



Perfluorinated compounds in sediment samples from the wastewater canal of Pančevo (Serbia) industrial area



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HIGHLIGHTS

- ▶ This is the first report of the presence of PFCs in the samples from Serbia.
- ▶ PFOS up to 5.7 ng g⁻¹ dw and total PFCs up to 6.3 ng g⁻¹ dw were detected.
- ▶ Compared to other worldwide reports high levels of PFOS were found in the sediment.
- ▶ A mass load of 1.38 kg year⁻¹ PFOS discharged in Danube River has been calculated.
- ▶ Our work contributes to identification of PFCs pollution of the Danube River Basin.

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ABSTRACT

Perfluoroalkyl sulfonates (PFASs) and perfluoroalkyl carboxylates (PFCAs) were analyzed in sediment samples from the wastewater canal draining the industrial complex of Pančevo, Serbia (oil refinery, petrochemical plant, and fertilizer factory). The canal is directly connected to Europe's second largest river, the Danube, which drains its water into the Black Sea. Perfluorooctane sulfonate (PFOS) up to 5.7 ng g⁻¹ dry weight (dw) and total Perfluorinated compounds (PFCs) up to 6.3 ng g⁻¹ dw were detected. Compared to other reports, high levels of PFOS were found, even though PFCs are not used in the industrial production associated with this canal. The PFOS concentration in water was recalculated using the adsorption coefficient, K_{OC} from literature. Using the average output of wastewater from the canal, a mass load of 1.38 kg PFOS per year discharged in the Danube River has been calculated, which undoubtedly points to the contribution to global persistent organic pollution of surface waters originating from this industrial place.

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1. Introduction

Perfluorinated compounds (PFCs) are chemicals that do not occur naturally, but have been widely used in chemical production since the 1950s. Because of their unique properties such as surface activity, water and oil repellency, thermal and acid resistance they are used in industrial processes such as in protective coatings for carpets, textiles, leather, food containers, wiring insulations for telecommunications, but also as components of consumer prod-

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ucts such fire-fighting foams, surfactants in cosmetics, electronics and medicals (Prevedouros et al., 2006). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the two PFCs most commonly used and found in the environment. Unique physical, chemical and biological properties of PFCs that arise from carbon–fluorine bonds (Table 1), are the reason why some of these compounds are resistant to hydrolysis, photolysis and degradation by acids, bases, oxidants, reductants, microbes, and metabolism (Olsen et al., 2005). However, there are some reports that mean concentrations of even-chain length perfluoroalkyl carboxylates (PFCAs) were higher than those of odd-chain length PFCAs in sludge samples from a wastewater treatment plant (Ma and Shih, 2010), which suggests that some type of microbial transformation occurs. That is also good confirmation of previous reports that

Table 1

The perfluorinated compounds (PFCs) investigated in this study. Two types of functional groups with variable CF₂ chain length were included: perfluoroalkyl sulfonates and perfluoroalkyl carboxylates.

Formula/Name/Acronym	No. of CF ₂ groups	Analyte	Acronym
CF ₃ (CF ₂) _n SO ₃ ⁻ Perfluoroalkyl sulfonates (PFASs)	n = 3	Perfluorobutane sulfonate	PFBS
	n = 5	Perfluorohexane sulfonate	PFHxS
	n = 7	Perfluorooctane sulfonate	PFOS
	n = 9	Perfluorodecane sulfonate	PFDS
CF ₃ (CF ₂) _m CO ₂ ⁻ Perfluoroalkyl carboxylates (PFCAs)	m = 2	Perfluorobutanoate	PFBA
	m = 3	Perfluoropentanoate	PFPeA
	m = 4	Perfluorohexanoate	PFHxA
	m = 5	Perfluoroheptanoate	PFHpA
	m = 6	Perfluorooctanoate	PFOA
	m = 7	Perfluorononanoate	PFNA
	m = 8	Perfluorodecanoate	PFDA
	m = 9	Perfluoroundecanoate	PFUnDA
	m = 10	Perfluorododecanoate	PFDoDA
	m = 11	Perfluorotridecanoate	PFTTrDA
m = 12	Perfluorotetradecanoate	PFTeDA	

PFCAs are produced as biodegradation products of fluorotelomer alcohols (FTOHs) under aerobic conditions in the activated sludge process (Dinglasan et al., 2004; Wang et al., 2005). Studies have found PFCs in all segments of environment across our planet; air (Chaemfa et al., 2010; Shoeib et al., 2010), water (Ahrens et al., 2009a,b; Wang et al., 2012), and sediment (Higgins et al., 2005; Becker et al., 2008b; Zushi et al., 2010; Pico et al., 2012; Theobald et al., 2012). A number of studies have reported the ubiquitous distribution of PFCs in wildlife and humans (Kärman et al., 2010; Ahrens, 2011; Haug et al., 2011; Theobald et al., 2011; Croes et al., 2012; Domingo, 2012). Besides normal PFCs branched PFCs have also been produced and used, but our study were focused on linear chain PFCs.

