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Temporal trend of perfluorinated compounds in untreated wastewater and surface water in the middle part of the Danube River belonging to the northern part of Serbia

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Abstract: The occurrence and temporal variation of selected priority substances and contaminants of emerging concerns, *i.e.*, eleven perfluorinated compounds (PFCs, belonging to perfluorosulphonates, perfluorocarboxylic acids, and perfluorinated sulphonamides) have been investigated in composite surface water samples of the Danube River at the upstream and downstream locations from the discharge point of wastewater. Among the analyzed compounds, six PFCs (PFOA, PFOS, PFHxA, PFNA, PFDA and PFUnA) were quantified. Overall, the detection frequency for most quantified compounds was very high (>90 %), only PFDA and PFUnA were quantified with less frequency, 33 and 67 %, respectively. The highest quantified concentrations of PFOA and PFOS were 14.9 ng/L (average 12.1 ng/L) and 14.2 ng/L (average 6.11 ng/L), respectively. These ones together with PFHxA (average 10.0 ng/L) were quantified at the highest concentrations in comparison to the other investigated compounds. However, the determined levels of PFOS during investigated sampling period, for all samples analyzed, were always lower than the maximum allowable concentration set for inland river waters but always higher than the environmental quality standard threshold value-AA-EQS of 0.65 ng/L sets by the Directive of European Parliament. Moreover, the levels of PFOA were always several times lower than the set AA-EQS value.

Keywords: emerging contaminants; PFCs occurrence; PFOS; PFOA; environmental pollution.

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INTRODUCTION

It is well known that the contamination of fresh water with numerous toxic compounds is a global problem.^{1,2} Unregulated chemicals gathering a wide range of so-called “emerging” or “new” contaminants have appeared as an environmental problem and become a priority topic in environmental analysis.³ Among them, perfluorinated compounds (PFCs) attract considerable attention as they are globally distributed, environmentally persistent, bioaccumulative and potentially harmful.^{2,4} A fully fluorinated hydrophobic alkyl chain attached to a hydrophilic end group is a common feature of these contaminants.⁵ As a consequence, PFCs have been found ubiquitous in the environment and in biota.⁶ However, despite being first synthesized back in 1940, PFCs have only recently been designated as contaminants of emerging concern.⁷ PFCs include perfluorocarboxylic acids (PFCAs), perfluorosulphonates (PFSAs) and perfluoro sulfonamides (PFASAs) and other polyfluorinated compounds, such as fluorotelomer sulphonates (FTSs), perfluoro phosphonic acids (PFPAs, *i.e.*, fluorotelomer).⁵ The most important and widely-studied representatives of PFCAs and PFSAs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), respectively. PFOS and PFOA were the first PFCs recognized as global pollutants because of their extended use during the past decades.⁴ Surface water is considered to be the major environmental reservoir for PFCs,⁵ because the surface water is a final sink for most PFCs. However, the presence of PFCs was determined also in groundwater,⁸ sediment,^{9,10} sludge samples,¹¹ agricultural plants,¹² food commodities,^{13,14} and even in the human body.⁵ Moreover, it is found that in every 20 children tested 19 had blood contaminated with PFOA which is extremely alarming.¹⁵ Thus, among selected PFCs, PFOS and PFOA were of particular concern since they account for the major proportion of PFCs contamination worldwide, thanks to their high solubility in the aquatic environment.¹⁵ Namely, PFOS and PFOA have high solubility of 570 and 9500 mg/L, respectively. The European Commission (EC) has declared PFCs as emerging organic contaminants, and PFOS and its derivatives as priority hazardous substances which must be monitored in the European Union (EU) water bodies. Namely, in the EU strong restrictions on the use and import of PFOS were introduced in 2006, while in 2012, through European Water Framework Directive, the EC established a threshold concentration in drinking water and fish for environmental quality assessment, and in 2013, it established Environmental Quality Standards¹⁶ against which to measure PFOS concentrations in inland surface waters and biota. The maximum allowable concentration (*MAC-EQS*) for surface water and biota (*EQS*) is set at 36.0 and 9.1 ng/L, respectively; after a risk assessment study, the mean annual concentration (*AA-EQS*) limit is set to be 0.650 ng/L for inland surface water.¹⁶ Moreover, PFOA, its salts and related substances are restricted with certain derogations within the EU with a transitional period until 2020. PFOA, its salts and

