

CONCENTRATIONS OF PERFLUOROCTANOATE AND PERFLUOROCTANE SULFONATE IN SEDIMENT OF WESTERN CAPE RIVERS, SOUTH AFRICA

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Abstract: In this study, we report for the first time, concentrations of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in sediments from a South African environment, particularly for the largest catchment areas of the Western Cape, South Africa, an area associated with the largest agricultural sector with some of the produce and end-products intended for the international markets. Sample preparation and analysis were based on the ISO 25101: 2009(E) method, using solid phase extraction (SPE) followed by liquid chromatography combined with electrospray tandem mass spectrometry (LC-MS/MS). Sediment grain size analysis, core water characteristics and percent total organic carbon were also quantified. From the results, PFOS and PFOA were observed in all the river sediment samples and were found in concentrations up to 19 ng/g and 187 ng/g for Salt River, 121 ng/g and 772 ng/g for Diep River, and 75 ng/g and 193 ng/g for Eerste River, for both PFOS and PFOA, respectively. Some of these concentrations are higher than those previously reported in similar studies in various countries; this suggests there is cause for concern. Although sediment has a poor sorption capacity for both PFOS and PFOA in comparison with plants, the prevalence of PFOS and PFOA in sediment samples from rivers from which irrigation water is sourced for agricultural purposes, indicates a risk of agricultural produce contamination.

Keywords: Perfluorooctanoate (PFOA); Perfluorooctane sulfonate (PFOS); Perfluorinated compounds; River sediment

1. INTRODUCTION

Perfluorinated compounds are used in aqueous fire-fighting foams, while their lipid-and-water-repellent properties make them useful in stain repellents for carpets, textiles, leather, home furnishings, paper products, non-stick cookware and cleaning products (EFSA, 2008). They are also used as emulsifiers and surfactants in mining and oil well drilling operations (Renner, 2001). Moreover, PFCs are applied in products used in metal plating, photography, gasoline and hydraulic fluids. The Agency for Toxic Substances and Disease Registry has estimated PFCs (PFOS and PFOA) half-life as follows: > 41 and > 92 years in water, and > 4 years

and > 1 year in photolytic conditions, respectively.

Previous studies have focused on the analysis of PFCs in biota and aqueous systems. Little attention has been paid to their distribution in solid matrices, such as river sediment. This is because of PFCs' low occurrence in river sediment and also because their analysis is difficult (Yang et al., 2011). However, sediments are considered major adsorbents for various contaminants in the aquatic environment (De Boer et al., 2001; Ahrens et al., 2011). Yang et al. (2011) and Ahrens et al., (2009) have indicated that river sediment is an important component in a water system as it plays an important role in the environmental transportation and fate of persistent organic pollutants (POPs). Additionally,

Covaci et al., (2005) illustrated that well-laminated sediments can provide information on historical environmental contamination, as river sediment makes it feasible to assess the impact of societal activity, environmental degradation and pollution on localised ecosystems. Organic pollutants such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and others, are frequently found in the aquatic environment as they have an affinity for suspended organic matter which easily settles (Mokgadi et al., 2013).

Moreover, to date, there has been no pre-establishment of what is known as the 'minimal risk level' (MRL) for PFOS or PFOA for humans; however, 0.2 µg/L for PFOS and 0.4 µg/L for PFOA have been provisionally recommended by the EPA as the upper safe limit for their presence in drinking water (EPA, 2011).

Since river sediment has been suggested as a reservoir for non-ionic hydrophobic organic pollutants, such as PCBs and OCPs (Yang et al., 2011), emerging POPs such as PFCs can be quantified in river sediment to determine the extent of environmental pollution in an ecosystem. Additionally, it has been established that their non-ionic hydrophobic properties facilitate their partitioning behaviour between water and sediment (Yang et al., 2011). This suggests that their prevalence in the aqueous phase should be high for the contaminants to be detectable in the sediment. Furthermore, in a study by Becker et al., (2008) conducted on the Roter Main River (Bayreuth, Germany), PFOA and PFOS concentration in sediment samples was frequently below detectable limits for PFOA, while PFOS concentration was determined to be in the range of <0,05 to 0,57 ng/g dry weight (DW) with high concentrations observed in the river water. Furthermore, the quantification of both PFOS and PFOA in sediment of the Liao River system (China) suggested that PFOS and PFOA concentrations were 1.2 to 1.7-fold higher than the average determined below a 10 cm sediment depth (Bao et al., 2009). This suggested enhanced PFOA and PFOS mobility onto the mobile phase in aquatic systems. Additionally, a study conducted in Shanghai (China) to quantity of short- and long-chain perfluorinated acids in solid matrices, indicated that PFOA concentration in collected sediments was always higher than PFOS (Li et al., 2011). These studies suggested that for an environmental risk assessment to be successful, the quantification of pollutants in sediment is the most appropriate method to initially determine historical deposition of environmental pollutants in a river.