In December 2006, the European Parliament and the Council decided to restrict marketing and use of PFOS, with a few exceptions, by amending Council Directive 76/769/EC on dangerous substances for PFOS (EC, 2006). Since these compounds are extremely persistent, bioaccumulative and of toxicological concern (Jensen and Leffers, 2008; Kovarova and Svobodova 2008), PFOS and perfluorooctane sulfonyl fluoride (POSF) are added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs) (Stockholm Convention on POPs, 2009). The EU is currently assessing PFOA.

Although industrial facilities that still use fluorochemicals are the largest sources of emissions for PFCs (Prevedouros et al., 2006), municipal and industrial wastewater treatment plant effluents are important contributors to PFC levels in the environment (Becker et al., 2008a; Guo et al., 2010; Ma and Shih, 2010). It has been shown that PFCs remain stable in wastewaters after treatment and are released into the environment (Kima et al., 2012). However, there is not sufficient data concerning the level of PFCs in wastewaters from industry that does not use PFCs directly in production. Released PFCs are distributed between water, suspended particulate matter and sediment (Ahrens et al., 2010). Sediments have been suggested as one of two final sinks of PFCs, the other being the deep oceans (Prevedouros et al., 2006). Since sediment can be considered as a reservoir of PFC, the distribution between water and sediment is described with partition coefficient (K_d) which depends on parameters such as pH (Higgins and Luthy, 2006) and organic carbon fraction (f_{oc}) (Ahrens et al., 2009a).

The Danube is the second longest river in Europe (after the Volga) and is a vital environmental and economic resource to central and eastern Europe. It supports drinking water supply, agriculture, industry, fishing, tourism and recreation, power generation, navigation, etc. (Liska et al., 2008) Its source is in the Black Forest region of Germany, and it flows eastwards for a distance of some

2850 km and drains an area of 817 000 km², before emptying into the Black Sea. In the scientific literature, there is little information available on the occurrence of polar organic contaminants such as PFCs in river water and sediment of the Danube River and its tributaries (Clara et al., 2009; Loos et al., 2009, 2010).

The wastewater canal Vojlovica (WWCV) was built in 1962 to collect the wastewater discharges from the industrial complex of the city of Pančevo in Serbia (Fig. 1). The WWCV is located 20 km northeast of Belgrade, capital of Serbia downstream on the River Danube. The industrial complex consists of a chemical fertilizers factory (HIP Azotara), petrochemical factory (HIP Petrohemija) and oil refinery (NIS Rafinerija Nafta, Pančevo) and covers about 290 hectares. The chemical fertilizers factory produces and/or handles many chemicals including ammonia, nitric acid, urea, calcium ammonium nitrate fertilizers, and nitrogen, phosphorus, and potassium fertilizers. The petrochemical factory produces ethylene dichloride (EDC) which is used to make vinyl chloride monomer that is polymerized to make polyvinyl chloride. The Polyethylene Pipes and Fittings Plant is also situated in the petrochemical factory in Pančevo. Finally, the oil refinery in Pančevo, the largest in the former Yugoslavia, is a facility that produces oil and gasoline products that are used by a variety of industries (Gopal and Deller, 2002).

The WWCV is an artificial canal with no natural flows, about 2 km long, around 70 m wide (from the crown to the crown of the embankment) and carries wastewater from several effluents and stormwater runoff from the complex directly into the Danube River (IMET, 2006). The water depth is around 1–2 m during mean flow of the River Danube. The environment surrounding the canal has been strongly affected for a long time by the presence of the industrial complex. Additionally serious destruction during the NATO military bombing campaign in 1999 resulted in contamination of air, soil, groundwater and the WWCV itself by various hazardous substances.

