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Organic geochemical approach in the identification of oil-type pollutants in water and sediment of the River Ibar

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Abstract: In this paper an applied organic geochemical approach in studying the nature of organic matter (OM) in water and sediments of the River Ibar (upstream and downstream of towns Kosovska Mitrovica and Kraljevo) was used. A forensic approach that relies on the fact that the composition of OM of recent sediments and oil varies due to geological age and maturity was applied. The content of bitumen, its group composition of saturated, aromatic and NSO compounds (nitrogen, sulphur, and oxygen compounds) and the distribution of *n*-alkanes in saturated fractions identified by gas chromatography–mass spectrometry (in almost all samples incorporated into the colloidal micelles formed by water and NSO compounds) could not answer the question whether OM in isolated extracts has native or anthropogenic origin. However, the presence of sterane and terpane, with the distribution of structural and stereochemical isomers characteristic of oil, as a form of most mature OM in sediments, unambiguously confirmed presence of oil type pollutants in analyzed samples. Based on significant differences in the distributions of these polycyclic alkane (water–water, sediment–sediment and water–sediment), it was concluded that they have more than one source of pollution, and that the River Ibar is permanently exposed to this form of pollution.

Keywords: petroleum pollutants; biomarkers; urban pollution; environment.

INTRODUCTION

The generation of oil is now fully understood due to geochemical analyses of the organic substances transformations in sedimentary formations in the Earth's

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crust. These investigations which were most intensive during the 1980s and 1990s proved that a very small part (only 0.01–0.1 %) of the organic matter that originates from the biosphere remains in the surface of the Earth's crust – lithosphere. Its macromolecules (polysaccharide, lignin, protein and complex lipids) under the action of microorganisms decompose to form a lower molecular weight (usually corresponding to the monomer units). At the stage of diagenesis they polymerize to fulvic and humic acids, and then to humin, and finally to kerogen. In the catagenesis phase, under the influence of heat, pressure, mineral catalyst and over a long geological time, bitumen is produced by the pyrolysis process. Under favorable conditions this complex hydrocarbon mixture migrates from the source rocks to the reservoir, where it is concentrated, and forms oil.^{1–3}

From the fundamental point of view, oil is only one of the forms of organic substances in the geosphere. However, its importance is commercially incomparably greater compared to other compounds. Together with the natural gas and coal, oil today represents the most important fossil fuel.⁴

Since in the diagenetic-catagenetic sequences oil is at the end of the transformation of organic substances, it consists of hydrocarbons that have the highest degree of thermodynamic stability. During the geological history the oil compounds undergo change aiming to take the most stable structural and configuration status. This is especially true for biological markers (biomarkers, or molecular fossils) for which the exact biological precursor is determined.^{1–4}

Due to the characteristic biomarker distribution, oil is easily distinguished from other forms of organic substances in the geosphere. This is especially true for the bitumens in recent sediments, coal and oil shales, including bitumen in source rocks. They all contain *n*-alkanes, isoprenoid aliphatic alkanes, polycyclic alkanes of sterane and terpane type, oil-aromatics, polycyclic aromatic hydrocarbons (mainly naphthalene and phenanthrene type) and others. However, due to highest level of maturity, oil contains the highest amount of thermodynamically stable isomers, which makes the distribution of these biomarkers typical only for this type of organic substances in sediment formations.

Described unique characteristics of oil have a distinct role in the area of chemistry and environmental protection. A certain amount of bituminous type of organic substance (soluble in conventional organic solvents) is found in ground and surface waters, soil and recent sediments. Since it is located at the beginning of the organic carbon cycle in the geosphere, this organic substance contains mainly compounds of the low-level thermodynamic stability. Their distributions are typical for the immature organic substance.