In South Africa, the occurrence of these

organic chemicals, that is, PFOS and PFOA, in aquatic systems, for example, rivers, wetlands, riparian areas, drinking and irrigation water sources, has yet to be reported and documented. Although, Hanssen et al., (2010) reported the presence of PFOS and PFOA in South African maternal serum and cord blood in humans, their source is largely unknown as there is no environmental study which reports their prevalence and/or concentration in the South African aquatic environment, including agricultural produce.

In this study, we report for the first time, the presence of PFOA and PFOS in the South African aquatic environment, a result indicating PFC contamination of major rivers in the region. Moreover, there have been few studies conducted in the identified rivers, that is, the Salt, Diep and Eerste Rivers, for the presence of emerging persistent organic pollutants such as PFCs, although several studies have focused on metal contamination (Ayeni et al., 2010; Shuping et al., 2011).

2. MATERIALS AND METHODS

2.1. Rivers under evaluation

The three rivers, namely the Diep, Eerste and Salt Rivers, were selected as they: 1) are part of the three biggest catchment areas in the Western Cape, with the largest surface water network; 2), have a similar mean annual surface water runoff range of 1305 to 2085.10⁶ m³ (Midgley et al., 1990), while each of the rivers has several tributaries; and 3) have similar soil/sediment characteristics, that is, structured sediment with a sandy texture, which facilitates sub-surface accumulation of organic matter including organic chemicals.

The Salt River is periodically polluted by effluent from industrial and residential areas in and around Cape Town (Scarfe et al., 1985). Pollutants have included hexane and associated compounds, oils and paraffins from industrial sources, and algacides as well as herbicides used in vegetation control along the river. Algacides and herbicides have been suspected of being sources of PFCs (Wang et al., 2009). The river has a rich effluent emanating from the Athlone WWTP (DWAf, 2005; Brown & Magoba, 2009). Additionally, the Salt River receives plant debris from the Black River, which is one of its major tributaries. The name 'Black River' was derived from the fact that it naturally carries water darkly stained by organic material leached from the *fynbos* vegetation through which it flows (Brown & Magoba, 2009), including a rich effluent emanating from the Athlone WWTP.

Tributaries converging into the Salt River include the Black River, the Liesbeeck River and the Elsiekraal River (DWAF, 2005).

The Diep River is located in the South-Western Cape region, north of Cape Town. Agriculture, mainly temporary commercial dry land agriculture, permanent commercial irrigated agriculture and commercial forestry account for about 74% of the catchment land-cover area of the river. Approximately 2% of the watershed area consists of degraded bush and shrubs, while 17% is natural, consisting of land shrub, bush land, grassland and water bodies and wetlands, for example, the Rietvlei wetland and the Milnerton lagoon. The soil type in the catchment area comprises Malmesbury shale, Cape granite, and Klipheuwel conglomerates, giving the sediment in the catchment area its sandy texture. According to the DWAF *State-of-Rivers' Report*, about 95% of the area has waterborne sewage systems with the remainder served by septic tanks and soak-away areas.

The Eerste River is generally a rocky and narrow river; the river's headwaters rise in the Jonkershoek mountains and the Forest Reserve (Somers & Nel, 2003). From its sources, the river flows in a north-westerly direction towards Stellenbosch, and through the Cape Flats, a residential area in which waste material, including sewage, is dumped into the river, to where it discharges into False Bay at Macassar beach. Additionally, the river comprises a mountain stream zone (Jonkershoek), 7km long from its headwaters: the upper zone, which starts 5km from the lower end of the Jonkershoek valley to its confluence with the Plankenburg River in Stellenbosch; and the lower zone which stretches from Stellenbosch to the estuary at False Bay. The Eerste River is joined at its lower region by several tributaries, namely, the Kuils, Veldwagters and Blouklip Rivers.

The Eerste River is a typical urban river that has been physically and biologically modified owing to urban activity. Maccassar and Stellenbosch wastewater treatment plants discharge into the river (Brown & Magoba, 2009). These WWTPs contribute to the pollution of the river. In addition, along its course, the river traverses an array of used land indicated to have progressively impacted negatively on the quality of its water. Furthermore, the water quality has deteriorated downstream, starting at the Eerste River's confluence with the Plankenburg River. It is at this downstream point that the river receives treated municipal effluent (8.4 million m³/annum) from the Stellenbosch WWTPs.

The prevalence of organic carbon in river water and sub-surface runoff from plant material,

WWTP's effluent, including anthropogenic activities, can sustain the accumulation of both PFOA and PFOS as suggested by other studies (Higgins et al., 2005; Bossi et al., 2008). This includes leachates from municipal waste dumps (Eggen et al., 2010; Weinberg et al., 2011) and contaminated wetlands including riparian ridges for each of the rivers (Quinete et al., 2009; Pico et al., 2012).