WWCV investigations conducted jointly by the United Nations Environment Programme (UNEP) and the United Nations Centre for Human Settlements (UNCHS) in 1999 (UNEP/UNCHS, 1999) and 2001 (UNEP/UNCHS, 2001) showed long-term pollution from the industrial complex. The main conclusion was that the water in the canal was not significantly polluted. In contrast, the sediments were classified as hazardous wastes (class H-11) due to their high content of mineral oil, mercury, polycyclic aromatic hydrocarbons, EDC and benzene, toluene, ethylbenzene and xylene. The United Nations Office for Project Services (UNOPS) performed another study on the Pančevo canal in 2002, and it was found that the pollutants were strongly bound to sediment



Fig. 1. Map and Google Earth image showing the wastewater canal of Pančevo industrial area in Serbia with marked sampling locations.

particles, while sediment pore-water was not significantly affected (UNEP, 2004).

The last in the series of official assessments, was performed in 2005/6 by D'Appolonia S.p.A Genoa, Italy, appointed by the Italian Ministry of the Environment and Territory (IMET, 2006). This document eventually resulted in a feasibility study for remediation of the wastewater canal. A preliminary ecotoxicological assessment of contaminated sediment from the WWCV was conducted during 2011 and this study justified the well-known status of the WWCV as a contamination hot spot (Planojević et al., 2011).

To our knowledge this is the first study and report of the presence of PFCs in samples from the WWCV and also from this part of the Danube River Basin. The aim of this study was to determine the possible presence of PFCs, compare the level of contamination with other known locations from literature and to assess the annual mass flow of PFOS from the canal to the River Danube having in mind sediment–water distribution and average water flow through the canal.

2. Experimental

2.1. Standards and reagents

Mass-labeled PFCA and PFAS (MPFAC-MXA) were obtained from Wellington Laboratories (Guelph, ON, Canada). All solvents and reagents were HPLC grade. Effective procedure for reducing blank level called Retention Gap Technique was used to avoid the increase of blank level from elution solvent (Ezaki et al., 2009).

2.2. Sediment sampling

Surface sediments layer of 15 cm were taken from WWCV using a Van Veen grab sampler (0.5 L capacity). In order to take samples

that would reflect the most average chemical composition of individual locations, 10 samples were taken from each of the five locations by “zig-zag” sampling from an area 5×5 m. These individual samples were homogenized directly at the sampling site in a previously methanol-rinsed polypropylene barrel. Every composite sample was representative of 25 m^2 area, depth 0.15 m and held an average value of PFCs concentration.

Composite samples were collected, transferred in glass jars and stored at 4°C during transport to the laboratory. Microbiological and chemical analyses were conducted immediately. For long-term storage, samples were stored in 500 mL polypropylene bottles and frozen (-20°C). In total, five sediment samples were collected. Four samples were taken from the WWCV itself, and for comparative purposes the same type of sediment sample was also taken from the navigation canal flowing parallel to WWCV but not receiving any direct discharge of industrial wastewaters. No water samples were analyzed because during the sampling campaign (November 11th, 2011), water was released from the effluents irregularly, and due to drought the level of the water in the WWCV was at the lower limit, so results were not expected to be representative. Details about sampling sites are listed in Table 2.

2.3. Basic physicochemical and chemical analysis of the sediment

Samples were analyzed for: content of clay, sand, and silt, moisture (for original material), pH, total, organic and inorganic carbon, sulfur and nitrogen using standard methods (Wilke, 2005; Pansu and Gautheyrou, 2006). The content of total petroleum hydrocarbons (TPH) in the sediment was extracted as per method ISO 16703 (2004) and determined gravimetrically in accordance with DIN EN 14345 (2004) as previously described (Beškoski et al., 2011).

Table 2
Sampling locations–coordinates.

Designation of the sample	Location	Water depth (m)	GPS	
			Latitude (N)	Longitude (E)
P-1	Navigation canal	6	44 50.404	20 39.650
P-2	Confluence of the WWCV with the Danube River (downstream from the industrial area and all effluents)	1.2	44 50.098	20 38.678
P-3	Mouth of the fertilizer factory outlet in WWCV and downstream	0.1–0.4	44 50.260	20 39.844
P-4	Mouth of the petrochemical factory WWTP outlet in WWCV and downstream	0.1–0.5	44 50.340	20 39.327
P-5	Mouth of the oil refinery new outlet for emergency situations in WWCV and downstream	0.1–0.6	44 50.338	20 39.143

2.4. Microbiological analysis

The number of microorganisms was determined by plating appropriate serial dilutions on agar plates incubated at 28 °C. The media used were: nutrient agar for total chemoorganoheterotrophs (TC); nutrient agar with 0.5% glucose for total anaerobic chemoorganoheterotrophs (TAC); malt agar for yeast and molds (YM) and a mineral base medium containing 2 g of standard D2 diesel fuel in 1 L of medium (Bossert et al., 2002) for hydrocarbon degraders (HD).