Oil contains the same classes of organic compounds. However, the relations between thermodynamically stable geolipid isomers and less stable biolipid precursors are different (with a pronounced domination of geolipid forms). Therefore, the presence of petroleum pollutants in different segments of the

environment can be determined very efficiently. This was confirmed by testing the composition of oil belonging to the south-eastern part of the Pannonian basin (Serbia),^{5–8} but also the composition of organic substances in coal^{9–11} and organic substance in oil shale deposits in Serbia.^{12,13} Previous studies of the fate of petroleum pollutants in the environment, which belongs to the territory of Serbia, have also given direct confirmation of the correctness of this approach.^{14–17}

In this study, water and sediment of the Ibar river on locations of special importance were analyzed. Samples were taken upstream and downstream from the towns of Kosovska Mitrovica and Kraljevo. The “forensic” approach for determining the presence and assessment of the origin and fate of oil pollutants in aqueous systems was applied, which is based on theoretical and empirical organic-geochemical foundation.

EXPERIMENTAL

Samples

Details related to the samples and sampling locations are given in the Supplementary material to this paper.

Separation and instrumental techniques

Sediment samples were first air-dried, homogenized and pulverized. The soluble organic matter (bitumen) was extracted (42 h) from sediments by Soxhlet’s method with an azeotropic mixture of methylene chloride and methanol (88:12 volume ratio) and quantified. The liquid–liquid extraction was used for the isolation of bitumen fractions from the water samples using chloroform as a solvent and quantified. This process is described in previous papers.^{19,20}

The bitumen extracts were separated into saturated, aromatic and NSO (polar fraction, which contains nitrogen, sulfur and oxygen compounds) fractions using column chromatography over SiO₂ and Al₂O₃. The saturated hydrocarbon fraction was eluted with *n*-hexane, the aromatic hydrocarbons with benzene, and the NSO fraction with a mixture of methanol and chloroform (1:1 volume ratio). The saturated hydrocarbons of bitumen were analyzed by gas chromatography–mass spectrometry (GC–MS). GC–MS was performed using an Agilent 7890A gas chromatograph (HP5-MS column, 30 m×0.25 mm, 0.25 μm film thickness, He carrier gas, 1.5 cm³ min⁻¹), coupled to an Agilent 5975C mass selective detector (70 eV). The column was heated from 80 to 310 °C, at a rate of 2 °C min⁻¹, and the final temperature of 310 °C was maintained for additional 25 min. Detailed analyses of the target compounds were conducted using the following ion chromatograms: *m/z* 71 (*n*-alkanes and isoprenoids), *m/z* 217 (steranes) and *m/z* 191 (terpanes). The individual peaks were identified by comparison with literature data and on the basis of the mass spectra (library: NIST5a). Biomarker parameters were calculated from GC–MS chromatogram peak areas (GC–MS Data Analysis software). The individual peaks were identified on the basis of comparison of the mass spectrum obtained with those from the literature.^{1,2}

RESULTS AND DISCUSSION

Group parameters

Results of determination of soluble organic substance in organic solvents (bitumen fraction) in the analyzed water and sediment samples are given in Table I.

TABLE I. Content of bitumen in analyzed water and sediment samples

Sample	Sample mark	Bitumen, mg L ⁻¹
Zubin Potok – water	ZP-W	132
Veliko Rudare – water	VR-W	40
Konarevo – water	K-W	97
Ratina – water	R-W	86
Bitumen, mg kg ⁻¹		
Zubin potok – sediment	ZP-S	830
Veliko Rudare – sediment	VR-S	810
Konarevo – sediment	K-S	730
Ratina – sediment	R-S	710

The content of the bitumen in water and sediment samples are in relatively narrow ranges. As expected, the content of bitumen in water samples is much lower (40–132 mg L⁻¹, Table I) than in sediment samples (710–830 mg kg⁻¹, Table I) thanks to deposition, and adsorption on minerals.

Results of group composition of the isolated bitumen (content of saturated hydrocarbons, aromatics and NSO compounds) in the tested water and sediment samples are given in Table II.

