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Investigation of Per- and Polyfluoroalkyl Substances (PFAS) Adsorption onto the Medium Size Quartz Gravel

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Abstract: Poly- and perfluoroalkyl substances (PFAS) are persistent chemicals that may pose risks to ecosystems and human health. Understanding the environmental fate and transport of PFAS is challenging due to their ability to migrate across air, water, and soil. In surface waters, PFAS can interact with sediments, organic matter, and plants, influencing the mobility of these compounds and posing potential risks to the environment. This study provides the first analysis of the adsorption of PFAS, including perfluoro-carboxylic acids (PFCA, C4–C10), perfluoro-sulfonic acids (PFSA, C4–C8), per-/poly-fluoroalkylether acids (PFEA C4–C8) and fluorotelomer sulfonates (FTS, C8 and C10) to medium-sized quartz gravel (pebbles), commonly found in the UK river systems. The effects of exposure time (1, 3 and 7 days) and mechanical disturbance (shaking) on PFAS adsorption were evaluated. The degree of PFAS adsorption indicated a clear dependence on the compound's functional group and carbon chain length. Long-chain PFAS, perfluorodecanoic acid (PFDA), exhibited the highest adsorption, while PFCA showed the least sorption compared to corresponding PFEA, PFSA and FTS of homologues (C5–C8). Mechanical disturbance (shaking) of gravel in PFAS-contaminated water did not significantly influence the extent of adsorption on most of the studied analytes except 9 Cl-PF3OUdS, 8:2 FTS, and PFDA, onto the gravel. The study demonstrates, for the first time, that medium-sized quartz gravel can adsorb PFAS, including new-generation substitutes from water. In riverine systems, these pollutants can be remobilised from gravel surfaces during e.g., flooding, dredging, or changes in water chemistry, potentially reintroducing them into the water and impacting water quality and ecosystem.

Keywords: quartz; PFOS; PFOA; PFHxA; water pollution

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals used for manufacturing of various consumer goods [1]. These compounds also belong to a group of new and emerging and persistent organic pollutants (NEPs and POPs) that may pose significant risks to human health and ecosystem [2,3]. PFAS constitute a class of over 14,000 chemicals with different functionalities including perfluoroalkyl ether acids (PFEA), and fluorotelomer sulphonates (FTS) [4–6]. However, regulations have been set up to restrict the use and production of only a limited number of PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) [7] and monitor them in the environment [8,9]. PFAS have been widely observed in diverse environments including surface water [10–12] drinking water [11,13,14], air [15–17] and sediments [18–20].

PFAS can be released into surface waters via several sources e.g., atmospheric deposition [21], landfills [22,23], wastewater treatment plants (WWTPs) [24,25], and accidental release from aqueous film forming foams

(AFFFs) [25]. Once released into aquatic environments, the presence and long-term impact of PFAS can be challenging to predict. This is due to processes including but not limited to adsorption and desorption of PFAS from the surface of riverine sediments and plants. These processes can also potentially influence the mobility and availability of PFAS in surface waters [26,27].

Several studies have reported the adsorption of various PFAS including PFOA and PFOS, perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), perfluoropentanoic acid (PFPeA), perfluorononanoic acid (PFNA), perfluoroheptanoic acid (PFHpA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA) and perfluorohexanesulfonic acid (PFHxS) onto sediments [28–31] soils [32–35] and activated carbon [36,37] commonly used for water treatment. PFAS adsorption onto sediments are governed by the compounds diverse characteristics such as carbon chain length, molecular weight (MW), and functional group [34,38]. The characteristics of sediments, such as mineral composition [39,40], surface charge [34], particle size [28,30,41] and organic matter content [30,41,42] have also been reported to influence PFAS adsorption. These characteristics could affect the types of interactions between PFAS and sediments e.g., electrostatic, hydrophobic and ion-exchange interactions, and cause them to exhibit different adsorption capabilities [43]. For instance, several studies have reported hydrophobicity as a main adsorption mechanism for long-chain PFAS [34,42,44,45] whereas the adsorption of short-chain PFAS onto soils have been attributed to electrostatic interactions between the ionic groups of PFAS and soil surfaces [34,46].