2.5. PFCs analysis

2.5.1. Sediment extraction

For extraction of PFCs, 5 g of homogenized, previously 105 °C-dried sediments were extracted three times using 10 mL of methanol and ultrasonic extraction. MPFAC-MXA (each 100 ng mL⁻¹ in methanol), as mass-labeled surrogates, was spiked into the sample. Then, after reducing the volume to 5 mL under nitrogen purging, 100 mL of Milli-Q water and 20 µL of formic acid were added. The sample was extracted with SPE (Presep PFC II, Wako Pure Chemical Industries) which were preconditioned with 10 mL of 0.1% ammonium/methanol, 10 mL of methanol, and 15 mL of Milli-Q water. After the analyte-loading, the cartridges were washed with 10 mL of Milli-Q water. The glass beaker was rinsed with 5 mL of 0.1% ammonium/methanol; the rinsing solution was directly used for elution of the target compounds in the cartridge. The elution was concentrated to 1 mL by using a gentle nitrogen stream. Labeled 10 µL of ¹³C₉PFOA (100 ng mL⁻¹ in methanol) was added as a syringe spike.

2.5.2. Instrumental analysis

Each final solution was analyzed by liquid chromatography (LC)–tandem mass spectrometer (MS/MS) using Xevo TQ (Waters) coupled with ACQUITY UPLC (Waters). Analysis was conducted using negative electrospray ionization with multiple reaction monitoring. The analytical column was ACQUITY UPLC BEH (C18, 2.1 × 50 mm, 1.7 µm, Waters). Separation of instrumental blank was performed using a retention gap column (ACQUITY UPLC BEH (C18, 2.1 × 100 mm, 1.7 µm, Waters). For the LC mobile phase, 2 mM ammonium acetate and acetonitrile were used. At a flow rate of 0.3 mL min⁻¹, the mobile phase gradient was ramped from

1% to 95% acetonitrile in 8 min, kept at 95% for 1 min, and then ramped down again to 1%. The column temperature was set at 40 °C. The capillary voltage was set at 0.5 kV. The desolvation gas flow and temperature were kept at 1000 L h⁻¹ and 500 °C, respectively.

2.5.3. Quality control, method limits of detection and method limits of quantification

The instrumental limits of detection (LOD) were defined empirically as the concentration producing a signal to noise ratio of 3, and the limits of quantification (LOQ) were defined as the concentration producing a signal to noise ratio of 10. The method limits of detection (MDL) and method limits of quantification (MQL) were determined from LODs and LOQs. MDLs of PFCAs and PFASs were 0.02 ng g⁻¹ dw (dry weight) and 0.04 ng g⁻¹ dw respectively. MQLs of PFCAs and PFASs were 0.06 ng g⁻¹ dw and 0.12 ng g⁻¹ dw respectively. The sampling containers, glass jars, polypropylene bottles as well as all the glassware (glass syringe and syringe barrels, beakers, measuring flasks, measuring cylinders, test tubes, etc.) were rinsed with methanol and Milli-Q water prior to use. Teflon bottles and Teflon-lined caps were avoided throughout the analysis. HPLC water, SPE blank, solvents and sample bottle blank were all analyzed, and no analytes were detected.

2.6. Statistical analysis

All results were calculated according to dry matter, while percentages were calculated according to mass. The results were processed by the OriginPro 8.0 program, and SPSS 11.5 software was used for statistical analysis.

3. Results and discussion

3.1. Chemical and microbiological properties of sediments

Samples from the WWCV were characterized by neutral pH, relatively high content of organic carbon and high content of inorganic carbon (Table 3). Silt, particularly fine silt, was the dominant granulometric fraction in all samples. Stormwater that washes soil from the oil refinery was the cause of the extremely high TPH in sample P-5. A high content of carbonates was determined in samples P-3, P-4 and P-5 taken from the inner part of the canal.

A high number of all microbial groups tested was determined (Table 3). This confirms that intensive aerobic and anaerobic microbiological processes occur in sediment from the WWCV and that this material is a good matrix for studying possible biotic transformations of organic contaminants.