TABLE II. Group composition of bitumen fraction in water and sediment samples

Sample	Saturated fraction, %	Aromatic fraction, %	NSO fraction, %
ZP-W	28.7	14.3	57.2
VR-W	23.8	28.6	47.6
K-W	44.5	46.0	9.4
R-W	24.0	32.0	44.0
ZP-S	8.6	6.9	84.5
VR-S	10.9	19.8	69.3
K-S	8.1	23.3	68.6
R-S	15.0	15.9	69.0

NSO-fraction is dominant in seven out of eight samples. This is particularly true in the sediment organic matter (from 68.6 to 84.5 %, Table II). Significantly higher proportion of saturated and aromatic hydrocarbons (44.5 and 46.0 %, Table II) is only present in the organic substance of the water sample K-W. NSO fractions are dominant also in other water samples, but not to the same extent as in the sediment samples (from 44.0 to 57.2 %, Table II). This result is logical if one takes into account the higher adsorption capacity of mineral part towards the more polar NSO compounds compared to alkanolic fraction.²¹ Domination of NSO compounds in sediment organic substances formation is the characteristic of recent sediments. In oil and bitumen of older sediments (such as source rocks) saturated hydrocarbons are dominant.⁴ Bearing this in mind, and based on the results given in Table II, it can be concluded that in all water and sediment samples (besides the sample K-W) organic matter of native type is present.

Specific parameters – *n*-alkane

Distribution of *n*-alkanes in saturated fractions in tested water (fragmentograms m/z 71) and sediment samples are presented in Figs. 1 and 2, respectively. The range of *n*-alkanes, the most abundant members in their distributions, as well as the value of the parameter that indicate the relationship between the relative abundance of odd and even homologs (carbon preference index, *CPI*) are given in Table III.

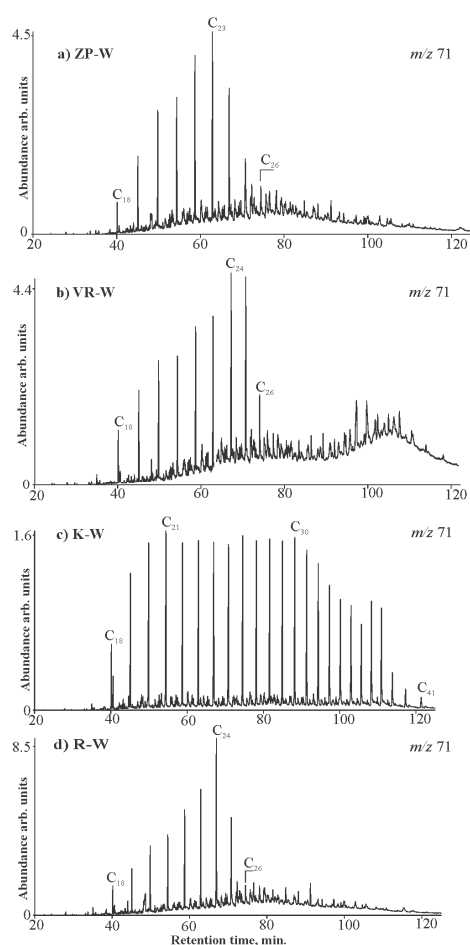


Fig. 1. Distribution of *n*-alkanes in saturated fractions in organic substance of analyzed water samples (fragmentograms m/z 71): a) Zubin Potok, b) Veliko Rudare, c) Konarevo and d) Ratina.

In three of the four tested water samples (ZP-W, VR-W and R-W) *n*-alkanes were identified with almost identical distributions in the range C_{18} – C_{26} (Fig. 2a, b and d and Table III). Distribution of odd and even homologues in fractions of saturated hydrocarbons is largely uniform which resulted in similar values for *CPI* close to the unit (Table III). The lack of homologs with a larger number of

carbon atoms ($> C_{26}$) is most likely the consequence of their low solubility in water. In addition, it is known that the NSO compounds and water build colloidal micelles in channel forms with a diameter of about 5 Å. Such channels are easily incorporated into *n*-alkanes with a long homologues building in that way inclusion compounds. Only with intensive extraction *n*-alkanes can be extracted from them.^{22,23} As already stated, fractions of NSO compounds is dominant in these samples (Table II). However, if this approach is accepted in the interpretation, it could be assumed that the NSO-fraction of bitumen sample extract ZP-W, VR-W and R-W are isolated by column chromatography, actually represent the sum of the masses of NSO-compounds and *n*-alkanes with more than 26 C-atoms.

