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## Sorption and partitioning of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) onto sediments of Diep and Plankenburg river systems Western Cape, South Africa



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### ABSTRACT

Partitioning behaviour of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in sediments obtained from river systems were investigated in this study. The partitioning coefficient ( $\log K_{OC}$ ) and distribution coefficient ( $\log K_D$ ) of PFOA and PFOS between sediments and the aqueous solution were estimated from the sorption data. Levels of PFOA and PFOS in the sediment samples ranged between 30.01–191.96 ng/g dw and 0.50–248.14 ng/g dw, respectively. The kinetic study showed that the time required for equilibrium was <400 min for the compounds. Sediment samples SS-C provided the highest sorption capacities (0.11 and 0.13 mg/g) for both PFOA and PFOS. Sorption studies revealed that the removal kinetics fitted well into the Elovich rate equation ( $R^2 = 0.98$  and  $0.92$ ) followed by the pseudo-second-order kinetic model ( $R^2 = 0.91$  and  $0.89$ ) for PFOA and PFOS, respectively. Mean values for the partitioning coefficient ( $\log K_{OC}$ ) in the river systems were  $1.04 \pm 0.26$  and  $1.85 \pm 0.65$  ( $\text{cm}^3/\text{g}$ ) for PFOA and PFOS respectively. Partitioning coefficient ( $\log K_{OC}$ ) significantly ( $p < 0.05$ ) increased over time. This study represents the first report on partitioning and distribution of PFOA and PFOS in sub-Saharan Africa, which provide data and a scientific base to understand the fate and sorption of PFOA and PFOS in an aquatic system. The findings showed that lower pH values and increasing ionic strength favours sorption and partitioning of perfluoroalkyl substances (PFAS) in aqueous solution onto sediments; hence, plays an important role in their availability in water. Presence of PFAS in the aquatic system sediments is a potential risk to organisms.

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## 1. Introduction

Pollution has been a major problem associated with industrialization and economic development. Contamination of environmental matrices by organic compounds is particularly important and ecologically significant. Perfluorooctanoic

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acid (PFOA) and perfluorooctane sulfonate (PFOS) are important derivatives of perfluoroalkyl acids (PFAAs) and have been listed among the emerging environmental contaminants. They have received considerable attention in recent times due to their persistence, bioaccumulation, and toxicity in the environment (DeWitt et al., 2012; Dong et al., 2018; Elmonznino, 2016; Podder et al., 2021). PFOA and PFOS are extremely resistant to natural degradation processes; their anionic nature enhances their solubility in aqueous media. PFAAs exhibit a unique characteristic different from non-ionizable contaminants due to hydrophobic and lipophobic moieties present on the compounds. The presence of hydrophilic and lipophilic moiety in their chemical structures renders them suitable as constituents in various domestic and industrial applications, such as surface coating, electronics, and the packaging industry (Ahmed et al., 2020; Castiglioni et al., 2015; Giesy and Kannan, 2002; Ng et al., 2021). Essentially, sources of PFOA and PFOS into the environment have been largely attributed to anthropogenic activities, through both point and non-point sources (Castiglioni et al., 2015; Fagbayigbo et al., 2018). Dispersion of PFOA and PFOS in ecological systems has been attributed to several factors, including atmospheric deposition, long-range transport in marine environments, and biochemical degradation of their precursors (Xiao et al., 2015). They also occur in the food chain across trophic levels and in various environmental matrices globally (Dalahmeh et al., 2018; Gredelej et al., 2020; Wilhelm et al., 2010; Zhang et al., 2020). Like many organic contaminants, PFOA and PFOS in environmental samples mostly occur at trace levels. However, their bio-accumulative effects on ecological systems over prolonged time periods may result in adverse environmental and health effects. Workers elsewhere have shown that PFOA and PFOS could lead to adverse health effects on exposed laboratory organisms (Ding et al., 2015; Lee et al., 2017). Some health implications associated with PFOA and PFOS exposure in humans and validated by laboratory studies include hepatotoxicity, immunotoxicity, reduced infertility, thyroid disruption, developmental toxicity and ultimately death (DeWitt et al., 2014; Navarro et al., 2020; Song et al., 2018).

Environmental fates and distribution of PFOA and PFOS may be influenced by the presence of solid-phase matrices in an aquatic system (Elmonznino, 2016; Giesy and Kannan, 2002). The physicochemical properties of the solid phase and prevailing environmental conditions could enhance the availability of the compounds in the environment (Campo et al., 2016). Sediment characteristics such as the organic carbon fraction ( $f_{oc}$ ), percentage clay content, and total organic matter (TOM), amongst other parameters, could influence the partitioning and distribution of organic contaminants in sediment (Chen et al., 2012; Higgins and Luthy, 2006; Li et al., 2019). Solution pH and the cation effect in solution have also been reported as influencing the sorption and partitioning of anionic fluorinated surfactants in aquatic systems (Chen et al., 2012; Xiao et al., 2015). Other studies suggested that partitioning of PFAS in aquatic systems could be influenced by their distribution, transportation, and fate in the environment (Ahrens et al., 2010; Perra et al., 2013). Partitioning and distribution coefficients of contaminants have been used as an indicator for assessing the mobility of organic contaminants, and the sorption mechanism might provide insights into the contaminants in the aquatic systems (Labadie and Chevreuil, 2011; Pereira et al., 2018; Wang et al., 2015). Hence, estimated values from distribution coefficient ( $\log K_D$ ), partitioning coefficient ( $\log K_{oc}$ ) and the organic carbon fraction ( $f_{oc}$ ) between sediment and water for organic contaminants in aqueous systems, have been used to establish their partitioning behaviour (Hong et al., 2013). In an earlier study by Pan and You (2010), the sorption and desorption of PFOS at water-sediment interfaces were remarkably enhanced by the cationic surfactant cetyltrimethylammonium bromide (CTAB) in the sediment compartment. Ahrens et al. (2010) reported that the values of  $\log K_{oc}$  and  $\log K_D$  was 4.74 and 1.20  $\text{cm}^3/\text{g}$  for PFOA, and 4.5 and 0.96  $\text{cm}^3/\text{g}$  for PFOS in sediments from Tokyo Bay. In a similar study, Li et al. (2014) reported the maximum partitioning value for  $\log K_{oc}$  was 1.5  $\text{cm}^3/\text{g}$  and for  $\log K_D$ , 0.77  $\text{cm}^3/\text{g}$ , in respect of PFOA in sediments from Bohai Bay and Laizhou Bay in China. The sorption mechanism of PFOA and PFOS in the aquatic system is yet to be fully understood due to the complex processes of sediment-water interaction. Most studies have focused on levels of PFAS in the environment matrices, with limited information on the distribution and partitioning of PFAS in aquatic systems. Environmental assessment in terms of their fate and distribution in the aquatic systems needs further investigation. Given that limited information is available on the sorption mechanism and partitioning of PFOA and PFOS in the aquatic systems, it is pertinent to carry out more investigations in this area. To date, this study represents the first investigation of sorption and partitioning of PFOA and PFOS in sub-Saharan Africa. The study aimed at investigating adsorption behaviour, including partitioning and distribution coefficient, as well as sorption mechanisms of PFOA and PFOS in sediments from the Diep- and Plankenburg rivers in Cape Town, South Africa. Data sets were analysed using kinetic models and partitioning and distribution coefficients. The influence of sediment properties, solution pH, and the presence of cation ( $\text{Ca}^{2+}$ ) as well as, fraction organic carbon was evaluated.