3.2. PFCs in sediments

Most of the environmental studies worldwide have determined PFCs in biota and water, while very few studies deal with PFCs in sediment, although sediment can be considered as a reservoir of different compounds in the environment.

The presence of PFCs was confirmed in all analyzed sediment samples from the Pančevo industrial zone, wherein PFOS was predominant (Table 4). In sediment P-1 taken from the navigation canal where no industrial wastewaters are discharged, the presence of PFOS (~49%), together with PFHxS (~39%) and PFOA (~12%) were confirmed. Since this navigation canal is used as a source of technical water for the industry and as a port to host ships that transport raw materials and products in/from the Pančevo industrial zone, a reasonable assumption is that PFCs are originating from these vessels. In sediment P-2 taken at the confluence of

Table 3
Basic chemical and microbiological properties of the sediment samples from the WWCV.

Parameter	P-1	P-2	P-3	P-4	P-5
pH	7.4	7.3	7.3	7.4	7.6
Total carbon (%)	4.3 ± 0.1 ^a	3.4 ± 0.1	12.7 ± 0.1	12.5 ± 0.1	12.9 ± 0.1
Organic carbon (%)	2.1 ± 0.1	1.8 ± 0.1	1.9 ± 0.1	2.1 ± 0.1	5.4 ± 0.1
Inorganic carbon (%)	2.2 ± 0.2	1.6 ± 0.1	10.8 ± 1.6	10.4 ± 1.4	7.5 ± 0.3
Total nitrogen (%)	0.28 ± 0.04	0.24 ± 0.02	0.13 ± 0.01	0.24 ± 0.01	0.15 ± 0.02
Total sulfur (%)	0.19 ± 0.02	0.16 ± 0.01	0.09 ± 0.02	0.32 ± 0.01	0.48 ± 0.03
Sand (%)	7.8	14.7	5.7	7.7	7.9
Silt + Clay (%)	92.2	85.3	94.3	92.3	92.1
TPH (g kg ⁻¹ dw)	1.6 ± 0.2	0.2 ± 0.1	4.1 ± 0.3	4.9 ± 0.6	35.6 ± 0.9
TC (CFU g ⁻¹)	1.3 × 10 ⁶	1.4 × 10 ⁶	1.4 × 10 ⁶	1.9 × 10 ⁶	1.3 × 10 ⁶
TAC (CFU g ⁻¹)	1.3 × 10 ⁶	4.0 × 10 ⁶	2.0 × 10 ⁶	8.0 × 10 ⁶	1.7 × 10 ⁶
YM (CFU g ⁻¹)	2.1 × 10 ⁵	1.4 × 10 ⁵	4.6 × 10 ⁴	7.0 × 10 ⁴	4.0 × 10 ⁴
HD (CFU g ⁻¹)	4.0 × 10 ⁵	1.2 × 10 ⁵	3.0 × 10 ⁵	2.0 × 10 ⁵	1.2 × 10 ⁵

^a Standard deviation for five measurements.

Table 4
PFCs content in the sediment samples from WWCV (ng g⁻¹ dw).

Sample	PFCAs											PFASs				
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS	ΣPFC
P-1	n.d.	n.d.	<MQL	<MQL	0.068	<MQL	n.d.	<MQL	n.d.	n.d.	n.d.	n.d.	0.23	0.29	n.d.	0.588
P-2	n.d.	n.d.	<MQL	<MQL	0.080	n.d.	<MQL	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	2.10	n.d.	2.180
P-3	n.d.	n.d.	<MQL	<MQL	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.17	5.30	n.d.	5.470
P-4	n.d.	n.d.	0.170	<MQL	0.130	<MQL	<MQL	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	5.70	0.29	6.290
P-5	n.d.	n.d.	0.066	<MQL	0.076	<MQL	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.42	n.d.	0.562

n.d. – Not detected.

MQL – method limits of quantification.

the WWCV with the Danube River, and located downstream from all industrial effluents, a relatively high level of PFCs, comprising of PFOS (96%) and PFOA (4%) were determined. Sediment P-3 was taken at the location which receives water from the fertilizer factory outlet. The fertilizer plant does not have any industrial wastewater or stormwater treatment facilities and effluent is discharged directly into a collection canal and subsequently to the open WWCV (UNEP/UNCHS, 1999). As in the sample from the navigation canal, in sample P-3, PFHxS was also present (3%) but the predominant PFC was PFOS (97%).