2.2. Chemical reagents, Sample collection sites, physico-chemical characteristics of core water samples and sediment characterisation

All reagents used in this study were of analytical grade standard. Methanol and Analytical Standards of PFOA and PFOS were purchased from Sigma-Aldrich (St. Louis, MO, USA) and stored at 4°C with appropriate dilutions made from stock solutions when needed. Acetic acid was purchased from Saarchem (Wadeville, South Africa). All the sediment samples used in this study were randomly collected using a stainless- steel AMS Multi-Stage Sediment Sampler (AMS Samplers, USA), with two core samples taken at each of the sampling sites, and up to a depth of 40cm from below the sediment surface, 80cm from the shoreline of the three rivers, that is, the Diep, Eerste and Salt rivers. Samples were transferred to and kept in polypropylene (PP) bottles. After collection, samples were then transported to the laboratory immediately and kept refrigerated (-20°C) before processing. Sampling point locations were noted and their geographical co-ordinates were recorded (two samples were taken for each sampling site). Sediment characterisation, that is, classification, was done using the American Society for Testing and Materials method (ASTM) coupled with the Unified Soil Classification System (USCS) chart. The sediment grain size distribution was determined by oven drying the samples for 24 hours followed by screening using different-sized meshes and a shaker (ASTM method DIN-4188) as previously described by Bentivegna et al., (2004).

The characteristics of core water samples were quantified using an YSI multi-function probe (YSI, USA) to quantify: pH, total dissolved solids, conductivity (salinity), dissolved oxygen, nitrates, and ammonium-N. Furthermore, the concentration of phosphates in the recovered core water samples was quantified using Merck phosphate cell test kits (Darmstadt, Germany; 0.05 to 9mg/L PO₄-P) and a Spectroquant NOVA 60. Prior to the analysis of Total Organic Carbon (TOC), samples were frozen at -20°C to reduce the degradation of organic compounds by either volatilisation or microbial degradation. The

samples were corrected for moisture/water content by drying them overnight at 60°C in a drying oven. Analysis of TOC was then quantified using the Loss-On-Ignition (LOI) method, which involves the thermal destruction of organic matter in the sediment at a temperature of 950°C (Heiri et al., 2001; Santisteban et al., 2004), after which the difference in gravimetric weight prior and after thermal treatment was used to determine the %TOC.

All samples were combusted in ceramic boats in a Nabertherm furnace (Germany), without accelerants. Some of the sediment cores samples, that is, samples not used for TOC determination and soil classification were used to extract core water so that its characteristics could be quantified as described above.

2.3. Sample Pre-treatment

Prior to analysis, the samples were thawed, and core water recovered and dried without sieving. Thereafter, 2g of dry samples were transferred to a clean 15mL PP centrifuge tube, to which 10mL of 1% (v/v) acetic acid solution had been added. Each tube was sonicated using a high-powered piston probe sonicator (Sonics, vibra-cell sonicator, 20 KHz \pm 50 Hz) for 1 min, at ambient temperature. After sonication the PP tubes were centrifuged at 3,000 rpm for 4 min and the recovered acetic acid-based extracts were decanted into an empty 50mL PP tube. An aliquot of 3mL of the 90:10 (v/v) methanol and 1% (v/v) acetic acid mixture was then added to the original tube to resuspend the sediment and the contents were again sonicated for 1 min, before being centrifuged and decanted into the second PP tube with the extracts from the first centrifugation cycle. This process was repeated using a 10mL acetic acid (1% v/v acetic acid) solution. All extracts recovered were combined and then filtered (0.22 μ m, polypropylene Cameo syringe filters, Sigma Aldrich) before passing through the Solid Phase Extraction (SPE) cartridges.

SPE was carried out using Supelco-Select HLB SPE cartridges (500mg solid phase, 12 ml tubes), a method similar to that proposed by the ISO 25101:2009(E), with minor changes. Cartridges were preconditioned by eluting 5mL of methanol followed by 5mL of Milli-Q water at a flow rate of 1-2 drops per second. The solid phase was kept wet for optimal extraction. A volume of 25mL of sediment extracts was loaded onto cartridges, so that a flow rate of 1–2 drop(s) a second was achieved. The cartridge was then washed with 5mL of a 40% (v/v) methanol solution in Milli-Q water, as reported by Naile et al., (2010), to rinse contaminants off the solid-phase;

thereafter, the cartridges were allowed to run dry while being kept cool. For the SPE extraction, a large volume sampler (24 port Visiprep sampler, Supelco) was used to process multiple samples at a time. The filtrate recovered was then discarded, prior to the use of analytical grade methanol for the recovery of both PFOA and PFOS. The cartridges were eluted with 10mL analytical grade methanol after which nitrogen gas flow was used to further reduce the methanol volume in the recovered eluents to a range of 0.5 to 1.9mL for the LC/MS/MS analysis.