## 2. Materials and methods

### 2.1. Standards and chemicals

Perfluorooctane sulfonate (PFOS, 98%) was purchased from Fluka Analytical (USA), perfluorooctanoic acid (PFOA, 96%) from Alfa Aesar (USA), and mass-labelled internal standards (IS) [ $^{13}\text{C}_4$ ]-PFOS and [ $^{13}\text{C}_4$ ]-PFOA used for analytical quantifications were supplied by Wellington Laboratories (Guelph, Canada). High performance liquid chromatography (HPLC) grade methanol (>99.9%) was purchased from Sigma-Aldrich (Germany), ammonium acetate and Milli-Q water were supplied by Merck Millipore (Germany). Laboratory contaminated water was prepared from a mixture of PFOA and PFOS stock solutions of 1000 mg/L in pure methanol. Working solutions were prepared with a mixture of PFOA and PFOS deionized water in a 500 mL polypropylene (pp) bottle.

## 2.2. Sample preparations and extraction procedures

Sediment samples were collected from the Diep and Plankenburg rivers in Cape Town, Western Cape, South Africa. Diep river flows through the Southern suburb of the Western Cape Region, Cape Town, while, the Plankenburg river system runs through the farms, industrial and informal settlement of the town of Stellenbosch, Western Cape. See Figure S1 in the supplementary information showing the map of the sampling area. Samples were collected in triplicate from seven sampling stations using aluminium foil pre-treated with methanol; they were placed in an ice chest in the field and transported to the laboratory. Samples were stored in a freezer at  $-4\text{ }^{\circ}\text{C}$  prior to preparation for analysis. The sediment samples were air-dried and sieved using a  $250\text{ }\mu\text{m}$  aperture stainless steel sieve, before the extraction procedure. Approximately 3 g of sediment was carefully weighed using a sensitive weighing balance into 15 mL centrifuge tubes. The extraction procedure was conducted using a solid-phase extraction-hydrophilic lipophilic balance (SPE-HLB) cartridge ( $0.5\text{ g}$ ,  $12\text{ cm}^3$ ) supplied by Sulpeco (Sigma Aldrich, Germany). SPE tubes were preconditioned using 10 mL of pure methanol and 5 mL of Milli-Q water, at a constant flow rate of 1 mL/min. Aliquots were collected after the partitioning and sorption experiments and filtered using  $0.45\text{ }\mu\text{m}$  polyethersulphone membrane syringe filters (Sigma-Aldrich, Germany). The aliquots were allowed to flow through a pre-conditioned SPE cartridge at a constant flow rate under gravity. The resultant effluent was discarded while the cartridges were allowed to drip to dryness. SPE tubes were rinsed with 5% methanol to eliminate possible interfering matrices. The recovery of PFOA and PFOS was achieved by allowing 5 mL of pure methanol to pass through the SPE cartridges. Recovered supernatants were concentrated and reconstituted back into 2 mL with pure methanol, and transfer into 2 mL vial for instrumental analysis. Sample extraction procedure is further described in the supplementary information (S1.1).

## 2.3. Fraction of organic carbon

The fraction of organic carbon ( $f_{oc}$ ) was estimated by transferring approximately 1 g sediment sample into a pre-cleaned conical flask. Approximately 10 mL of 1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  was added to the conical flask containing 1 g sediment and swirled. Concentrated sulphuric acid (20 mL) was added to the mixture and allowed to cool for 30 min. The mixture was diluted with 200 mL of Milli-Q water. Four drops of ferroin indicator were added and 0.4 N ferrous sulphates used to titrate until the endpoint was reached (yellow–blue–green colour). Control samples (CRS-sediment) were prepared in the same way alongside with the sediment samples. Each sample was titrated in triplicate. This method was adapted from Walkley–Black chromic acid wet oxidation method for the determination of organic carbon (Schumacher, 2002).

## 2.4. Total organic matter (TOM)

The TOM was estimated by weighing approximately 3 g (dw) of sediment samples into a pre-cleaned crucible (Kawasaki et al., 2011). The samples were transferred into the oven and heated at  $300\text{ }^{\circ}\text{C}$  for 36 h. The samples were then cooled to room temperature and weighed. The TOM of the sediments was estimated using Eq. (1) (Schumacher, 2002).

$$\text{Total organic matter (\%)} = (x - y) / x \times 100 \quad (1)$$

where  $x$  is the initial weight (g) of crucible and sediment before ignition and  $y$  is the final weight (g) of crucible and sediment after ignition.

## 2.5. Optimization procedure

Aggregate particle size for the sediment was estimated by weighing approximately 50 g air-dried, homogenized sediment samples using an analytical balance (Perkin Elmer, USA). The sample was sieved using three different mesh sizes (10, 125 and  $250\text{ }\mu\text{m}$ ) to obtain different particles sizes of the sediment. In addition, factors influencing the adsorption and partitioning of organic contaminants onto sediment in river systems (e.g. the solution pH and presence of cation  $\text{Ca}^{2+}$ ) were investigated. The solution pH was varied (pH 4, 6 and 9) and the effect of  $\text{Ca}^{2+}$  concentrations (0.005 M – 0.5 M) was optimized. Other conditions applied included initial concentration of analytes, agitation, and the shaking speed (Adeyinka and Moodley, 2019).

## 2.6. Sorption and partitioning experiments

Sorption studies were conducted using 50 mL polypropylene Nalgene tubes pre-cleaned with 100% methanol in order to eliminate possible impurities. Approximately 1 g of homogenized sediment sample was weighed into the Nalgene tubes containing 25 mL of contaminated water with a mixture of PFOA and PFOS (250 ng/L). Experimental data obtained were analysed using four kinetic models, including: pseudo-first-order; pseudo-second-order (Eqs. (2) and (3)).

$$t/q_t = 1/k_2q_e^2 + 1/q_e(t) \quad (2)$$

$$\ln(q_e - q_t) = \ln q_e - k_1t \quad (3)$$

where  $q_e$  and  $q_t$  represent the amounts adsorbed (mmol/g) at equilibrium and time  $t$  (min).  $K_1$  and  $K_2$  represent pseudo-first-order and pseudo-second-order rate constant, respectively. Adsorption kinetic constant  $K_1$  and  $K_2$  for pseudo-first- and second-order kinetics were derived from the linear Eq. (2) by plotting  $\ln(q_e - q_t)$  versus  $t$  (min) and Eq. (3) by plotting  $t/q_t$  against contact time  $t$  (min) (supplementary information).

$$q_t = 1/\beta \cdot \ln \alpha_E/\beta + 1/\beta \ln t \quad (4)$$

$$q_t = 1 + k_p t^{1/2} \quad (5)$$

Elovich rate equation and Webber–Morris intra-particle diffusivity equation is represented by Eqs. (4) and (5) where  $\alpha_E$  is the initial concentration of sorption rate and  $\beta$  is the desorption constant. The Webber–Morris intra-particle diffusivity was applied to derive the intra-particle diffusivity constant  $K_p$  and the boundary layer diffusion effect  $I$ .