PFOA-related substances shall not be manufactured or placed on the market as substances on their own from 4 July 2020.¹⁶ Accordingly, the mean annual concentration limit for PFOA is set to be 100 ng/L for inland surface water.¹⁶ For perfluorononanoic acid (PFNA), perfluorododecanoic acid (PFDoA), perfluoroundecanoic acid (PFUnA), and perfluorodecanoic acid (PFDA) in the EU, regulatory restrictions similar to the ones in place for PFOS and PFOA are currently under discussion. As the carbon-fluorine bond in PFCs is one of the most stable in nature, removal of these contaminants in wastewater treatment plants (WWTPs) and also in the environment under aerobic and anaerobic conditions is limited. They are not significantly removed during secondary biological treatment, while their concentrations in treated wastewater are often higher compared to raw sewage.⁴ Namely, it is observed that longer-related PFCs can biodegrade to short-chain PFCs which causes that WWTPs not only directly receive PFC loads from various inputs, but also enhance, *e.g.*, PFOS and PFOA concentration *via* degradation of their longer-related PFCs.¹⁸ The threat posed by the release of these contaminants through wastewater treatment plant effluents is particularly worrisome in streams or small rivers, where the dilution capacity of the receiving freshwater ecosystem is small.¹⁸

Relating the present situation in Serbia only the small portion (around 10 %) of WW is treated by any standardized WW treatment procedures implying a common practice of discharging untreated municipal wastewater into surface water recipients.¹⁹ Although the Danube River, the largest river in Serbia, has the greatest dilution capacity, even the worrisome problem is that 90 % of untreated wastewater is directly discharged into the rivers of Serbia. Since the surface water samples were collected upstream and downstream of the wastewater discharge point into the Danube River, the results obtained in this study were used to assess the impact of PFCs from discharged wastewater on surface water, as in the scientific literature, there is scarce information available on the occurrence of perfluorinated compounds in the Danube River and its tributaries. This is particularly important knowing that the Danube River is the second-largest river in Europe (2857 km long) that flows through 10 countries and receives a vast volume of untreated wastewater from domestic sources, industrial and agricultural activities, but, on the other hand, together with its tributaries, the Danube River provides a necessary resource for water supply, sustaining biodiversity, agriculture, industry, fishing, recreation, tourism, power generation and navigation.²⁰ Thus, in light of the present situation, the aims of this study were: *i*) to give a preliminary insight into the occurrence and levels of eleven perfluorinated compounds, which included two perfluorosulphonates; perfluorobutane sulfonic acid (PFBS) and perfluorooctane sulfonic acid (PFOS), eight perfluorocarboxylic acids; perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic

acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA) and one perfluorinated sulphonamides: perfluorooctane sulfonamide (PFOSA) in the surface water of the middle part of the Danube River belonging to Republic of Serbia by the method validated in this study, *ii*) to reveal hotspots in small-sized cities which might have a possible adverse effect on the environment as a consequence of the discharge of untreated wastewater, *iii*) to investigate the temporal variation in concentrations of studied PFCs and *iv*) to compare the determined levels with the ones found in the literature. To the best of our knowledge, there is no published data regarding the concentration of 11 PFCs in the surface water of the Danube in Balkan countries.

EXPERIMENTAL

Chemicals and standards

Eleven PFCs, *i.e.*, PFBS, PFOS, PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA and PFOSA were obtained from Chiron AS (Trondheim, Norway). Purities of the standards were >98 %. More details about eight surrogate compounds (SSs) could be found in the Supplementary material. Waters Oasis HLB Plus LP (225 mg, 60 μ m) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA). Grade GF/C glass microfiber filters (0.47 μ m) were purchased from Whatman International Ltd (Maidstone, Kent, UK). Ultra-pure water (resistivity 18.2 M Ω cm) was obtained from Milli-Q system (Millipore, Molsheim, France). Methanol and ammonium acetate (all LC-MS grade) were purchased from J.T. Baker (Deventer, Netherlands), and glacial acetic acid (trace analysis grade) was obtained from Fisher Chemicals (Fisher Chemicals, Loughborough, UK).