2.4. Analytical conditions and parameters for PFOA and PFOS quantification

A Universal High Pressure Liquid Chromatography (UHPLC) system (Nexera UHPLC, LC/MS-8030, Shimadzu, Japan) was used coupled with a tandem mass spectrometer (MS) to determine PFOA and PFOS concentration in each of the samples. Basically, for 1) the UHPLC system, a separation column (i.e. Shim-pack FC-ODS 150 x 2mm, 3.0 μ m, P/No: 228-40512-05) was maintained at 40°C, of which the Mobile phase constituents were, a) 100% Acetonitrile (ACN) and b) 2 mM Ammonium acetate (NH₄OAc) and pumped at a 0.3 mL/min flow rate. In this regard, a volume of 10 μ l from the recovered extracts was injected into the instrument for a total run time of 6.5 min; 2) the mass spectra were then taken by employing electrospray ionization (ESI) in a negative mode. After the processing of each sample, a methanol rinse was performed to limit cross-contamination after each injection. For calibration standards, that is, the accuracy and concentration range of 0, 0.5, 1, 5, 10, and 50 ng/L for both PFOA and PFOS were used achieving a correlation coefficient (R^2) of 0.99 for each run. Quantitative analysis was performed in the multiple reaction monitoring (MRM) modes and the collision gas was used at energies of 10v for PFOA and 45v for PFOS. PFOA and PFOS were then identified by their retention time, including the specific MRM settings used (413.10 > 368.90, PFOA; 499.00 > 80.05, PFOS). Sample extracts with a higher PFC concentration, meaning, those exceeding the range, were diluted with methanol. Furthermore, the recovery of PFOA and PFOS was > 70% using multiple injections. The limit of detection (LOD), described as the lowest concentration that the instrument can differentiate from blanks, at an S/N ratio \geq 3, was 0.03 ng/g for PFOS and 0.5 ng/g for PFOA for eluents used in the analysis. The gradient used was t = 0.01, 2% ACN; t = 4 min, 98% ACN; t = 6 min, 98%, which was reduced to 2% ACN thereafter, as previous performed, by Mudumbi et al., (2014).

3. RESULTS AND DISCUSSION

3.1. PFOA/PFOS in river sediment

Concentration of PFOS and PFOA was observed in all the river sediment samples, with PFOA concentration being the dominant contaminant. The results in table 1 indicated the prevalence of PFOA and PFOS as directly determined from sediment extracts after SPE treatment, that is, extraction and recovery from the solid phase using methanol. The concentration of PFOA and PFOS obtained after quantification was then correlated with the mass of sediment (2g) used during the extraction.

From these results, the Salt River's PFOS concentration ranged from below the detection limit to 19.98ng/g, and 38.6 to 187 ng/g for PFOA. For the Diep River, the concentrations ranged from 2.53 to 121.1 ng/g and 10.7 to 772.5 ng/g for PFOS and PFOA, respectively, while for the Eerste River they ranged from 0.72 to 75.1 ng/g and 15.2 to 193.2ng/g, respectively. The mass spectra for both PFOA and PFOS, including the calibration curves are shown in Figure 1, whereby the integrated peak area is related to the PFC concentration in the extracts. Overall, the Diep River had the highest concentration of PFOA and PFOS during the period under evaluation in comparison with the Eerste and Salt Rivers. As the three rivers receive discharge from WWTPs, the prevalence of PFOA suggested that WWTP effluent might be a contributing factor as previously suggested by Yu et al. (2009) and Oliaei et al., (2006). The concentration of both PFOA and PFOS is far higher

than those previously reported in similar studies in various countries, whereby the concentration of PFOA and PFOS, respectively, were found to be 0.06 ± 0.02 and 0.20 ± 0.2 ng/g (USA: Houde et al., 2006; Becker et al., 2008); 2.3 and 0.29 ng/g (Japan: Senthilkumar et al., 2007); 1.70 to 73.5 and 0.06 to 0.64 ng/g (China: Shi et al., 2012); 49 ± 3.0 and 28 ± 0.65 ng/g (Germany: Ahrens et al., 2011); $< 0.3 \pm 7.5$ and 0.02 to 85 ng/g (Canada: Stock et al., 2007; Becker et al., 2008); < 0.005 and 0.023 ng/g (Indonesia: Harino et al., 2012); 0.35 to 2.82 and 0.56 to 6.70 ng/g (Brazil: Quinete et al., 2009); and 0.004 to 1.24 and 0.10 to 4.80 ng/g (Spain: Pico et al., 2012).