During the 1999 military conflict, large quantities of oil, debris and other materials clogged and partly damaged the sewer pipes, oil separators and discharge pipelines at Pančevo Oil Refinery. Since then, some of the refinery's wastewater has been discharged directly into the canal and subsequently into the Danube River, without final treatment of oily wastewater, which had previously been conducted at the petrochemical plant's integrated wastewater treatment plant (WWTP) (UNEP, 2004). Today, effluent from the petrochemical plant and the oil refinery undergoes treatment in a petrochemical plant's integrated WWTP facility before discharge into the WWCV (IMET, 2006). Sample P-4, taken at the mouth of a drainpipe from the petrochemical factory WWTP was the most polluted sediment, not just with regard to concentration but also diversity of PFCs. The dominant compound in sediment P-4 was PFOS, with a contribution of ~90%. The other contributions were from long carbon chain PFDS (~5%) followed by short carbon chain PFHxA (~3%) and PFOA (~2%). Sampling place P-5, which receives collected atmospheric waters from oil refinery, was characterized by the presence of PFOS (~75%), PFOA (~13%) and PFHxA (~12%). The concentration of PFCs in P-5 was the lowest among the sediments studied, and the reason is very likely to be the high content of nonpolar TPH.

Interestingly no long-chain PFCAs ($m > 6$) were detected in the sediments in concentrations higher than MQL. Moreover, PFCAs ($m > 9$) as well as ($m < 4$) were not detected at all. PFHpA was de-

tected in all samples but in concentrations less than MQL. Likewise, the presence of PFHxA was also confirmed in sediments P-1, P-2 and P-3, but again at concentrations less than MQL. In the sediments P-4 and P-5 only even-numbered PFCAs (PFHxA and PFOA) were found, which is in accordance with the fact that even-chain length PFCAs are detected more frequently and are dominant in sediments (Higgins et al., 2005).

Significant difference between PFOS patterns from samples P-2, P-3 and P-4 was not found. However, P-1 sampled from the navigation canal showed different PFOS pattern which undoubtedly reflect different sources or pollution history. Furthermore, P-5 showed slight difference which can be result of different source of pollution but also can be result of different polarity i.e. different amounts of non-polar components and high TPH concentration comparing to other samples which could have an impact on sorption and desorption of different PFCs isomers from the sediment. Mass chromatograms of the molecular ion m/z 499 of PFOS are submitted as electronic [Supplementary material](#).

3.3. Comparison with other published PFCs results

If we compare concentrations of PFCs detected in the sediment from the WWCV with the levels of the same PFCs determined in other relevant papers (Table 5) there are significant differences. The maximum concentration of PFHxA was almost 30-fold lower than the one determined at the Danube River bank at Asten, and 10-fold lower than the one at the Formarin Alpine Lake in Austria. The maximum PFOA concentration in L'Albufera Natural Park was more than 80-fold higher than in the WWCV. In contrast, the concentrations of PFHxS determined in the WWCV were significantly higher than the highest levels found in other studies. Also, high levels of PFOS were found compared to other studies. PFOS levels were higher than those determined in the San Francisco Bay area and L'Albufera Natural Park, but lower than was measured in the Baltic Sea.

Table 5
Concentrations of PFCs in sediment (ng g^{-1} dw) reported in the literature.