Partitioning equilibrium parameters including partitioning distribution  $\log K_D$  and partitioning coefficient  $\log K_{OC}$  were evaluated and used to deduce their environmental distribution as presented in Eqs. (6) and (7), respectively.

$$K_D = C_{\text{sediment}}/C_{\text{water}} \quad (6)$$

$$K_{OC} = K_D \times 100/f_{OC} \quad (7)$$

where  $K_D$  represents partitioning coefficient,  $K_{OC}$  is the distribution coefficient and  $f_{OC}$  represents organic carbon fraction. Detailed sorption and partitioning experiments were presented in the supplementary data.

### 2.7. Analysis of PFOA and PFOS using UPLC-QTOF-MS

The determination of the target compounds PFOA and PFOS were performed using ultra-performance liquid chromatography-quadrupole time of flight-mass spectrometry (UPLC-QTOF-MS) technology by Waters Corporation, Milford, MA (USA). Samples were injected at a flow rate of 0.3  $\mu\text{L}/\text{min}$  into the guard column (4.6  $\mu\text{m}$  particle size, 5 mm long and 5.0 internal diameter) before passing into the Luna Phenomenex reverse phase C-18 column (4.6  $\mu\text{m}$  particle size, 150 mm length, 5.0 internal diameter), supplied by Sigma Aldrich (Germany). Analysis of PFOA and PFOS was the same as previously reported by Fagbayigbo et al. (2018).

### 2.8. Quality assurance and control

Standard laboratory practices were adhered to during the experimental procedures. Chemicals used were HPLC grade. Laboratory glassware were washed with detergent and rinsed with Mill-Q water and oven-dried at 55 °C. Blank and standard reference material (SRM) determination were conducted alongside the run standards to establish the contribution of analytical signals. These included the effect of mobile phase solvent, instrumental response, and human error. Samples were collected and analysed in triplicate. Labelled  $^{13}\text{C}$  PFOA and PFOS were added as internal standards to check instrumental variability and error of the analysis. The spike recovery calibration, instrumental parameters and blank of PFOA and PFOS are presented in the supplementary information (See Table S2–S6).

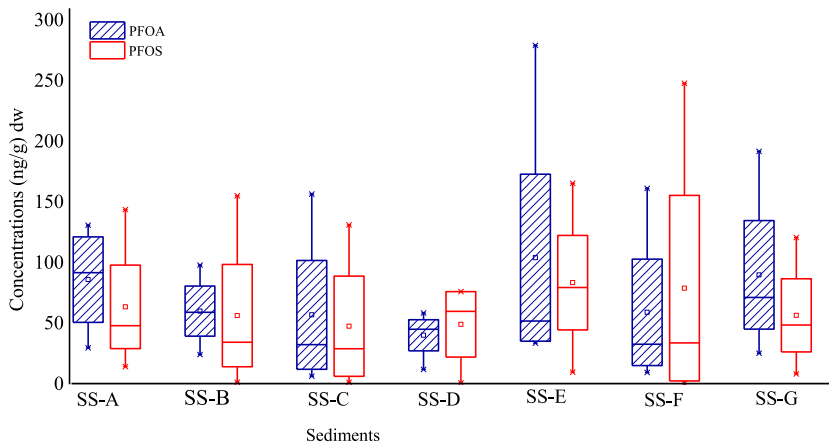
### 2.9. Statistical analysis

The data obtained were analysed statistically using SPSS 24 software. Two-way analysis of variance (ANOVA) was used to analyse data obtained; box and whisker plots were used to represent the levels of PFOA and PFOS in the sediment.

## 3. Result and discussion

### 3.1. Concentration of PFOA and PFOS in the sediment samples

Levels of PFOA and PFOS in sediment samples (SS-A, SS-B, SS-C, SS-D, SS-E, SS-F and SS-G) in this study are represented in (Fig. 1). The maximum concentration of PFOA was measured in sediment SS-E (279.37 ng/g dw) and the minimum concentration was detected in sediment SS-D (58.74 ng/g). In contrast, the maximum concentration of PFOS in sediment was detected SS-F (248.14 ng/g dw) and minimum in SS-D (74.42 ng/g dw). Mean concentrations of both PFOA and PFOS in all the sediments samples were <100 ng/g dw. This suggested they were available in trace concentrations in the sediment samples. Concentrations of PFOA and PFOS detected in the sediment were consistent with those in the previous report from Yangtze rivers, China where levels of these compounds varied between 72.90 and 536.7 ng/g (Pan and You, 2010). Also, concentrations of PFOA and PFOS in the sediment in this study were similar to sediment from the Baltic region, Latvia. The reported PFOA range was <LOD to 0.12 with a mean concentration of  $0.08 \pm 0.02$ , whereas PFOS ranged from <LOD to 0.17 with a mean concentration of  $0.55 \pm 0.54$  (Zacs and Bartkevics, 2016). Levels of PFOA (0.11–0.93 ng/g) and PFOS (<0.15–0.38 ng/g) were repeatedly found in sediment samples of East China sea (Wang et al., 2017). Concentrations of PFOA and PFOS in core sediments from Michigan-, Superior- and Huron Lakes were detected at a lower concentration than those reported in this study (Codling et al., 2018). Statistical analysis showed that there was no significant difference ( $p > 0.05$ ) in the levels of PFOA and PFOS among the sediment samples. See supplementary information (Table S10).



**Fig. 1.** Levels of PFOA and PFOS in the investigated sediments samples; SS-A, SS-B, SS-C, SS-D, SS-E, SS-F and SS-G.

**Table 1**

Physical characteristics of sediment samples.

Sediments	Mass of sand	Mass of silt	Mass of clay	Sand (%)	Silt (%)	Clay (%)	$f_{oc}$ (%)	Organic matter (%)
SS-A	39.76 ± 02	0.54 ± 18	0.05 ± 02	79.52	1.09	0.10	0.86	2.69
SS-B	30.79 ± 23	0.65 ± 57	0.40 ± 13	61.58	1.31	0.80	0.90	3.89
SS-C	12.34 ± 61	0.79 ± 08	2.20 ± 44	24.68	1.58	4.41	2.30	13.42
SS-D	14.65 ± 49	4.53 ± 25	1.01 ± 07	29.29	9.06	2.03	0.53	15.23
SS-E	31.34 ± 71	2.99 ± 08	1.47 ± 09	62.68	5.99	2.95	2.04	15.23
SS-F	33.50 ± 48	1.50 ± 11	0.85 ± 82	67.00	3.01	1.70	1.11	11.86
SS-G	25.79 ± 31	3.30 ± 06	0.46 ± 65	51.59	6.61	0.93	0.67	2.02

Note: Average mass of sand, silt and clay were measured in (g) ±SD.