Sampling sites and sample collection

Details related to sampling are given in Supplementary material to this paper.

Twelve composite surface water samples were collected down-D ($n = 6$) and up-U ($n = 6$) stream of the discharge point of the local municipal collecting wastewater unit. Additionally, eight composite 24 h wastewater (WW) samples were collected from the discharged unit. The sampling frequency is given in Supplementary material, Table S-I. More about sample collection could be found in the Supplementary material.

Sample extraction

During the samples handling and analysis Teflon bottles, Teflon-lined caps and any suspect fluoropolymer materials were avoided in order to avert cross-contamination of the samples. Analytical methods for the determination of PFCs in wastewater and surface water samples were developed by Duong *et al.*²² and re-validated by an “in-house” quality control procedure for purpose of the present study. More information could be found in the Supplementary material. The extract was then spiked with internal standards (ISs listed in Section *Chemicals and standards*) at the concentration of 2 ng/mL by transferring 20 μ L of IS stock solution (50 μ g/mL) into the 500 μ L of the final extract.

Instrumental analysis

Concentrations of PFCs in SW and WW samples were determined by using Thermo ultra-high-performance liquid chromatography (UHPLC) coupled with a Thermo TSQ Vantage triple quadrupole mass spectrometer (MS/MS) equipped with heated-electrospray ioniz-

ation probe, HESI (Thermo Fisher Scientific, San Jose, CA, USA), more details could be found in Supplementary material, Table S-II.

Method validation parameters

The sample preparation method used for the analysis of polar compounds on UHPLC-MS/MS was published earlier.²² Although the mentioned sample preparation methods were fully validated, an additional “in-house” quality control procedure was applied in order to check their applicability in the different laboratories and on different types of instruments. Parameters that were taken into account were: specificity, instrumental linearity, method limits of detection (*MDL*) and quantification (*MQL*), recovery, and precision (expressed as relative standard deviation). Criteria for PFCs identity confirmation by MS/MS were: *i*) the retention time, *ii*) the presence of two product ion transitions for each analyte and *iii*) the relative intensities of the detected products ions (ratio qualifier/quantifier transitions), which shall correspond to those of the calibration standards at comparable concentrations within tolerances ranging from 20 to 50 % depending on the relative intensity of the base peak.²³ To evaluate the linearity of the method mixed standard solutions were prepared in the expected concentration range of PFCs, *i.e.*, in accordance with available literature data. Acceptable linearity was achieved when the squared correlation coefficient (R^2) was higher than 0.99 for internal calibration curve. It's worth noting that the deuterium-labeled internal standards were provided for each studied PFCs. PFCs were quantified using an internal calibration procedure. In this way, preparation of matrix match calibration was avoided as the PFC residue-free matrix was really hard to obtain. Calibration solutions for internal calibration curves were prepared into previously analyzed ultra-pure water. The instrumental limit of detection (*IDL*) values were estimated as the concentration of each toxic compound that gives a signal that corresponds to three times the noise ($S/N = 3$). The instrumental limit of quantification (*IQL*) values was defined as the concentration of each toxic compound that gives a signal that corresponds to ten times the noise ($S/N = 10$). Then the method detection limits (*MDL*) and method quantification limits (*MQL*) were calculated taking into consideration the dilution factor and the volume of sample used (500 mL for surface water and 300 mL for wastewater).

Recovery tests were conducted by spiking a mixture of 11 PFCs (10 ng/L each) and a mixture of 8 surrogate compounds (10 ng/L each) into ultra-pure water. Spiked water was treated by the same procedures as real water samples. Before recovery experiments, unfortified water samples were previously analyzed in order to confirm that no PFCs were detected. Recovery of the method was determined for all compounds and defined as the ratio between the quantified and the spiked amount. The repeatability of the method was determined as relative standard deviation (*RSD* in %) of the PFCs in five fortified samples. Blank samples were included in every batch of samples to check for possible contamination. The accuracy of individual sample analysis was checked by examining the recoveries of the surrogate spiked into the samples before analysis. When reporting data, blank corrections were subtracted from sample concentration. The reporting values were corrected using recovery values. Whenever sample concentrations were below the *MQL*, a concentration equal to half of the limit of quantification was used for the calculations, according to Directive 2009/90/EC.¹⁶ Also, when the total sum was reported results below the *MQL* of the individual substances were set to zero.¹⁶

Statistical treatment of the data

Microsoft Excel 2010 for Windows was used for basic statistical treatment (mean, maximum, minimum, kurtosis, skewness) of the obtained data. Statistically significant difference

between means of samples taken upstream and downstream during the monitoring period and statistically significant difference in quantified concentrations among each analyzed PFCs during the monitoring period of one month were checked by student's *t*-test.