Surface waters, such as rivers, are typically associated with the presence of suspended and deposited sediments, consisting of various minerals (e.g., quartz, the second most abundant mineral on Earth) as a result of natural processes e.g., erosion and/or weathering of rocks [47–49]. A study by Cormier et al. [50] demonstrated that in an aqueous solution containing 10 ng/mL of PFOS, large-sized plastics (125–500 µm) can act as a more active adsorption surface for PFAS (PFOS) than fine-sized plastics (4–20 µm). These findings highlight the importance of both material composition and particle size in the efficiency of pollutant adsorption in aquatic environments that could influence contaminant retention and mobility. Most existing research has focused on PFAS adsorption to fine size sediments such as silt and sand (0.1 µm–5 mm) [34,35,39,41,51,52]. However, to the best of our knowledge, the adsorption of PFAS onto medium-sized sediments such as gravel (>8 mm) has not been investigated, despite being predominantly found in or around rivers [53] and its potential to serve as a surface for PFAS adsorption.

Considering recent reports on the occurrence and toxicity of PFAS, including new-generation substitutes, at trace levels [54–56], as well as the lack of information on the adsorption of these compounds onto commonly present in riverine systems medium-sized gravel (>8 mm), further studies are needed to understand the mobility of new-generation PFAS in aquatic environments. Therefore, the aims of this study were (1) to assess the extent of adsorption of 19 PFAS with four different functionalities including PFCA, PFSA, FTS and PFESA, onto medium-sized gravel, and (2) to assess the impact of exposure time and mechanical disturbances on the adsorption of PFAS to riverine gravel. Understanding these factors are needed for the PFAS transport assessment in riverine systems, and mitigating their potential environmental impact.

2. Materials and Methods

2.1. Materials

250 mL glass beakers (P/N FB3311, Boro 3.3 Fisherbrand^{TM}·, Fisher Scientific, Schwerte, Germany); 20 mL Head Space (HS) crimp top glass vials (P/N 12971231, Fisherbrand^{TM}, Thermo Scientific, Langerwehe, Germany) with aluminium crimp caps and silicone/PTFE septa (P/N11793127, Fisherbrand^{TM}, Thermo Scientific); 10 mL HS glass vials (Chromacol 10-HSV, Thermo Scientific) with metal screw caps (Chromacol 18-MSC, Thermo Scientific) and PTFE septa (Chromacol 18-ST101, Thermo Scientific); luer tapered filters (Iso-Disc PTFE-membrane, 13 mm × 0.45 µm, Thermo Scientific, Shanghai, China); Quartz gravel (8–12 mm) (source Germany, purchased from AK Kin Garden Supplies, Chichester, UK). The chemical composition of the quartz gravel is shown in Table S1.

2.2. Chemical Reagents

Optima^{TM} LC-MS grade: ammonium acetate (Fisher Chemical, Pittsburgh, PA, USA), water (Fisher Chemical, Loughborough, UK) and methanol (Thermo Fisher Scientific, Trinidad and Tobago); HiPerSolv CHROMANORM^{TM} (VWR Chemicals, Leuven, Belgium): methanol (super gradient grade for HPLC) and formic acid (for LC-MS); EPA-533PAR standard mixture consisting of 25 PFAS, including perfluoroalkane sulfonates (C4, C5, C7 linear, C6 & C8 linear and branched isomers), perfluoroalkyl carboxylic acids (C4–C12), 4:2