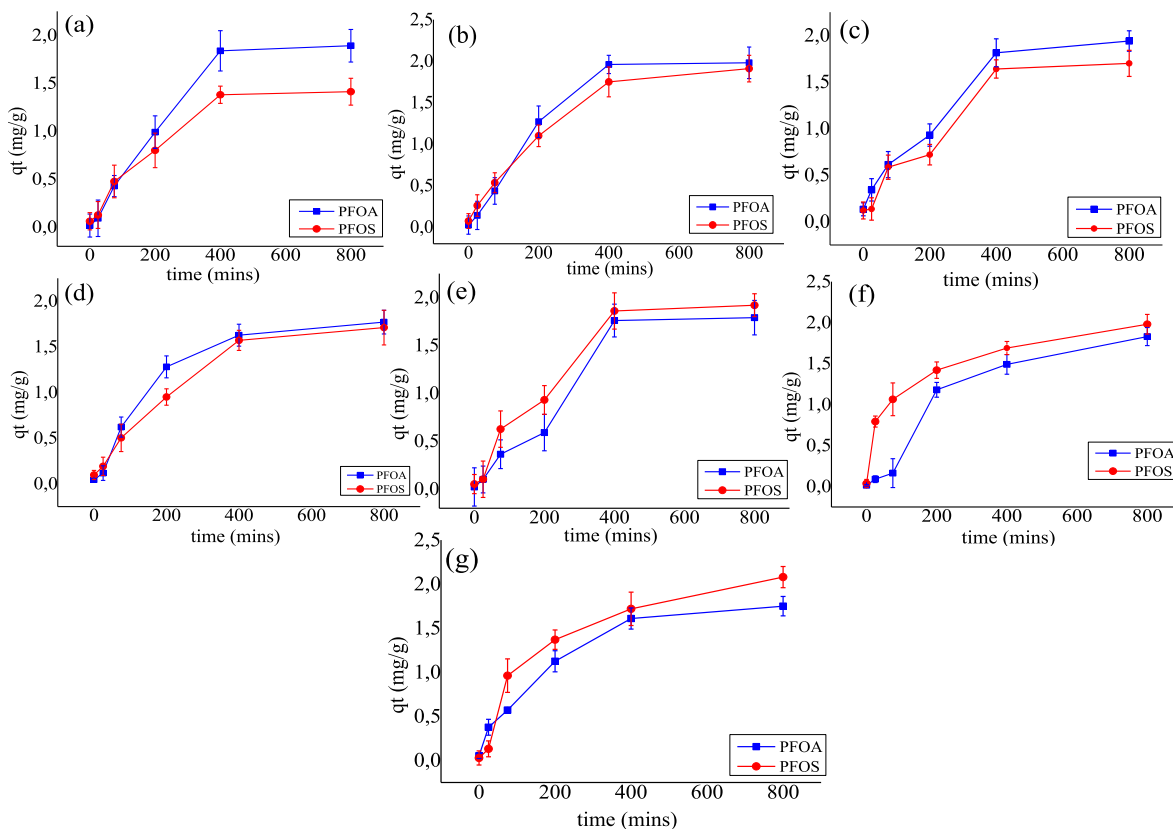
### 3.2. Physical characteristics of sediment samples

The physicochemical characteristics of the investigated sediment samples showed that sandy content was the dominant soil fraction, followed by silt and clay particles respectively (Table 1).

The results were consistent with a previous study on sediments samples from Cape Town, South Africa that revealed the dominance of sand relative to clay and silt (Daso et al., 2013). The percentage of clay and silt particles measured in the samples was used to propose possible sorption mechanisms of PFOA and PFOS in the environment. It was noted that the percentage of clay was relatively high in some of the sediment samples (SS-C, SS-D, SS-E, and SS-F) suggesting a suitable sediment condition for the decomposition of organic pollutants. There was a significant positive relationship ( $p < 0.05$ ) between organic matter (OM), clay particle and the fraction of organic carbon ( $f_{oc}$ ) of sediment samples. Higher clay content in the sediment samples positively correlated with high organic matter and organic carbon of the sediment samples. The values of the fraction of organic carbon ( $f_{oc}$ ) content in the samples indicate the degree of negatively-charged sites available on the surface of the sediments (Baldock et al., 2014). Also, the high organic matter content in the sediment samples indicated a high rate of biological activity in the system (SS-E, SS-F, and SS-D relative to those from SS-A, SS-B, and SS-C). Sediment sample SS-C has the highest clay content, 4.41% relative to other samples, clay is characterized with a large surface area and high sorption potential (Adeyinka and Moodley, 2019). Anthropogenic activities in the vicinity where sediments were collected such as improper waste disposal systems, decomposition of organic and inorganic wastes from urban, agricultural activities, effluent from industrial activities and sewage might have contributed to the high values of TOM content obtained.

### 3.3. Sorption mechanisms of PFOA and PFOS onto the sediment samples

The effects of contact time on the sorption of PFOA and PFOS onto sediment samples are presented in Fig. 2. The Kinetic study shows that sorption equilibria for all the sediment samples were achieved in less than 400 min contact time for both compounds. Kinetic plots of  $q_t$  (mg/g) versus  $t$  (min) showed that the sorption increased with increasing contact time. This observation was consistent with those previously reported elsewhere (Barton et al., 2007; Johnson et al., 2007; Zhou and Keller, 2010). The sorption kinetics of PFOA and PFOS onto the sediment samples was analysed using four kinetic models (pseudo-first-order, second-order, Elovich rate equation and intra-particle diffusible equation) to analyse the equilibrium data. The amount of PFOA and PFOS adsorbed by the sediments was influenced by the particulate size; lower particulate



**Fig. 2.** Sorption kinetics (pseudo-second-order) for PFOA and PFOS onto sediment samples (a) SS-A, (b) SS-B, (c) SS-C, (d) SS-D, (e) SS-E, (f) SS-F, and (g) SS-G. Other characteristics such as solution pH, presence of divalent cations and ionic strength, among others, contribute to the sorption and partitioning of PFAS in the environment (Li et al., 2019, 2018).