Location	PFHxA	PFOA	PFHxS	PFOS	PFDS	Reference
<i>America</i>						
The San Francisco Bay area, California	–	n.d.–0.625	n.d.– < 0.2	n.d.–3.07	n.d.–1.47	Higgins et al. (2005)
Corvallis, Oregon	–	0.184	n.d.	0.018	n.d.	Higgins et al. (2005)
Baltimore, Maryland	–	0.186 – 0.390	n.d.– 0.072	n.d.–0.846	0.202– 0.980	Higgins et al. (2005)
Georgia Coastal areas	n.d.–0.6	n.d.–0.2	–	0.1–0.8	n.d.–0.2	Senthil Kumar et al. (2009)
<i>Australia</i>						
Sydney Harbor	n.d.	n.d.–0.16	<0.10–0.10	0.80–6.2	<0.10–0.20	Thompson et al. (2011)
<i>Asia</i>						
Western coast of Korea	<0.1	<0.5	<0.5	<0.5	<0.5	Naile et al. (2010)
Dalai River System, China	–	<0.08–0.17	n.d.–<0.13	<0.12–0.37	–	Bao et al. (2009)
Zhujiang River, Guangzhou, China	–	0.09–0.29	–	n.d.–1.0	–	Bao et al. (2010)
Huangpu River Shanghai, China	–	0.20–0.64	–	n.d.–0.46	–	Bao et al. (2010)
The Ariake Sea, Japan (shallow water and tidal flat areas)	–	0.84–1.1	–	0.09–0.14	–	Nakata et al. (2006)
Tokio Bay, Japan	–	0.12–0.45	–	0.90–1.79	–	Zushi et al. (2010)
Rivers, (Kumo, Uji, Tenjin, Katsura, Osaka) Japan	–	<0.1–3.9	<0.1–<1.6	<0.33–11	–	Senthilkumar et al. (2007)
Liao River, China	–	0.02–0.18	<0.02–0.10	0.04–0.48	n.d.	Yang et al. (2011)
Taihu Lake, China	–	<0.02–0.52	n.d.–0.03	0.06–0.31	n.d.	Yang et al. (2011)
<i>Europe</i>						
Lake Constance, Alpine Lakes, Austria	0.27–1.7	<0.13–0.82	–	n.d.–<0.94	n.d.	Clara et al. (2009)
Danube riverbank from Aschach to Wildungsmauer, Austria	0.19–4.6	0.65–2.8	–	n.d.–0.91	n.d.–<0.17	Clara et al. (2009)
Orge River (nearby Paris), France	0.06	<0.07	0.10	4.3	0.12	Labadie and Chevreuil (2011)
Roter Main River, Bayreuth, Germany	–	<0.02–0.175	–	0.05–0.537	–	Becker et al. (2008b)
L'Albufera Natural Park, València, Spain	<0.02–0.1	0.03–10.9	–	0.10–4.80	n.d.–2.00	Pico et al. (2012)
North Sea	<0.03– 0.087	0.079–1.575	<0.03– 0.040	0.038– 2.425	–	Theobald et al. (2012)
Baltic Sea	0.037– 0.049	0.061–0.684	<0.03	0.025– 0.666	–	Theobald et al. (2012)
WWCV (P-2, P-3, P-4 and P5)	<0.02–0.17	0.076–0.13	n.d.–0.17	0.42–5.7	n.d.–0.29	Present study

The maximum determined concentration of PFDS was almost 7-fold lower than that determined at the L'Albufera Natural Park. If we compare the concentrations of all PFCs isolated from the WWCV, clearly that their levels are almost the same as the levels of the PFHxA, PFOA, PFHxS, PFOS and PFDS in the sediment from Sydney harbor (Thompson et al., 2011).

The sampling method used provided assurance that the concentrations of PFCs determined were very representative of the whole sediment in the WWCV. Concentration of Σ PFCs in sediments from the WWCV (P-2–P-5) were between 0.56 and 5.47 ng g^{-1} dw (mean value = 3.63 ng g^{-1}), which is consistent with levels reported in Europe (Pico et al., 2012). The highest contribution was that of PFOS (83.4%), followed by long-chain sulfonate PDFS (7.2%), PFHxS (4.2%) and the short chain carboxylic acids PFHxA (2.9%) and PFOA (2.3%). The total contribution of PFSAs and PFCAs to PFCs was 94.8% and 5.2%, respectively.

In most environmental studies, PFOA and PFOS were the predominant compounds found, but different results have been reported as well. Clara et al. (2009) found PFHxA, PFHpA and PFOA in all Danube River sediment samples at concentrations ranging from 0.1 to 5.1 ng g^{-1} , whereas PFOS was only detected occasionally ranging from n.d. to 0.91. In our study, PFOS were the dominant PFC in the WWCV. Although the aqueous phase is a major sink for PFCs, we found relatively high concentrations of PFOS in sediments from the WWCV.

The question that arises is the source or place of origin of the PFCs in the WWCV. Since these compounds are not used in daily production in the fertilizer, petrochemical or oil refinery industries, there are two possible explanations. One is that they originate from fire fighting foams used in spring 1999 to extinguish fires caused by a military bombing campaign (more than 12 years before the sampling period). The other is that the pollution is recent, and that the possible sources of PFCs are fittings that contain these compounds, for example, insulators for electric wires, occasionally-used fire fighting foams, surfactants or cleaning chemicals. One of the possible sources of PFCs in sediment P-4 is the potential

Table 6
 $\text{Log}K_d$ and C_{aq} of PFOS in WWCV.