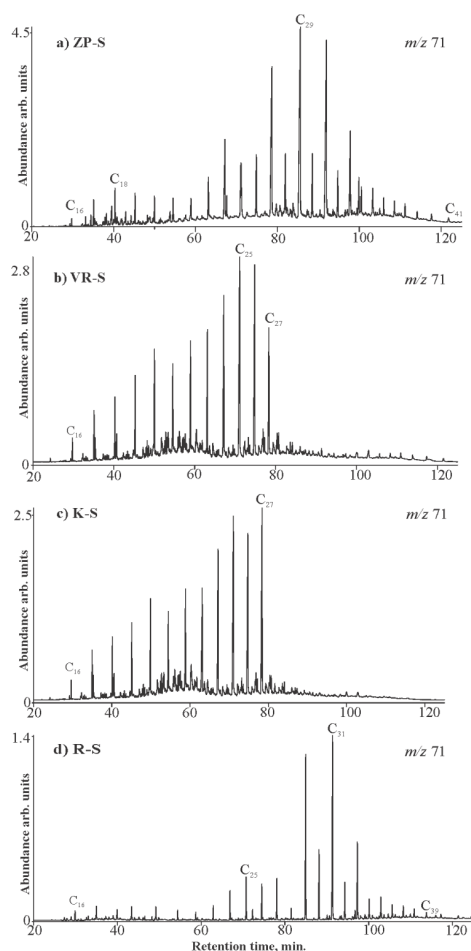


Fig. 2. Distribution of *n*-alkanes in saturated fractions in organic substance of analyzed sediment samples (fragmentograms m/z 71): a) Zubin Potok, b) Veliko Rudare, c) Kona-revo and d) Ratina.

In the K-W sample using column chromatography NSO fraction of only 9.4 % (Table II) was isolated. Only in this sample *n*-alkanes with more than 26

carbon atoms were identified in a relatively high concentration (Fig. 2c). Applying this approach in the interpretation, it could be concluded that only in this sample total amount of *n*-alkanes (including $>C_{26}$ homologues) was extracted, which resulted in such a low percentage of the NSO fraction, and high percentage of the saturated fraction (44.5 %, Table II).

TABLE III. Parameters that characterize the distribution of *n*-alkanes in saturated fractions in water and sediment samples

Sample	Range of <i>n</i> -alkanes	The most abundant <i>n</i> -alkane	<i>CPI</i>
ZP-W	C ₁₈ –C ₂₆	C ₂₃	1.03
VR-W	C ₁₈ –C ₂₆	C ₂₄	1.09
K-W	C ₁₈ –C ₂₆	C ₂₁ (C ₃₀)	1.07
R-W	C ₁₇ –C ₂₆	C ₂₄	1.00
ZP-S	C ₁₆ –C ₃₅	C ₂₉ (C ₁₈)	2.56
VR-S	C ₁₇ –C ₂₇	C ₂₅	1.05
K-S	C ₁₇ –C ₂₇	C ₂₇	1.26
R-S	C ₁₇ –C ₃₇	C ₃₁ (C ₂₅ , C ₁₈)	2.83

In sediment samples VR-S and K-S the distributions of *n*-alkanes in saturated fractions is very similar to distributions in water samples (Figs. 2a, b, d, 3b and c and Table III). On the other hand, the *n*-alkanes found in sediment samples ZP-S and R-S are characterized by a bimodal distribution (Fig. 3a and d). In the second part of these chromatograms, peaks correspond to higher homologues with *n*-alkane maximum at C₂₉ and C₃₁ with distinct domination of odd homologues. This is also contributed to high values of the “total” Carbon Preference Index (*CPI* > 2.5, Table III). These distributions are characteristic for the organic substance of recent sediments that have terrestrial origin.¹⁻⁴ However, in the first parts of the chromatograms are peaks that correspond to the lower homologues with uniform abundance of odd and even members (Fig. 3a and d). Such distributions can be found in oil.¹⁻⁴ Therefore, it can be assumed that anthropogenic organic matter of oil type participated in the total organic substances in the sediment samples taken at both sites. However, the explicit conclusion about the presence of polluting substances in the oil type in tested water and sediment samples, including samples of ZP-S and R-S, based on the *n*-alkanes distribution in alkanolic fractions cannot be drawn.