sediments SS-C provided the maximum sorption capacities (0.11 and 0.13 mg/g) for both PFOA and PFOS respectively. It was observed that ( $K_2$ ) pseudo-second-order constant that indicates slow sorption rate is higher than ( $K_1$ ) first-order kinetic (fast sorption rate) for both PFOA and PFOS in the sediment. This implies that the sorption rate is dominated by chemisorption being a major controlling step (Adeyinka and Moodley, 2019). Elovich kinetic equation data revealed that PFOS was adsorbed more rapidly and the initial adsorption rate ( $\alpha_E$ ) values ranged between 6.04 and 30.44 g/mg min<sup>-1</sup> relative to PFOA with respective values between 0.44 and 6.85 mg/m min. Desorption rate,  $\beta$  values ranged between 2.98 and 8.19 g mg<sup>-1</sup> for PFOS and were higher than values for PFOA (2.92 and 3.85 g mg<sup>-1</sup>) for the sediments suggesting a fast initial transfer onto the sediments. Webber–Morris intra-particle diffusivity constants  $K_p$  and the boundary layer diffusion effects  $I$  were disparate among the sediments for both compounds, possibly due to differences in their physicochemical characteristics. The results indicated slow diffusional transport of organic matter into the internal pores of the sediment. Also, the aqueous phase and solid interface were easily accessible by the molecules of both adsorbates (PFOA and PFOS) with consequent enhancement of equilibrium. Equilibrium data obtained for the sorption of both compounds fitted well into Elovich rate equation kinetic models followed by pseudo-second-order, with correlation coefficient ( $R^2$ ) values above >0.90 for most of the sediment samples. It was established that both physisorption and chemisorption mechanisms are the controlling steps in the sorption process; intra-particle diffusivity also played some role in PFOA and PFOS removal. The correlation coefficient  $R^2$  values for the models ranged between 0.54 and 0.97 for PFOA and values were 0.73 and 0.87 for PFOS. A summary of kinetic models for the sorption of PFOA and PFOS into different sediment from river systems is presented in Table 2.

### 3.4. Partitioning and distribution of PFOA and PFOS in the environment

The fate of PFOA and PFOS in an aquatic environment was estimated by simulating partitioning and distribution studies in the laboratory. Information on the distribution and partitioning of PFOA and PFOS in the environment may be indicative of their availability to organisms, and possible threats that they pose to aquatic life. Theoretically, when estimated values of  $\log K_{OC}$  and  $\log K_D$  are above 1 cm<sup>3</sup>/g, the sediment compartment is considered a repository for contaminants in aquatic

**Table 2**  
Kinetic models for PFOA and PFOS sorption on to sediment samples.

Compounds	Sediments	Pseudo 1st order kinetics			Pseudo 2nd order kinetics				Elovich equation rate			Intra-particle diffusion		
		$K_1$	$q_e$	$R^2$	$K_2$	$q_e$	$h$	$R^2$	$\beta$	$\alpha_E$	$R^2$	$K_p$	$I$	$R^2$
PFOA	SS-A	$6.0 \times 10^{-5}$	4.08	0.60	1.19	0.01	0.02	0.84	3.13	5.17	0.98	0.09	1.53	0.86
	SS-B	$5.0 \times 10^{-5}$	4.44	0.63	0.79	0.02	5.05	0.84	2.92	1.02	0.94	0.09	1.71	0.87
	SS-C	$4.0 \times 10^{-5}$	4.31	0.56	0.18	0.13	$3.4 \times 10^{-3}$	0.90	3.63	6.76	0.98	0.07	1.44	0.81
	SS-D	$4.0 \times 10^{-5}$	4.22	0.57	0.53	0.04	1.06	0.92	3.85	6.85	0.98	0.07	1.25	0.83
	SS-E	$4.0 \times 10^{-5}$	4.42	0.49	0.47	0.02	$6.4 \times 10^{-4}$	0.85	3.37	5.86	0.97	0.07	1.32	0.76
	SS-F	$4.0 \times 10^{-5}$	4.39	0.54	2.19	0.01	4.62	0.97	3.05	1.50	0.90	0.09	1.51	0.78
	SS-G	$3.0 \times 10^{-5}$	4.49	0.50	0.37	0.05	1.09	0.82	4.10	0.44	0.93	0.06	1.22	0.73
PFOS	SS-A	$2.0 \times 10^{-5}$	4.09	0.30	0.27	0.04	0.11	0.99	8.19	19.39	0.83	0.02	1.12	0.54
	SS-B	$4.0 \times 10^{-5}$	4.44	0.65	0.29	0.07	$1.7 \times 10^{-3}$	0.87	3.29	6.04	0.98	0.08	1.59	0.89
	SS-C	$4.0 \times 10^{-5}$	4.31	0.55	0.33	0.11	$4.4 \times 10^{-3}$	0.98	3.82	6.99	0.98	0.07	1.33	0.83
	SS-D	$4.0 \times 10^{-5}$	4.22	0.81	0.21	0.09	$2.3 \times 10^{-3}$	0.84	4.45	8.83	0.94	0.06	1.44	0.96
	SS-E	$4.0 \times 10^{-5}$	4.42	0.57	0.49	0.05	$1.3 \times 10^{-3}$	0.93	3.25	19.41	0.98	0.08	1.48	0.82
	SS-F	$5.0 \times 10^{-5}$	4.39	0.94	0.48	0.03	0.69	0.79	3.92	30.46	0.80	0.08	1.82	0.97
	SS-G	$5.0 \times 10^{-5}$	4.49	0.78	0.70	0.02	$1.6 \times 10^{-4}$	0.85	2.98	5.54	0.90	0.10	1.88	0.94

Note:  $K_1$  ( $\text{min}^{-1}$ ) = pseudo first order kinetic,  $q_e$  ( $\text{mg g}^{-1}$ ) = ,  $K_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $K_p$  = Webber–Morris intra-particle diffusivity constants,  $q_e$  ( $\text{mg/g}$ ) = concentration adsorbed,  $\alpha_E$  ( $\text{g}^{-1} \text{mg} \text{min}^{-1}$ ) = initial adsorption rate,  $\beta$  ( $\text{g mg}^{-1}$ ) = desorption rate,  $I$  = boundary layer diffusion effects,  $R^2$  = correlation coefficient.

**Table 3**  
Water–sediment partitioning parameters for PFOA and PFOS.

	Sediments	$C_s$ ( $\text{mg/L}$ )	$C_w$ ( $\text{mg/L}$ )	% $f_{oc}$	$K_D$	$\log K_D$ ( $\text{cm}^3/\text{g}$ )	$K_{OC}$	$\log K_{OC}$ ( $\text{cm}^3/\text{g}$ )	
PFOA	SS-A	1.72	0.12	0.86	13.67	1.13	11.82	1.07	
	SS-B	1.77	0.12	0.91	14.41	1.15	12.99	1.11	
	SS-C	1.65	0.15	2.30	10.4	1.02	24.02	1.38	
	SS-D	1.36	0.17	0.53	8.03	0.91	4.30	0.63	
							Mean $\pm$ SD	1.04 $\pm$ 0.31	
	SS-E	1.60	0.16	2.04	10.03	1.00	20.47	1.31	
	SS-F	1.62	0.16	1.11	9.95	0.99	11.11	1.04	
	SS-G	1.45	0.15	0.67	9.55	0.98	6.40	0.80	
							Mean $\pm$ SD	1.05 $\pm$ 0.25	1.04 $\pm$ 0.26
PFOS	SS-A	16.74	0.16	0.86	102.6	2.01	88.21	1.95	
	SS-B	4.06	0.11	0.91	36.04	1.56	32.44	1.51	
	SS-C	20.82	0.11	2.30	177.90	2.25	409.20	2.61	
	SS-D	36.62	0.18	0.53	201.70	2.30	106.9	2.02	
							Mean $\pm$ SD	2.02 $\pm$ 0.45	
	SS-E	32.88	0.16	2.04	196.3	2.29	400.40	2.60	
	SS-F	3.53	0.14	1.12	24.45	1.38	27.38	1.43	
	SS-G	1.82	0.16	0.67	11.18	1.05	7.48	0.87	
							Mean $\pm$ SD	1.63 $\pm$ 0.82	1.85 $\pm$ 0.63