The highest concentration in PFC contamination observed in the Diep River, can be attributed to the size of the catchment, which is considerably the largest catchment under evaluation in comparison with both the Eerste/Kuils and the Salt catchments. Although, the Diep River might receive larger run-off surface water owing to its size, the catchment is mostly populated by shrub and agricultural land, thus it was expected that both the Salt and the Eerste Rivers would have the highest PFOA and PFOS contamination due to urban and industrial-based anthropogenic activities in both catchments. Furthermore, as the Diep River catchment has the largest percentage of land used for agricultural purposes, there is a pertinent risk of PFC-related contamination in the area as other studies have suggested that PFOA and PFOS can accumulate in legumes and vegetative parts of agricultural produce when river water is used for irrigation (Stahl et al., 2009).

Table 1: Concentration of PFOA/PFOS in sediment (ng/g dry wt.) and Sampling points geographic coordinates

River	Sample Site	Latitude	Longitude	PFOA	PFOS
Diep	S.1	S34°01'50.9"	E18°44'51.9"	497,5 ± 20,4	52,2 ± 1,8
	S.2	S34°01'51.1"	E18°44'52.1"	10,7 ± 2,0	32,4 ± 2,1
	S.3	S34°01'50.5"	E18°44'51.5"	772,5 ± 3,04	119,3 ± 9,31
	S.4	S34°01'49.9"	E18°44'51.8"	100,2 ± 2,7	121,1 ± 4,6
	S.5	S34°01'50.9"	E18°44'51.9"	227,5 ± 8,82	87,78 ± 11,6
	S.6*	S34°01'51.1"	E18°44'52.1"	176,3 ± 5,92	2,53 ± 0,0
Eerste	S.1	S33°49'47.4"	E18°31'13.2"	23,9 ± 0,0	69,9 ± 4,0
	S.2	S33°49'51.9"	E18°31'14.4"	75,1 ± 2,0	75,1±2,0
	S.3	S33°49'52.6"	E18°31'14.7"	15,2 ± 0,9	60,0 ± 3,7
	S.4	S33°49'53.3"	E18°31'14.9"	100,0 ± 5,04	6,08 ± 0,36
	S.5	S33°49'47.4"	E18°31'13.2"	162,4 ± 0,39	0,715 ± 0,2
	S.6	S33°49'51.9"	E18°31'14.4"	193,2±13,9	0,72 ± 0,12
Salt	S.1	S33°56'14.4"	E18°28'89.2"	86,9 ± 1,7	ND
	S.2	S33°56'14.1"	E18°28'88.9"	38,6 ± 0,24	ND
	S.3	S33°56'08.4"	E18°28'53.2"	64,6 ± 2,52	ND
	S.4	S33°56'04.6"	E18°28'49.7"	94,0 ± 2,34	19,98 ± 0,54
	S.5	S33°56'01.2"	E18°28'48.4"	187,0 ± 3,04	16,32 ± 3,52
	S.6	S33°56'59.9"	E18°28'48.3"	156,0 ± 2,03	0,225 ± 0,08

*Repeat samples, ND: concentration was below the detection limit. Samples were collected in duplicate for PFOA and PFOS quantification. Injections duplicated for each sample.

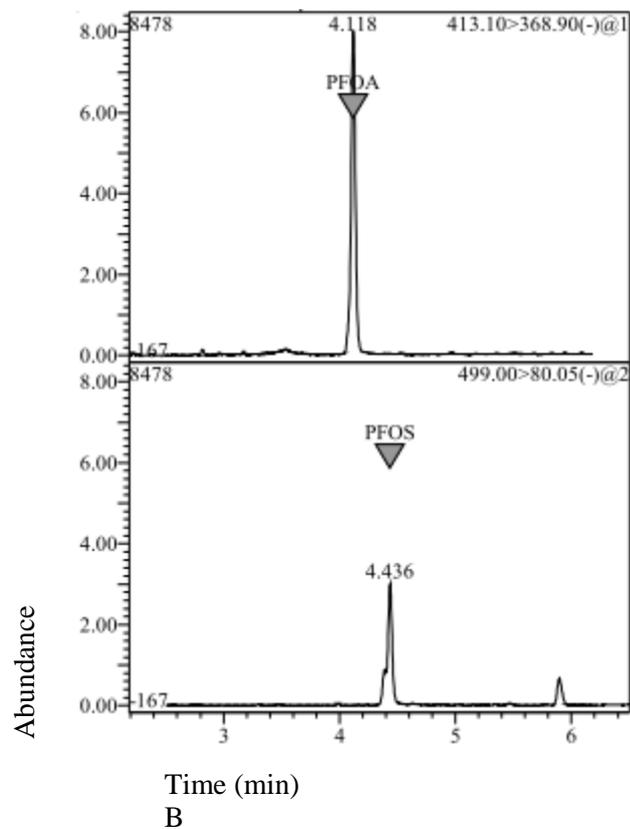
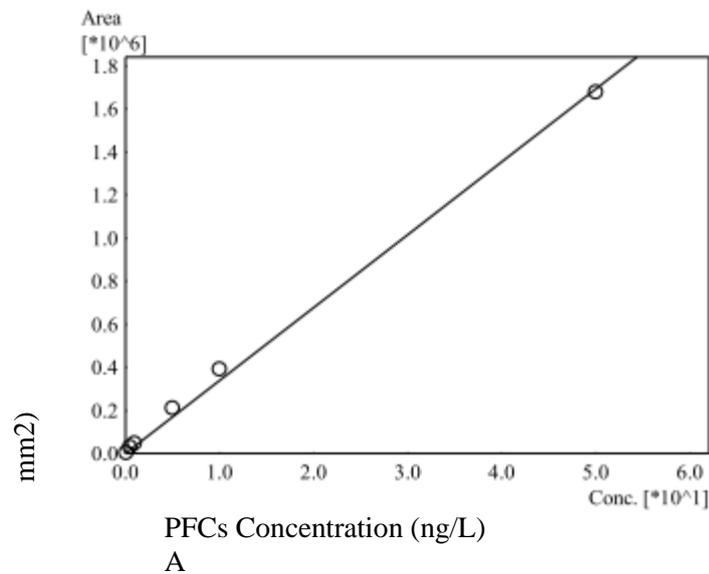