Specific parameters – sterane and terpane

Polycyclic alkanes of sterane and terpane type in the alkane fractions of the extracted organic substances in tested water and sediment samples of the river Ibar were analyzed. The characteristic sterane (*m/z* 217) fragmentograms are given in Fig. 3, and characteristics terpane (*m/z* 191) fragmentograms are given in Fig. 4. Identification of the peaks is given in Tables S-I and S-II of the Sup-

plementary material to this paper. The parameters that characterize distribution of sterane and terpane are given in Tables IV and V, respectively.

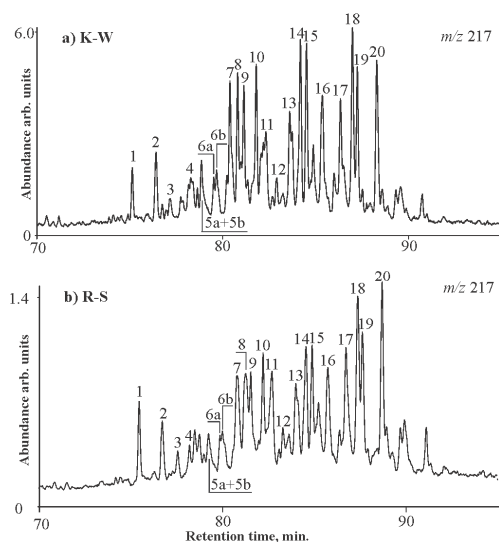


Fig. 3. Sterane distribution (m/z 217) of representative samples: a) water and b) sediment.

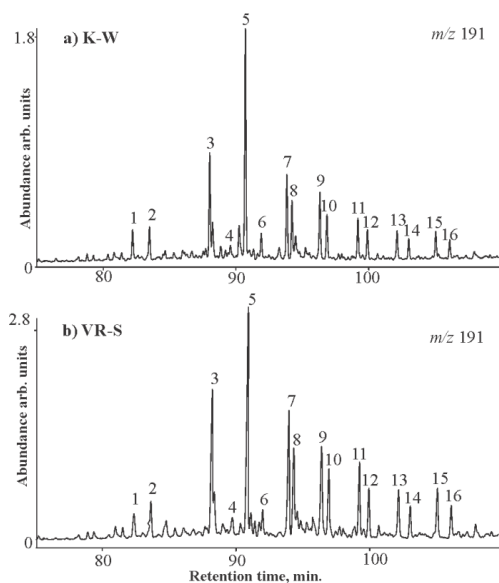


Fig. 4. Terpane distribution (m/z 191) of representative samples: a) water and b) sediment.

In all tested water and sediment samples polycyclic alkanes of sterane and terpane type with distributions that are characteristic for oil were identified (Fig. 3 and 4 and Tables S-I and S-II).

In sterane fragmentograms, besides C_{27} – C_{29} $14(H)\alpha 17(H)\alpha 20(R)$ isomere biolipide peaks, peaks originating from the thermodynamically more stable iso-

mer geolipide β configuration at the fourteenth and seventeenth carbon atoms and with the configuration of the twentieth carbon atom are also present. Also, in these fragmentograms dominant are peaks originating from typical geoisomere, diasterane. These configuration types are generally not found in bitumen of recent sediments which are at a low level of thermal maturity degree.