RESULTS AND DISCUSSION

Quality assurance and quality control

In Table I are given the results obtained during the validation procedure carried out in order to prove that the applied sample preparation method and instrumental analysis fit the purpose for PFCs determination in surface and wastewater samples.

TABLE I. Validation parameters for PFCs determination; reproducibility (inter-day precision) was calculated as the relative standard deviation, %, of the analytes (ten replicates) of blank surface water fortified with 11 analytes at three concentrations (10, 20 and 50 ng/L) on three consecutive days

PFCs	Linearity	MDL / ng L ⁻¹	MQL / ng L ⁻¹	Recovery, %	RSD / %	Inter-day, %
PFBA	0.9985	0.430	1.43	89.4	12	9.2
PFBS	0.9975	0.0100	0.0402	86.6	13	12
PFHxA	0.9933	0.195	0.630	73.2	7.4	14
PFHpA	0.9914	0.124	0.398	79.0	8.2	8.8
PFOA	0.9933	0.0602	0.218	76.5	13	15
PFOS	0.9925	0.100	0.321	81.8	11	9.6
PFOSA	0.9982	0.281	0.932	120	9.4	12
PFNA	0.9925	0.393	1.32	84.3	14	12
PFDA	0.9964	0.172	0.584	80.4	13	9.4
PFUnA	0.9994	0.125	0.397	72.1	15	10
PFDoA	0.9935	0.104	0.332	73.8	14	11

Identification of PFCs after UHPLC–MS/MS analysis was carried out using the retention time of the targeted compounds, precursor ion and at least two selective product ions. The validation process showed that the reported transitions for PFCs were the same as was published in the previous study²² although different UHPLC–MS/MS instruments were used. The linearity of the calibration curves was higher than 0.9900 for all studied compounds covering the range from 0.100 to 30 ng/L for surface water and from 0.170 to 50 ng/L for wastewater samples. Precision was lower than 15 % for all analyzed compounds. The efficiencies of extraction were in the range from 72 to 120 % obtained by analyzing five fortified replicates.

Relating the *MQL*, they were all lower than 1.43 ng/L. The obtained method validation parameters were comparable with the previously published data in which similar compounds were analyzed in surface and wastewater samples.²² The obtained validation parameters are comparable, *e.g.*, with the results obtained during the analysis of PFCs in the Danube River where the range of *MQL* was

from 0.551 ng/L (PFBS) to 3.20 ng/L (PFHpA).²⁶ It is worth mentioning that there are no reports in which a significant number of PFCs (eleven) were analyzed.

PFCs in surface water in the middle part of the Danube River, belonging to Republic of Serbia

Out of eleven analysed PFCs four of them (PFNA, PFOS, PFOA and PFHxA) were detected in all surface water samples, whereas PFDA and PFUnA were detected sporadically (Table II). Namely, PFUnA and PFDA were detected with the frequency of detection of 33 and 67 %, respectively, while the other detected PFCs showed a high frequency of occurrence (100 %) with a uniform level of occurrence during the monitoring period. The quantified concentrations of PFOA and PFHxA were in all analysed samples higher than 5 ng/L. PFOA and PFHxA account between 27 and 46 % and 25 to 36 % of the total PFCs concentrations. PFOS accounts between 9.4 and 37 % of the total PFC concentrations. This distribution is similar to data reported for surface water in the Europe²⁴ and Sri Lanka²⁵ where PFOS and PFOA were dominant, but PFNA was a minor component, yet different to those in river from Japan and Vietnam where PFOA and PFNA were more abundant than PFOS. In particular, PFOA is used as adjuvant in the production of fluoropolymers such as Teflon[®] or similar products, and occurs in these applications as aqueous and gaseous process emission.²⁴ All the other quantified PFCs account for less than 10 % of the total PFC concentrations. There was no statistically significant difference in quantified concentrations among each analyzed PFCs during the monitoring period. The highest quantified concentrations of PFOS and PFOA were 14.9 ng/L (average 6.11 ng/L) and 14.2 ng/L (average 12.1 ng/L), respectively. These ones together with PFHxA (average 10.0 ng/L) were quantified at the highest concentrations in comparison to the other investigated compounds. The quantified concentrations of other detected compounds (PFUnA, PFDA and PFNA), were all lower than 5 ng/L. The concentration of PFOS exceeded the AA-EQS of 0.65 ng/L for each analyzed surface water sample during the whole sampling campaign. However, relating the maximum allowable concentration of PFOS in surface water sets for biota, the determined level was higher only for one sample analyzed upstream of the discharge point. Moreover, none of the analyzed samples showed a level that exceeds the AA-EQS of 100 ng/L set for PFOA in inland water. The Final Report of Joint Danube Survey 3²⁷ reports 8.10 ng/L as the average concentration of PFOA in the Danube River downstream Budapest and 7.20 ng/L as the average concentration of PFOS in the Danube River in Szob before Budapest.