Figure 1. Examples of a chromatogram for A) the calibration regression curves and B) PFOA and PFOS obtained during analysis.

Additionally, as there are five WWTPs discharging into the river (Potsdam, Malmesbury, Kraaifontein, Klappmuts, and Kalbaskraal) and several landfills, including general waste disposal sites, it is prudent to hypothesise that some of these sites' leachates contribute to PFC contamination in the river.

3.2. Sediment and core water characteristics

Sediment characteristics were previously determined to influence the sorption capacity of PFOS and PFOA in different types of sediments (Higgins &

Luthy, 2006; Ahrens et al., 2011; Chen et al., 2012). Sandy sediments with a low organic content were determined to have the lowest sorption capacity for various organic pollutants, with a higher sorption capacity being observed for sediments with a higher organic content. This is of particular interest when the sorption of PFOA was considered for different types of sediments. In several studies (Becker et al., 2008; Li et al., 2010; Pan et al., 2011), PFOA was determined to be a contaminant which is sorbed easily when compared with PFOS for sediment with a high organic content. However, there is limited information about

the role of core water characteristics from the sediments, as the organic content can be attributed to the promotion of microbial activity and the attachment of microorganisms to sediment particulate matter, thus influencing the sorption of PFCs such as PFOA.

The association between the physico-chemical characteristics of the core water and sediment samples (Table 2) in relation to PFOA/PFOS sorption was studied. As such, it was observed that all three rivers had a salinity greater than 5.10-6 mg/L permissible for rivers, lakes and ponds (Niu & Cabrera, 2010) and the observed range was 1.39 ± 0.7 mg/L for Diep River, 223 ± 13 mg/L for Eerste River, and 418 ± 58 mg/L for Salt River. Furthermore, both the Eerste and Diep Rivers had low nitrate concentration ranging between 2.2 ± 0.4 ng/L and 3.4 ± 0.5 ng/L, respectively; while the Salt River had the highest, that is, 15.4 ± 6.1 ng/L, which was greater than the 10 ng/L permissible for freshwater by the EPA (2011).

Additionally, the ammonium concentration was high for all the three rivers as it exceeded the EPA allowable limit of 0.2 mg/L: 3.16 ± 0.67 mg/L, Diep River; 2.11 ± 0.43 mg/L, Salt River; 1.19 ± 0.11 mg/L, Eerste River. Previous studies have indicated that nutrients (e.g. ammonium, phosphorus, nitrates, etc.) support microbial growth (Benner et al., 1995; Pascoal & Cassio, 2004; Anne et al., 2006), although other factors such as pH, temperature and osmotic pressure may also play an important role in the sustainability of microbial growth and attachment to different types of sediment. Phosphate fertilizers are widely used in the agricultural sector. Its concentration was low for both the Diep and Eerste Rivers, 1.095 ± 0.115 mg/L and 1.015 ± 0.025 mg/L, respectively, but its concentration was greater than the 2 mg/L permissible by the IFC environmental health and safety guidelines and was 3.56 ± 0.11 mg/L for the Salt River. These results indicate that the three rivers under evaluation had high nutritional components which support microbial growth. The TOC, on the other hand, was high in grain sediment size of > 0.5 mm for the Salt River, followed by the Diep River, with grain sediment size of < 0.1 mm and ranging from 25.1 to 20.88% (w/w), respectively. However, for grain sediment size of < 0.5 to > 0.1 mm for the Eerste River, TOC was observed to be high (8.85%). This study has also observed that the high %TOC for the Salt River (25.1%) was due to the high plant material content in this river. The eutrophication described by Brown & Magoba (2009) was evidenced in this study by observed large plant material in situ. This phenomenon is associated with low dissolved oxygen, and high nitrate and phosphate levels, as observed for the Salt River. Therefore, it was justifiable to conclude that plant decomposition was low for both the Eerste and Diep Rivers as a lower