Note:  $C_s$  = concentration in sediment,  $C_w$  = concentration in aqueous phase,  $f_{oc}$  = fraction of organic carbon,  $\log K_D$  = partitioning distribution,  $\log K_{OC}$  = partitioning coefficient. Plankenburg river sites: SS-A, SS-B, SS-C and SS-D; Diep river sites: SS-E, SS-F and SS-G.

systems (Zhao et al., 2014). The partitioning parameters for both PFOA and PFOS in the different sediment samples from the two river systems are presented in Table 3.

The distribution coefficient ( $\log K_D$ ) ranged between 0.98 and 1.15  $\text{cm}^3/\text{g}$  for PFOA, and between 1.05 and 2.29  $\text{cm}^3/\text{g}$  for PFOS. The partitioning coefficient ( $\log K_{OC}$ ) for both compounds was determined relative to the organic carbon fraction ( $f_{oc}$ ) in the sediment (Lodge and Cook, 2016). Maximum  $\log K_{OC}$  values for PFOA and PFOS were 1.38 and 2.61  $\text{cm}^3/\text{g}$  respectively in sediment SS-C, while minimum  $\log K_{OC}$  values were observed in sediment SS-G. Low values of  $\log K_{OC}$  imply that PFOA and PFOS exist predominantly in the dissolved phase and can be rapidly dispersed and diluted within the aqueous solution. High  $\log K_{OC}$  values ( $> 1.0 \text{ cm}^3/\text{g}$ ) would imply higher concentrations of the compounds in sediments, with a strong association with particulate/sediment and consequently less mobility. It was also noted that values for  $\log K_{OC}$  increased over time (Fig. 3). This observation showed that sorption rate of hydrophobic organic compounds such as PFOA and PFOS onto sediment is controlled by diffusion processes (Chalhoub et al., 2013). Statistically, there was no significant difference ( $p > 0.005$ ) in values of  $\log K_{OC}$  among the sediments (see supplementary information Table S12 and 13). The partitioning coefficient  $\log K_{OC}$  provides a realistic representation of the partitioning of pollutants in an aqueous solution (Chen et al., 2012; Higgins and Luthy, 2006). Higher values of  $\log K_{OC}$  (above 1.0  $\text{cm}^3/\text{g}$ ) indicate that the investigated contaminants are also available in the solid phase (Lodge and Cook, 2016). It is important to note that prevailing conditions in the aqueous medium, such as the influence of the sediment aggregates and the dilution effect, might lead to disequilibrium in the system. This is due to the influx of additional surface water, which could lead to higher

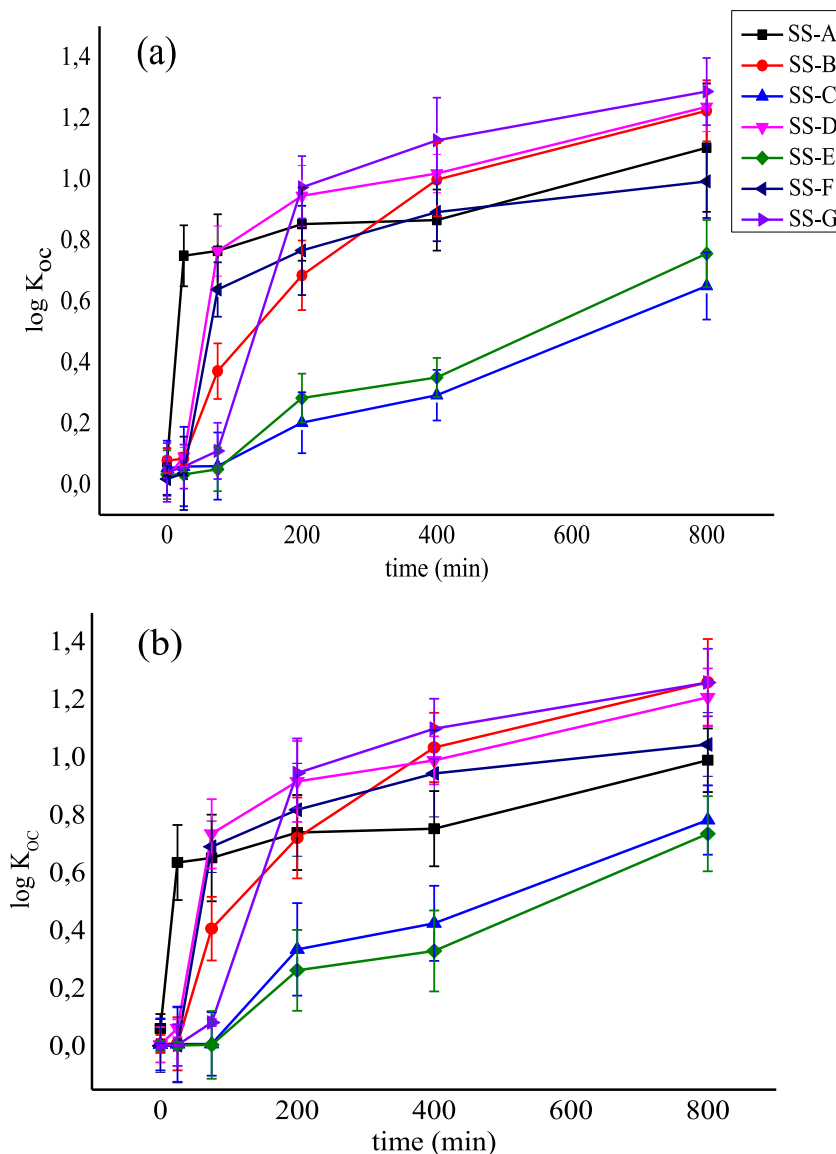


Fig. 3. Partitioning coefficient ( $\log K_{OC}$ ) of (a) PFOA and (b) PFOS for different investigated sediments.

$\log K_{OC}$  values. Dilution due to surface water runoff and precipitation in the moist or wet season could enhance the value of  $\log K_{OC}$  in river systems.

