sources, petrogenic, and pyrogenic are present both in water and sediment samples.

In water samples, a slightly pyrogenic signature occurs mainly in the warm period while in cold period, a petrogenic signature is emphasized.

In sediment samples, petrogenic and pyrogenic sources, originated by petroleum leaks and burning of petroleum products, biomass, and coal, were found.

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