Interestingly, PFHxA was detected in relatively high concentration (relative to other detected PFCs) in this study but not in the other mentioned papers, but still lower than the PFOA. Namely, besides some companies have switched to C6

PFCs such as perfluorohexanoic acid (PFHxA) to replace C8 PFCs as PFOA this trend is still not evidenced in the Danube River.

TABLE II. PFCs quantified in surface water samples

Sample	Concentration, ng/L					
	PFHxA	PFOA	PFOS	PFNA	PFDA	PFUnA
12.11.3-U	5.94	8.85	3.23	1.53	2.06	1.03
12.11.3-D	11.4	11.1	2.98	3.73	2.39	0.195 ^a
20.11.5-U	8.37	13.9	3.82	1.54	1.97	0.96
20.11.5-D	11.8	13.8	3.53	4.95	0.292 ^a	0.195 ^a
21.11.6-U	11.1	12.9	4.08	4.17	2.03	0.195 ^a
21.11.6-D	10.3	10.9	14.9	3.66	0.290 ^a	0.195 ^a
25.11.8-U	11.0	11.9	5.27	1.42	4.42	0.195 ^a
25.11.8-D	8.38	14.2	6.27	1.69	1.89	0.94
27.11.10-U	9.49	11.8	4.64	1.62	1.71	0.195 ^a
27.11.10-D	8.89	11.6	3.4	1.99	2.10	0.195 ^a
29.11.12-U	12.0	11.4	9.53	2.36	0.290 ^a	0.195 ^a
29.11.12-D	11.8	13.0	11.7	4.6	0.290 ^a	4.60
Mean	10.0	12.1	6.11	2.77	1.64	0.758
Median	10.6	11.8	4.36	2.18	1.93	0.195
Min	5.94	8.85	2.98	1.42	0.290	0.195
Max	12.0	14.2	14.9	4.95	4.42	4.60
Frequency of occurrence, %	100	100	100	100	67.3	33.2

^aNon-detected values were set to half the *MQL* for these calculations (in accordance with Directive 2009/EC)

Moreover, the obtained results were compared with the previously published data from the Joint Danube Survey 3²⁷ organized by the International Commission for the Protection of the Danube River (ICPDR) in 2013. JDS3 included in analysis six PFCs: PFBS, PFHxA, PFHpA, PFOA, PFOS and PFNA in the Danube River and its tributaries.²⁷ Of the mentioned ones, PFBS, PFHxA, PFOA and PFOS, were quantified with average and maximum value of 1.60 and 3.70, 4.00 and 8.50, 8.10 and 36.5 and 7.20 and 26.2, respectively. PFOS, PFOA and PFHxA were quantified with frequency over 90 %, which is in accordance with the results obtained in this study. The average concentrations of PFOS (7.2 ng/L), PFOA (8.1 ng/L) and PFHxA (4.0 ng/L) were of the same order as the results obtained in this study. PFOS exceeded the target value of 0.651 ng/L sets by EU Environmental Quality Standard at 94 % of the sampling sites during JDS3 survey and for all samples analysed in this study. The ICPDR had also organized, in 2007, a monitoring program²⁶ on the occurrence of some polar organic pollutants among them six PFCs (PFHpA, PFOA, PFNA, PFOS, PFDA, PFUnA) in the Danube River. Again, PFOS and PFOA were quantified with frequency over 90 % with the average concentrations of 8 and 20 ng/L, respectively. Additionally, the mean value of PFOA and PFOS obtained in this study was compared with the data of a few studies investigating the vulnerability of European river systems

such as Kampen IJssel (Netherland),²⁸ Ebro River (Spain),²⁹ Thames River (United Kingdom),³⁰ and Rhine River (Germany)³¹ in order to assess PFCs pollution levels, Table III.