	P-2	P-3	P-4	P-5	Mean P
C_{sed} (ng g^{-1})	2.10	5.30	5.70	0.42	3.38
f_{oc} (%)	1.8	1.9	2.1	5.4	2.8
$\text{Log}K_d$	1.96	1.98	2.02	2.43	2.15 ^a
C_{aq} (ng L^{-1})	23.28	55.65	54.16	1.56	24.09 ^a

^a Calculated using mean C_{sed} and f_{oc} values.

use of these compounds in the Polyethylene Pipes and Fittings Plant, located in the petrochemical factory. However, this fact does not explain the high concentration of PFCs also found upstream from sampling place P-4.

3.4. PFCs mass flow from WWCV to River Danube

The largest amounts of wastewater in the canal came from the chemical fertilizer factory, which releases cooling water mixed with sanitary and industrial wastewater at the very beginning of the canal. When the entire factory is in operation, the plant discharges about 6000 $\text{m}^3 \text{h}^{-1}$ of wastewater. The petrochemical factory and oil refinery together release about 650 $\text{m}^3 \text{h}^{-1}$. The total volume of water in the canal at the time of sampling was estimated to be around 32000 m^3 and retention time in the canal is 6–9 h.

The PFCs mass flow reaching Danube River and Black Sea from this place can be estimated if we assume that the determined concentrations of PFCs and other analytes in the sediment samples found in this study and approximated concentrations in water from the WWCV are constant throughout the whole year.

From Eqs. (1) and (2), using a sediment concentration of PFOS in the WWCV (C_{sed}), organic carbon normalized sediment–water distribution coefficient (K_{OC}) from literature ($\text{log}K_{OC} = 3.7$) (Ahrens et al., 2010; Labadie and Chevreuil, 2011; Pico et al., 2012) and organic carbon fraction (f_{oc}), the sediment–water distribution coefficient (K_d) (L kg^{-1}) and also the concentration of PFOS in water (C_{aq})

of the WWCV were calculated (Table 6). $\log K_d = 2.15$, calculated from mean C_{sed} and f_{OC} values, correlated very well with $\log K_d$ values reported in the literature (Ahrens et al., 2010; Labadie and Chevreuril, 2011; Pico et al., 2012).

$$K_{OC} = K_d \times 100/f_{OC} \quad (1)$$

$$K_d = C_{sed}/C_{aq} \quad (2)$$

The average output of wastewater from the WWCV is $6500 \text{ m}^3 \text{ h}^{-1}$, and the mean PFOS C_{aq} concentration is 24.1 ng L^{-1} . Using these data, calculation of the annual Σ PFOS discharge results in 1.38 kg per year. Since PFOS is the predominant PFC in the WWCV, we can compare this with predictions in other reports. The annual discharge of PFCs from Elbe River in Germany to North Sea was estimated by Ahrens et al. (2009b) to be 802 kg for the dissolved phase and 152 kg for the particulate phase per year and mass flow reaching L'Albufera lake and the Mediterranean Sea is approximately $\sim 5600 \text{ kg per year}$ (Pico et al., 2012). The mass flow of PFCs from the WWCV to the River Danube is much lower but it undoubtedly points to the contribution to global POPs pollution of surface waters just from this one industrial area.

4. Conclusions

This study is the first to report the presence of PFCs in sediment from Serbia. PFOS was predominant among the PFCs, present in all analyzed samples. Compared to other reports, high levels of PFOS were found, even though PFCs are not directly used in the industrial production associated with this canal. Further investigations are necessary to clarify whether concentrations of PFOS determined are sufficient to potentially cause adverse effects to some wildlife present in WWCV and subsequently to the River Danube. The total estimated flux per year was calculated with the wastewater discharge of $6500 \text{ m}^3 \text{ d}^{-1}$, which represents an average discharge of 1.38 kg of PFOS per year. Adsorption of polar organic compounds is also partially controlled by electrostatic effects. Therefore, inorganic materials should also be taken into account in future research. To understand PFC distribution, transforming mechanisms, the exact mass balance and the potential sinks of PFCs in the environment, further studies regarding the measurements of levels in the water, biota, and sediment compartments within the WWCV are needed. Although our study did not clarify major sources of PFCs in the WWCV it contributes to knowledge and awareness of the presence of PFCs in the environment of the Danube River basin on the way to the Black Sea. Monitoring data in various countries will contribute to better assessing risks of PFCs pollution on the global environment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.12.079>.

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