presence of nitrates, including phosphates, was observed in comparison with the concentrations observed in the Salt River. For the Diep River, it can be surmised that the low presence of nitrates and dissolved oxygen (DO) concentration was due to aerobic-type microbial contamination, while the water of the Salt and Eerste Rivers can be associated with photosynthetic-type microorganism blooms, as a high level of DO and a low ammonium concentration were observed. In certain instances, low dissolved oxygen and a high pH in the aquatic environment encourage the release of phosphates in the aqueous phase which assist in the growth of algae, thus contributing to a high TOC in grain sizes which are < 0.1 mm. In a study by Oliaei et al., (2006) on the Mississippi River, PFCs were investigated in floating algae, and the PFC prevalent was PFOS, which suggested either entrapment or sorption by the algal blooms. This study indicates that the bioconcentration of PFOS was from water to algae. Furthermore, Ding et al., (2012) indicated that PFCs' accumulation in algae increases with increasing fluorinated carbon chain length.

All sediments from the Diep, Eerste and Salt Rivers were observed to be poorly graded, gravelly with coarse grains, with more than half of the screened samples being retained by a 75 μ m sieve while most of the grains passed the 4500 μ m sieve. Furthermore, minimal fines were obtained for all samples screened, with $>50\%$ being retained on screen sizes between 2000 to 106 μ m.

Previous studies (Higgins & Luthy, 2006; You et al., 2010; Ahrens et al., 2011; Chen et al., 2012) have indicated PFOA and PFOS sorption onto sediment being associated with physico-chemical characteristics such as salinity, %TOC, and pH. In this study, it was observed that PFOA sorption onto the sediment was high at a higher pH (> 8), high %TOC in smaller grain size (< 0.1 mm), and high salinity, instead of low salinity including pH (< 8) as observed for the Diep River, while the prevalence of PFOS concentration was lower under similar conditions, a phenomenon previously reported by You et al., (2010).

For the Eerste River, PFOS concentration in the sediment samples was lower at a lower pH (> 7.95), %TOC ($> 16\%$ and 20% w/w) for sediment grains < 0.1 mm and > 0.5 mm, respectively, with low nitrate, phosphates and ammonium concentrations under a high salinity.

Table 2: Characteristics of the core water recovered and the sediment samples.

Core water								
Sampling site	pH	Conductivity μS/cm	Salinity (mg/L)	TDS (mg/L)	NO ₃ ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	DO (mg/L)	NH ₄ ⁺ -N (mg/L)
Diep River	8.08 ± 0.33	#2.72 ± 0.14(e10 ³)	%1.39 ± 0.07(e10 ³)	*1.93 ± 0.1(e10 ³)	3.42 ± 0.54	1.1±0.12	7.36±0.68	3.16 ± 0.67
Eerste River	7.91 ± 0.3	464.5 ± 26.5	223 ± 13	330 ± 19	2.16 ± 0.44	1.02±0.03	7.81±0.56	1.19 ± 0.11
Salt River	7.43 ± 0.18	857.5 ± 114.5	418 ± 58	609 ± 82	15.43 ± 6.06	3.58 ± 0.11	7.44 ± 0.86	2.11 ± 0.43
Control (rain water)	7.17 ± 0.31	65.05 ± 27.45	35.65 ± 11.85	46.1 ± 19.6	0.3 ± 0.045	0.06 ± 0.01	8.23 ± 0.12	0.36 ± 0.23
Sediment granulometry								
Sampling site	%TOC (w/w) > 0.5mm	%TOC (w/w) < 0.5 mm to >0.1 mm	%TOC (w/w) < 0.1mm	Classification/Observation				
PFOA/PFOS range								
Diep River	12.5	2.38	20.88 ± 4.2	Observation: coarse-grained sediment with more than half the sample mass being retained on sieve sizes with aperture sizes greater than that of no. 200 sieve (75μm), with more than half the fraction passing no. 4 sieve (4500μm). With very little fine grains. Class: Poorly graded and/or gravelly sediment with most of the sediment being retained by sieve nos 10 to 400 (2000 to 106 μm grain size).				
Eerste River	15.51	8.85 ± 0.9	20					
Salt River	25.1	6.3 ± 2.3	8.3					

- mS/cm; % - g/L; * - g/L

For the Salt River, although high salinity was measured as 418 mg/L with a high %TOC in grain sediment of size > 0.5 mm, and a high phosphate content, PFOS were below the detection limit in samples S1, S2 and S3 with PFOA and PFOS concentrations being high in sample S5 as ionic organic chemicals, such as PFOA and PFOS, salinity and pH largely increase their extent of sorption onto solid matrices (You et al., 2010).