TABLE IV. Parameters that characterize the distribution of sterane in alkane fractions extracted organic substances in analyzed water and sediment samples of the River Ibar

Sample	$C_{27}\alpha\alpha(R):C_{28}\alpha\alpha(R):C_{29}\alpha\alpha(R)$	$C_{27}\beta\alpha S \text{ dia-} / C_{27}\beta\alpha R \text{ dia-}$	$C_{29}\alpha\alpha S / C_{29}\alpha\alpha R$
ZP-W	35.0:30.6:34.4	1.44	0.67
VR-W	25.1:24.1:50.8	1.38	0.36
K-W	32.7: 27.1:40.2	0.72	0.61
R-W	40.6:20.6:38.8	1.33	0.60
ZP-S	39.3:21.4:39.3	1.61	1.00
VR-S	27.4:24.1:48.5	1.32	0.58
K-S	30.1:22.0:47.9	1.28	0.47
R-S	26.1:24.5:49.4	1.40	0.56
Parameter	1	2	3

TABLE V. Parameters that characterize the distribution of terpane in alkane fractions extracted organic substances in analyzed water and sediment samples of the River Ibar

Sample	Ts/Tm	$C_{30} \text{ hopane} / C_{30} \text{ moretane}$	$C_{32}(22S) / C_{32}(22R)$
ZP-W	1.13	13.90	1.42
VR-W	1.28	12.17	1.32
K-W	0.89	10.15	1.52
R-W	1.42	12.00	1.36
ZP-S	1.06	8.12	2.17
VR-S	1.56	8.33	1.64
K-S	0.75	13.30	1.64
R-S	0.63	10.83	1.35
Parameter	1	2	3

In all eight terpane fragmentograms, a peak which represents C_{27} $18\alpha(H),22,29,30$ -trisorneohopane (Ts) geoisomere located only in oil and the bitumen of old mature sediments is present. C_{29} and C_{30} $17\alpha(H)21\beta(H)$ -hopanes are significantly more abundant than C_{29} and C_{30} $17\beta(H)21\alpha(H)$ -moretane, and in homologous series of C_{31} – C_{35} homohopanes, $22(S)$ isomers are more abundant than less stable $22(R)$ form. Based on these results, it can be clearly concluded that in water and sediment samples taken at the selected sites along River Ibar the oil type pollutants are present.

However, the parameters of Tables IV and V, which specifically define the distribution of these biological markers show that they differ significantly. This is the case with the distribution of the biolipide sterane isomere (parameter 1, Table IV), which is considered as one of the most reliable correlation parameters for

assessing the origin of organic matter in sediments and oil,¹⁻⁴ but also with all others parameters which are used in the organic geochemical correlation studies for assessment of the maturity (sterane parameters 2 and 3 in Table IV and terpane parameters 1-3 in Table V). These differences are also visible when comparing water and sediment samples with each other, when comparing water and sediment samples taken at the same sites, but also samples from the river flow that belongs to the same town. In this way, the parameter values from Tables IV and V show that petroleum pollutants of the River Ibar have more sources of pollution.

CONCLUSIONS

In this paper, a “forensic” approach was applied for determining the presence and assessment of the origin and fate of oil pollutant in the water and sediment of the River Ibar (samples are taken upstream and downstream from the towns of Kosovska Mitrovica and Kraljevo).

Owing to deposition, and then the mineral adsorption, the amount of organic substances (bitumen fraction) in sediment is significantly higher than in water (710 to 830 mg kg⁻¹ vs. 40 to 132 mg l⁻¹).

Prevalance of NSO compounds in seven out of eight samples (68.6 to 84.5 % in the sediment organic substance and 44.0 to 57.2 % for the three samples of water) leads to the conclusion that in these samples organic substance of native origin is present.

In three out of the four tested water samples *n*-alkanes in the range of C₁₈–C₂₆ are identified with an uniform distribution of the odd and even homologue (*CPI* values are close to the unit). The absence of homologs with a larger number of carbon atoms (>C₂₆) may be explained by their low solubility in water. Furthermore, since NSO compounds and water are building colloidal micelles in a channel form with a diameter of about 5 Å in which *n*-alkanes with longer series (thus establishing the inclusion compounds) can be incorporated, it can be assumed that the third fraction of the bitumen extract of these samples represent the sum of the NSO compounds and *n*-alkanes with more than 26 carbon atoms masses.