### 3.5. Influence of pH

The influence of pH is one of the determinants of partitioning and sorption of pollutants in the environmental compartments. Slight changes in pH in an aquatic system can significantly influence the sorption of organic contaminants in the aquatic system. It was observed that low pH (pH 4) favoured the uptake of PFOA and PFOS in the aqueous medium due to the presence of abundant hydrogen ions ( $H^+$ ). The interaction between the charged molecules present in the solution might also contribute to the availability of hydrogen ion in the solution. The results indicated a significant difference ( $F = 66.04$ ,  $p$ -value  $< 0.05$ ) in the maximum adsorption capacities obtained for PFOA and PFOS at pH 4 in comparison to those obtained at higher pH values (pH 6 and 9) in the sediments, which corresponds with a previous report by Higgins and Luthy (2006). The estimated  $pH_{PZC}$  values were slightly acidic for the sediment samples, ranging between 5.3 and 6.4 pH (detailed results were presented in the supplementary information). Sorption of PFOA and PFOS below  $pH_{PZC}$  values suggests the positively charged surface of the sediments, which indicated adsorption of anions onto positively charged surfaces. This poses a greater tendency that electrostatic attraction between the contaminants and solids could be



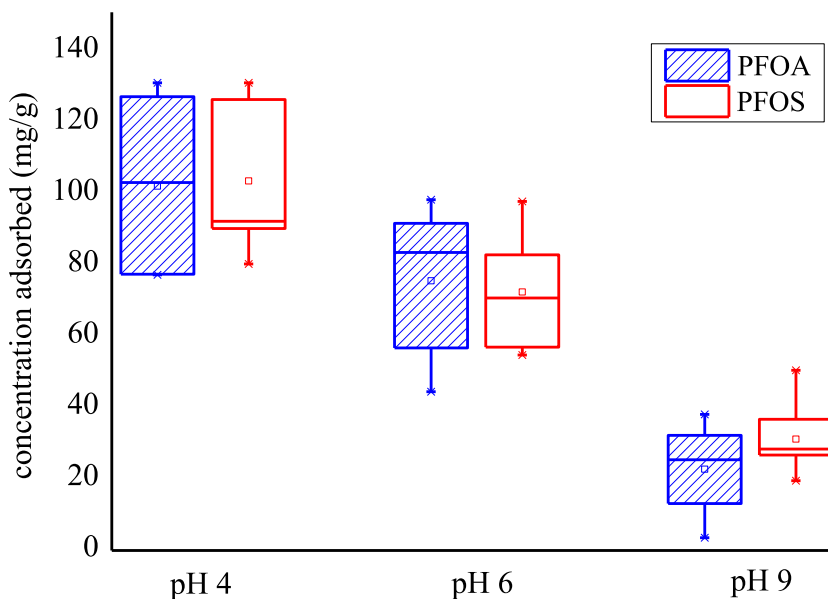


Fig. 4. Sorption of PFOA onto sediments at varied pH values at pH 4, 6 and 9.

enhanced. It is therefore deduced that an abundance of  $\text{OH}^-$  ions present in alkaline media hinder the diffusion of PFOA and PFOS molecules onto the porous surface of the sediment, thus reduces sorption processes (Fagbayigbo et al., 2020; Wang et al., 2021). Similarly, this report is consistent with other studies which demonstrated that sorption is favoured at lower levels of pH (4.0 and 7.5) than values  $> 8$  (Brooke et al., 2004; Wang and Shih, 2011). The effect of pH on the partitioning and sorption of organic compounds in aquatic systems could be attributed to the reactivity of hydrogen bonds which exist as hydroxyl ( $\text{OH}^-$ ) and hydrogen ( $\text{H}^+$ ) present in the aqueous solution. Previous investigations confirm that the partitioning behaviour of perfluoroalkyl substances onto solid surfaces demonstrated that sediment–water distribution depends on solution pH (Higgins and Luthy, 2006; Johnson et al., 2007; Wang et al., 2018). Fig. 4 illustrates the sorption of PFOA and PFOS at varied pH values on sediments samples.

### 3.6. Influence of cations ( $\text{Ca}^{2+}$ )

The presence of cations could be used as a determinant of the survival of the organisms in the aquatic environment. The influence of  $\text{Ca}^{2+}$  was investigated for the adsorption of PFOA and PFOS into the sediment samples. Solution pH 4 was maintained in the system, while the concentration of  $\text{Ca}^{2+}$  ranged from 0.005 M to 0.5 M and the concentration of adsorbate (PFOA) ranged between 0.5 and 2.5 mg/l. It was noticed that an increase in the concentrations of  $\text{Ca}^{2+}$  in the solution enhanced the sorption of PFOA and PFOS into sediment samples. It was also observed that sorption rates differ markedly for PFOA and PFOS at higher  $\text{Ca}^{2+}$  concentrations of 0.5 M and were significantly higher ( $p > 0.05$ ) than the lower  $\text{Ca}^{2+}$  concentrations (see supplementary information in Table S13). The electrostatic interaction and solubility properties of the compounds increased as the  $\text{Ca}^{2+}$  in the aqueous solution increased, thereby creating a charged environment that enhances the sorption of PFOA and PFOS onto the sediments. Similar studies have reported that the presence of divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in aqueous solutions enhanced the adsorption of PFAS onto negatively charged sediment particles (Higgins and Luthy, 2006; Senevirathna et al., 2010). Ionic strength was found to influence the sorption of PFAS between the aqueous phase and solid phase (sediment). Adsorption of PFOA and PFOS at increasing  $\text{Ca}^{2+}$  concentration is represented in Fig. 5.

The environmental distribution of organic compounds such as PFOA and PFOS have been reported to be mostly influenced by phase partitioning and electrostatics interaction processes (Li et al., 2018). Higher concentrations of PFOA and PFOS in the sediment compartment than concentrations in the aqueous phase imply that sorption was favourable into the sediment compartment. Based on this study, background concentrations of PFOA and PFOS in sediment used in this study were slightly lower than the levels reported in sediment in similar studies elsewhere (Liu et al., 2015; Rankin et al., 2016). The partitioning coefficients ( $\log K_{oc}$ ) obtained for PFOA and PFOS were generally lower than values obtained by Ahrens et al. (2015), where  $\log K_{oc}$  for PFOA and PFOS was 4.5 and 4.7  $\text{cm}^3/\text{g}$ , respectively. Values of  $\log K_{oc}$  for most of the sediment samples suggest extensive adsorption of PFOA and PFOS. Table 4 presents  $\log K_D$  and  $\log K_{OC}$  values obtained as compared to those from other studies. Also, water quality parameters such as pH and the presence of ionic substances have been reported to influence the sorption of PFOA and PFOS in aquatic environments (Pan et al., 2009). The mobility of PFOA and PFOS in the aquatic system could lead to bioaccumulation in the environmental