TABLE III. Comparison of PFOA and PFOS levels in European river systems; n.d. – not detected, n.e. – not estimated

System	Concentration, ng/L	
	PFOA	PFOS
This study	12.1	6.11
Wastewater canal in Pančevo (Serbia) ^{a10}	n.e.	24.09 ^b
Joint Danube Survey 3 ²⁷	8.50	7.20
Kampen IJssel (Netherland)	n.d.	9.90
Ebro River (Spain) ²⁹	125	27.0
Thames River (United Kingdom) ³⁰	11.7	18.9
Rhine River (Germany) ³¹	3.66	8.56

^aThe analyzed soil and sediment samples are from within and around the Petrochemical Industry of Pančevo;
^brecalculated based on published concentration level in sediment sample¹⁰

It can be concluded that concentrations of PFOS in Kampen IJssel²⁸ and Rhine River³¹ were of the same order, but a bit higher than the concentrations obtained in this study being 9.90 and 8.56 ng/L, respectively while concentrations in Ebro River²⁹ and Thames River³⁰ were 4.4 and 3.1 times higher than concentrations obtained in this study. In respect of PFOA concentrations in Rhine River and Thames River were lower being 3.66 and 11.7 ng/L while concentrations in Ebro River were 10.3 times higher.^{29–31} The study published by Beškoski *et al.* (2013) represents the first data on the presence of PFCs in sediment samples in Serbia.¹⁰ The study deals with the determination of PFCs in sediment samples of wastewater canal draining wastewater from the industrial complex of Pančevo, Serbia. PFOS was quantified in a concentration up to 5.7 ng/g dry weight (dw), while the total PFCs content was up to 6.3 ng/g (dw). The recalculated PFOS concentration in water using the adsorption coefficient from the literature was 24.09 ng/L. The mean recalculated PFOS concentration (24.09 ng/L) was almost four times higher than the mean concentration of PFOS (6.11 ng/L) reported in the present study. Furthermore, it is interesting to note that the sum of identified PFCs determined in the Danube River surface samples during the sampling campaign was always a few times lower than the action limit for drinking water sets in Denmark, by the Environmental Protection Agency of 100 ng/L for the sum of 11 PFCs compounds including perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, 6:2 fluorotelomer sulfonic acid (6:2 FTSA), PFBA, perfluoro-*n*-pentanoic acid (PFPeA), PFHxA, PFHpA, PFOA, PFNA and PFDA; as well as, the sum of PFCs in the Danube surface water samples were lower than the concentration limit sets in Sweden by National Food Agency of 90 ng/L for sum of seven PFCs including PFOA, PFOS,

PFBS, PFPeA, PFHxA, PFHpA and PFHxS. Besides, it is worth mentioning that the United Kingdom Drinking Water Institute sets the action limit only for PFOA and PFOS of 10.0 ng/L for each of them, in 2021, while in the Netherlands, the concentration limits of 390 ng/L for PFOA and 90 ng/L for PFOS are set, in 2020.

PFCs in wastewater

Among 11 analyzed PFCs, only PFOS and PFOSA were quantified in WW samples (Fig. 1). PFOS was quantified in the concentration range from 0.321 to 3.54 ng/L, while PFOSA was quantified in the concentration range from 0.140 to 7.38 ng/L. PFOS and PFOSA were quantified with the frequency of occurrence of 50 and 88 %, respectively. Since PFOSA was not detected in surface water samples it could be concluded that untreated wastewater does not have an influence on PFOSA content in the Danube River.

