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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 (PFSAs) 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.

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 products 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

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Table 1
The perfluorinated compounds (PFCs) investigated in this study. Two types of functional groups with variable CF_2 chain length were included: perfluoroalkyl sulfonates and perfluoroalkyl carboxylates.

Formula/Name/Acronym	No. of CF_2 groups	Analyte	Acronym
$CF_3(CF_2)_nSO_3^-$	$n = 3$	Perfluorobutane sulfonate	PFBS
	$n = 5$	Perfluorohexane sulfonate	PFHxS
Perfluoroalkyl sulfonates (PFSAs)	$n = 7$	Perfluorooctane sulfonate	PFOS
	$n = 9$	Perfluorodecane sulfonate	PFDS
	$m = 2$	Perfluorobutanoate	PFBA
	$m = 3$	Perfluoropentanoate	PFPeA
$CF_3(CF_2)_mCO_2^-$	$m = 4$	Perfluorohexanoate	PFHxA
	$m = 5$	Perfluoroheptanoate	PFHpA
	$m = 6$	Perfluorooctanoate	PFOA
Perfluoroalkyl carboxylates (PFCAs)	$m = 7$	Perfluorononanoate	PFNA
	$m = 8$	Perfluorodecanoate	PFDA
	$m = 9$	Perfluoroundecanoate	PFUnDA
	$m = 10$	Perfluorododecanoate	PFDoDA
	$m = 11$	Perfluorotridecanoate	PFTrDA
	$m = 12$	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 (Kärrman 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 km^2, 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 Nafte, 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