In most cases in which the quantification of PFOS and PFOA was conducted, PFOA concentration in the aqueous phase was high, indicating poor binding mechanism to coarse sediments, with a low %TOC. Additionally, for muddy sediments, consisting of clay and silt granules, including a larger size of fines and with a high organic carbon, a higher sorption capacity of organic chemicals such as PFOA and PFOS is expected. Previously, it was determined that the partition variations for PFCs in sediment-free water studies were minimal when the partitioning coefficients were normalised against the organic carbon, suggesting that the binding and/or sorption mechanisms of PFC in sediments were strongly related to the organic carbon content of the sediment, with minimal influence of other parameters such as salinity, pH, and conductivity.

Although a large percentage of studies associated with the determination of PFOS and PFOA partitioning and/or distribution in river studies neglects to account for detailed characterisation of the sediment as a function of either organic content for different fractions in the studied sediment, it was imperative to assess and account for plant- and microbial-based organic content in sediments in association with the sorption of PFOA and PFOS. From this study, it was logical to hypothesise that for larger-sized sediment fractions (> 0.5mm) having a high %TOC associated with abiotic decay of plant-based materials, minimal PFC adsorption will occur in comparison with sediment fraction sizes < 0.1mm and having a high %TOC associated with microbial-based attachment onto the sediment. It is for these reasons that it was logical to surmise that sediment with a high microbial content, in which the microorganisms are attached to the sediment, will contribute largely to the sorption of PFOA in comparison with PFOS in sandy sediments, which generally have a poor sorption capacity for PFCs, particularly for PFOS. Additionally, others (Ahrens et al., 2010; Ahrens et al., 2011) have concluded that PFOS-associated adsorption is moderately meagre and losses from the sediment are based largely on river outflow losses, that is, washout from the sediment.

3.3. PFOA/PFOS pathways, tolerable daily intake (TDI) and associated health risks

From the literature reviewed, the major source of PFC exposure to humans is not well understood. Dietary intake is thought to be a major source of PFCs in humans; for instance, Moore (2010) stated that the exposure pathways for PFCs outside manufacturing might be related to ingestion, inhalation or possible adsorption through dermal contact. Prevedouros et al. (2006) also report that exposure can be as a result of eating animals exposed to PFCs through water, soil and dust contaminated by PFCs, as well as the degradation of consumer products containing PFCs. Furthermore, PFCs were determined to bioaccumulate in edible agricultural produce. A study in Spain found PFCs in a wide variety of food sources, with fish and dairy products representing the most significant source of exposure (Tittlemier et al., 2007). On the other hand, Ericson et al. (2008) reported in a study from Canada that beef products were the most significant dietary source of PFOS. As the catchments in which PFCs were determined in this study are associated with the largest agricultural sector, the use of river water for irrigation can result in the bioaccumulation of these compounds in agricultural produce.

The literature reviewed led to the notion that there is limited knowledge in respect of the safe Total Daily Intake (TDI) for PFOA and PFOS. In 2006, the BfR (Federal Institute for Risk Assessment) in Germany and the Committee on Toxicity (COT) in the United Kingdom suggested a 0.1µg/kg bw/day for PFOS and 3µg/kg bw/day for PFOA (EFSA, 2008). These values were based on the NOAEL in rats and the effects of these compounds on animal kidneys. These values were revised and set at 0.15µg/kg bw/day for PFOS and 1.5 µg/kg bw/day for PFOA, respectively.

In addition, PFCs were suggested to have adverse health effects (Alexander et al., 2003; Oliaei et al., 2006). It was found that women with a higher PFOA and PFOS concentration in their sera have an increased risk of infertility (Fei et al., 2009). Similarly, men who have high levels of PFCs were determined to have poor semen quality, with fewer than half the number of normal sperm than men with low levels of PFOA and PFOS (Joensen et al., 2009).

With such an insight, it is obvious that PFCs (i.e. PFOA and PFOS) in South African rivers pose a significant threat to communities using river water in riparian areas.

4. CONCLUSIONS

The Western Cape is one of the industrialised regions of South Africa. Previous studies in this region have focused mainly on heavy metal concentration in sediments. Nothing has been reported previously on PFC concentration in the province. The present study determined the concentrations of both PFOA and PFOS in sediments from the Diep, Eerste and Salt Rivers. PFOA and PFOS were observed in all samples collected, with PFOA being the predominant contaminant. Results also indicated the relationship between PFOA and PFOS sorption on sediments with both sediment and core water physicochemical characteristics. In certain instances, the concentrations are higher than those previously reported in other countries. This is the first study in South Africa in which these contaminants have been investigated and reported in environmental matrices.

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