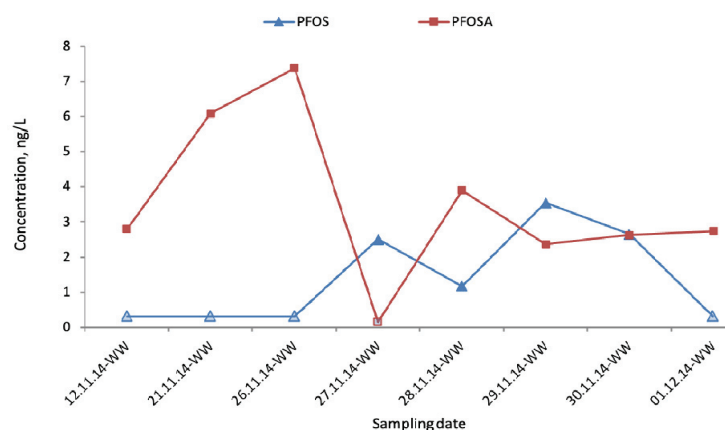


Fig. 1. Concentrations of PFOS and PFOSA in wastewater samples.

A similar conclusion can be drawn for PFOS, since its mean value (6.1 ng/L) for surface water samples upstream and downstream of the wastewater discharge into the Danube River is almost 2.5 times higher than in wastewater samples (2.50 ng/L).

CONCLUSIONS

The obtained results contributed to the previous two EU studies on the occurrence of perfluorinated compounds in Danube River water. The method, developed in this study, is capable to detecting perfluorobutane sulfonic acid (PFBS); perfluorooctane sulfonic acid (PFOS); perfluorooctane sulfonamide (PFOSA); perfluorobutyric acid (PFBA); perfluorohexanoic acid (PEHxA); perfluoroheptanoic acid (PFHpA); perfluorooctanoic acid (PFOA); perfluorononanoic acid (PFNA); perfluorodecanoic acid (PFDA); perfluoroundecanoic acid

(PFUnA); perfluorododecanoic acid (PFDoA). SPE technique was chosen for the clean-up step in the analytical procedures used for analysis of PFCs in water. The concentrations of PFOS were quite constant in the Danube River, while the concentrations of PFOA have been in decreasing trends probably as a consequence of strong restrictions on the use and import. Regarding the other investigated PFCs, although the data on their presence is still limited, the levels of occurrence were in stagnation or in slightly increase over time in the Danube River (*e.g.*, PFNA was quantified in average concentration of 1.00, 1.20 and 2.77 ng/L during JDS2,²⁶ JDS3²⁷ and in this study, respectively). There was no statistically significant difference between the mean values obtained for the PFCs in upstream and downstream water samples indicating that the discharge of wastewater from small-sized towns (Indija, Stara Pazova and Nova Pazova, with total population of about 150.000) had not influenced the water quality.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/11811>, or from the corresponding author on request.

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ИЗВОД

СЕЗОНСКЕ ПРОМЕНЕ У КОНЦЕНТРАЦИЈАМА ПЕРФЛУОРОВАНИХ ЈЕДИЊЕЊА У НЕПРЕЧИШЋЕНИМ ОТПАДНИМ И ПОВРШИНСКИМ ВОДАМА СРЕДЊЕГ ДЕЛА РЕКЕ ДУНАВ НА СЕВЕРУ СРБИЈЕ

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Сезонске промене у концентрацијама једанаест перфлуорованих једињења (PFCs) испитиване су у композитним узорцима површинске воде реке Дунав, узводно и низводно од места испуштања отпадних вода. Међу једанаест анализираних PFCs квантификовано је шест PFCs једињења (PFOA, PFOS, PFHxA, PFNA, PFDA и PFUnA) у дванаест испитиваних узорака. Највеће концентрације одређене су за PFOA и PFOS и то 14,9 ng/L (средња вредност 12,1 ng/L) и 14,2 ng/L (средња вредност 6,11 ng/L), редом, у поређењу са осталим испитиваним PFCs једињењима. Међутим, добијене концентрације PFOS током испитиваног периода узорковања биле су ниже од максимално дозвољених концентрација прописаних за реке, али су биле веће од граничних вредности концентрација (0,65 ng/L) за квалитет животне средине, прописаних Директивом европског парламента. Додатно, добијене концентрације за PFOA биле су неколико пута ниже од концентрација прописаних поменутом Директивом.

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