Relatively high concentration and *n*-alkanes with more than 26 carbon atoms have been identified only in one sample (K-W). It contains only 9.4 % NSO compounds. The implication is that that total amount of *n*-alkanes (including >C₂₆ homologues) was extracted only in this sample which resulted in a low percentage of the third fraction, and high percentage of the saturated hydrocarbons fraction (44.5 %).

n-Alkane identified in the sediment samples ZP-S and R-S are characterized by a bimodal distribution. Since besides *n*-alkanes with a distinct domination of members with an odd number of carbon atoms (which is characteristic of organic

substances of recent sediments) in the first part of the chromatogram in these fractions are peaks that correspond to the lower homologues with uniform abundance of odd and even members it may be assumed that anthropogenic organic matter of oil type participated in the total organic substances in the sediments of the two sites.

In all tested water and sediment samples, polycyclic alkanes of sterane and terpane type with distributions that are characteristic for oil were identified. Geolipide isomers with β configuration at the fourteenth and seventeenth carbon atoms and the S configuration at the twentieth carbon atom as well as diasteranes as typical geoisomers were identified in sterane fragmentograms. In the terpane fragmentograms C_{27} 18 α (H), 22,29,30-trisnorneohopane (*Ts*), C_{29} and C_{30} 17 α (H)21 β (H)-hopanes (which are significantly more abundant than C_{29} and C_{30} 17 β (H)21 α (H)-moretane), as well as the homologous series of C_{31} – C_{35} homohopanes at which 22(*S*) isomers is more abundant than the thermodynamically less stable 22(*R*) configuration were identified. Such distributions of sterane and terpane clearly indicate that in the water and sediment samples of the River Ibar pollutants of oil type are found.

However, based on the significant differences in the distributions of these polycyclic alkane (water–water, sediment–sediment and water–sediment) can be concluded that petroleum pollutants of the River Ibar have more than one source of pollution. On the other hand, the presence of oil type organic pollutants in all tested samples of water in the vicinity of Kosovska Mitrovica and Kraljevo that are at a relatively large distance, suggests that the River Ibar is permanently exposed to this form of pollution.

SUPPLEMENTARY MATERIAL

Sampling details and identification of the peaks from Figs. 3 and 4 are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ОРГАНСКО–ГЕОХЕМИЈСКИ ПРИСТУП У ИДЕНТИФИКАЦИЈИ ЗАГАЂУЈУЋИХ СУПСТАНЦИ НАФТНОГ ТИПА У ВОДИ И СЕДИМЕНТИМА РЕКЕ ИБАР

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У раду је примењен органско–геохемијски приступ у проучавању природе органске супстанце вода и седимента реке Ибар (узводно и низводно од градова Косовска

Митровица и Краљево). Примењен је „форензички“ приступ који се ослања на чињеницу да се састав органске супстанце рецентних седимената и нафте разликује као последица њихових различитих геолошких старости и матурираности. Садржај битуменске фракције, њен групни састав засићене, ароматичне и NSO фракције (једињења азота, сумпора и кисеоника) и расподеле *n*-алкана у засићеним фракцијама, идентификовани су гасно-хроматографско–масеноспектрометријском техником (у скоро свим узорцима инкорпорирани у колоидне мицеле које су формирали вода и NSO једињења) нису могле да дају одговор на питање да ли се у изолованим екстрактима налази нативна или антропогена органска супстанца. Међутим, присуство стерана и терпана са расподелама структурних и стереохемијских изомера, какве су карактеристичне за нафту, као најматуриранији облик органске супстанце седиментних формација, недвосмислено је потврдило присуство загађујућих супстанци нафтног типа у испитиваним водама и седиментима. На основу значајних разлика у расподелама ових полицикличних алкана (вода–вода, седимент–седимент и вода–седимент) закључено је да они имају више извора загађења и да је река Ибар перманентно изложена овом виду загађења.

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