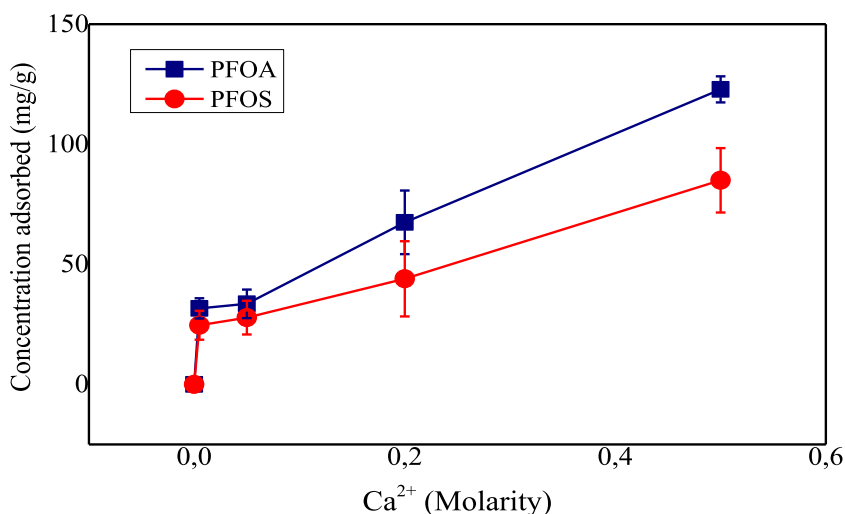


Fig. 5. Sorption of PFOA and PFOS into sediment at increasing concentrations of ( $\text{Ca}^{2+}$ ) in the aqueous solution.

Table 4

Comparison of distribution coefficient ( $\log K_D$ ) and partitioning coefficient ( $\log K_{OC}$ ) with other studies.

Sample locations	PFOA			PFOS		
	$\log K_D$ ( $\text{cm}^3/\text{g}$ )	$\log K_{OC}$ ( $\text{cm}^3/\text{g}$ )	Reference	$\log K_D$ ( $\text{cm}^3/\text{g}$ )	$\log K_{OC}$ ( $\text{cm}^3/\text{g}$ )	Reference
Sediment, Sweden	1.20	4.7	Ahrens et al. (2010)	0.96	4.5	Ahrens et al. (2010)
Sediment, USA	NA	2.06	Higgins and Luthy (2006)	7.42	2.8	Johnson et al. (2007)
Liao river, China	2.30	NA	Yang et al. (2011)		2.57	Higgins and Luthy (2006)
Yangtze River, China	0.77	1.5	Li et al. (2011)		3.7	Labadie and Chevreuil (2011)
Tokyo Bay Japan		2.4	Ahrens et al. (2011)		3.70	Ahrens et al. (2011)
Pearl River, South China	2.58–4.75		Zhao et al. (2014)		3–6.26	Zhao et al. (2014)
Youngsan and Nakdong water shed, Japan	$0.35 \pm 0.3$	$2.0 \pm 0.5$	Hong et al. (2013)	$0.83 \pm 0.3$	$2.5 \pm 0.5$	Hong et al. (2013)
Selected surface waters, The Netherlands	$1.83 \pm 0.40$	$2.63 \pm 0.34$	Kwadijk et al. (2010)	$2.35 \pm 0.35$	$3.16 \pm 0.7$	Kwadijk et al. (2010)
Dalian coast china				$1.44 \pm 0.11$	$3.47 \pm 0.07$	Chen et al. (2011)
Yangtze River china				$3.2 \pm 0.5$	$4.3 \pm 0.5$	Pan and You (2010)
Sub-Tropical sea South China sea	2.18	4.54	Xiao et al. (2021)	2.80	5.15	Xiao et al. (2021)
Songhua River China					$4.49 \pm 0.24$	Dong et al. (2018)
Plankenburg River, SA	$2.06 \pm 0.12$	$1.04 \pm 0.31$	This Study	$2.0 \pm 0.33$	$2.02 \pm 0.45$	This Study
Diep River, SA	$1.99 \pm 0.11$	$1.05 \pm 0.25$	This Study	$1.57 \pm 0.64$	$1.63 \pm 0.82$	This Study

components, which means they could easily be picked up by living organisms, with consequent environmental and health implications. Distribution, degradation, reactivity, and mobility contribute significantly to the fate of PFOA and PFOS in the environment. Anthropogenic activities adjacent to these rivers make them highly susceptible to contamination. In addition to the unrestricted application of chemicals from agricultural practices (Paulse et al., 2009), other activities that may contribute to the contamination of the investigated rivers include inadequate waste management systems, littering, the improper dumping of waste, industrial release and the occasional application of firefighting chemicals to combat wildfires.

#### 4. Conclusion

This study provides data on the sorption mechanism, partitioning and distribution of PFOA and PFOS onto sediments from river systems in Cape Town, South Africa. Physicochemical characteristics of sediment such as sediment aggregates comprise one of the dominant factors responsible for the adsorption of PFOA and PFOS onto the sediments. Batch adsorption studies showed that sediment samples from the sampling stations indicated different percentages of particle sizes and sorption capacities for PFOA and PFOS. Sediment samples SS-C provided the highest sorption capacities for both PFOA and PFOS relative to other investigated sediments samples. Sorption behaviour of PFOA and PFOS were significantly influenced by a decrease in solution pH and increased in  $\text{Ca}^{2+}$  concentrations. Sorption kinetics reveals that

equilibrium was attained between 200 and 400 min for most of the sediment samples. The data obtained from the sorption mechanism fitted well with the pseudo-second-order and followed by Elovich rate equation kinetic models, suggesting that a chemisorption process and slow sorption rate is among the controlling factors. The partitioning and distribution of PFOA and PFOS evaluated using data obtained for  $\log K_{OC}$  and  $\log K_D$  in laboratory-scale simulated experiments showed that values for  $\log K_{OC}$  were mostly above  $1.0 \text{ cm}^3/\text{g}$ . This suggest that PFOS and PFOA have strong association with sediments and consequently less mobility; hence, adsorbed more rapidly onto the sediments, indicating a potential sink for PFOA and PFOS in the aquatic systems. The findings showed that sediments characteristics play an important role in the availability of PFOA and PFOS in water systems. Consumption of polluted water by people living close to the water bodies may pose as health risk and potential hazard to the aquatic ecological system. This study represent the first investigation of partitioning and distribution PFOA and PFOS in sub-Sahara Africa, as such, it provides the much needed insight and scientific basis to understand the fate and sorption of PFOA and PFOS s in the aquatic environment.

### CRediT authorship contribution statement

**B.O Fagbayigbo:** Conception and design of study, Acquisition of data, Analysis and/or interpretation of data, Writing – original draft, Writing – review & editing. **B.O. Opeolu:** Conception and design of study, Writing – original draft, Writing – review & editing. **O.S. Fatoki:** Conception and design of study, Writing – original draft. **O.S. Olatunji:** Conception and design of study, Acquisition of data, Analysis and/or interpretation of data, Writing – original draft, Writing – review & editing. **M.O. Akharam:** Acquisition of data, Analysis and/or interpretation of data, Writing – review & editing. **I.S. Human:** Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2021.102110>.

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