fluorotelomer sulfonate (4:2 FTS), 6:2 fluorotelomer sulfonate (6:2 FTS), 8:2 fluorotelomer sulfonate (8:2 FTS), perfluoro-3-methoxypropanoic acid (PFMPA), perfluoro-4-methoxybutanoic acid (PFMBA), perfluoro (2-ethoxyethane) sulfonic acid (PFEESA), perfluoro-3,6-dioxaheptanoic acid (3,6-OPFHpA), sodium dodecafluoro-3H-4, 8-dioxanonanoate (NaDONA), hexafluoropropylene oxide dimer acid (HFPO-DA), 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS) & 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS), at concentrations of 0.5 μg/mL and EPA-533ES ^{13}C isotope mixture containing 16 (^{13}C) PFAS (including 4:2 fluorotelomer sulfonate $^{13}C_2$ (M2-4:2FTS), 8:2 fluorotelomer sulfonate $^{13}C_2$ (M2-8:2FTS), 6:2 fluorotelomer sulfonate $^{13}C_2$ (M2-6:2FTS), perfluorohexanoic acid $^{13}C_5$ (M5PFHxA), perfluorobutanoic Acid (MPFBA), perfluoropentanoic acid $^{13}C_5$ (M5PFPeA), perfluorononanoic acid $^{13}C_9$ (M9PFNA), perflurooctanoic acid $^{13}C_8$ (M8PFOA), perfluoroheptanoic acid $^{13}C_4$ (M4PFHpA), (M7PFUdA), perfluorodecanoic acid $^{13}C_6$ (M6PFDA), perfluorododecanoic acid $^{13}C_2$ (MPFDoA), perfluorohexane sulfonic acid $^{13}C_3$ (M3PFHxS), perfluorobutane sulfonic acid $^{13}C_3$ (M3PFBS), perfluorooctane sulfonic acid $^{13}C_8$ (M8PFOS), and hexafluoropropylene oxide dimer acid $^{13}C_3$ (M3HFPO) at 0.5–2.0 μg/mL (Wellington labs, Canada). The full names for the abbreviated n-PFAS (and ^{13}C PFAS used as internal standards (ISs)) are detailed in Table S2 of the Supplementary Data.

2.3. Sample Preparation and Cleaning Procedures

Before conducting all experiments, quartz gravel was (1) pre-washed with deionised water, (2) sonicated with methanol for 20 min and (3) rinsed with LC-MS grade water (each step three times). The glass beakers, caps, vials and pipette tips were also washed to reduce contaminants and residues. For example, the glass beakers were sonicated with 150 mL of 70:30 methanol:water (*v*/*v*) solution for 20 min. Pipette tips, vials and caps were pre-washed and rinsed three times each with methanol and LC-MS grade water, respectively.

2.4. PFAS Extraction from the Surface of Gravel

Recent research indicated that when compared to high-density polyethylene and polypropylene, glass material provides lower adsorption losses of long-chain PFAS (e.g., PFOA, PFNA, PFOS, and PFDA) in highly aqueous solutions (i.e., with 100% water) [57–59]. Therefore, beakers made of glass material were selected as vessels for adsorption experiments. Exposed to PFAS gravel was transferred into a prewashed 250 mL glass beaker and extracted with 18 mL of LC-MS Grade methanol (HiPerSlov CHROMANORM^{TM}) in an ultrasonic bath for 20 min (10 min × 2 times). The methanolic extracts were filtered using 0.45 μm membrane filters, into prewashed 20 mL crimp top glass vials. The PTFE filters used in this study were previously assessed for PFAS leachability [17]. Purging of PTFE filters with methanolic solution was encouraged to reduce potential PFAS artefacts to a background level. Therefore, in this study, the filters were purged before use with 20 mL of LC-MS Grade methanol. The filtered methanolic gravel extracts were spiked with a mixture of 16 ^{13}C PFAS IS at 20 pg/mL for three FTS and 5 pg/mL for other analytes. The spiked extracts were then evaporated to 1 mL under a gentle flow of nitrogen, topped up with 4 mL of water (LC-MS grade), and vortexed to achieve 80:20 water:methanol (*v*/*v*) ratio necessary for online SPE analysis [17]. IS was added prior to the evaporation step, ensuring they account for variations during the latter part of the extraction process, as well as matrix effects and instrumental fluctuations. Recovery experiments by spiking pebbles directly with n-PFAS mixture and ^{13}C-PFAS provided high recoveries (80.2 ± 3.9% to 109.5 ± 4.1%). The experiments were performed in four replicates.

Extraction Efficiency of PFAS from Gravel Surfaces

The extraction efficiency of the method was evaluated by spiking 5.1 g quartz gravel with PFAS analytes (EPA-533PAR mixture containing 25 native PFAS) at 7 pg. The samples were then extracted, reduced by volume and analysed as described in Section 2.3. Following the first extraction, the same quartz gravel was subjected to second and third extraction steps and processed in a similar way as described in Section 2.3. The recovery experiments were performed in four replicates. The recoveries of PFAS were obtained by calculating the ratios of the mass of PFAS recovered at each extraction step to that of the theoretical mass of PFAS (7 pg) spiked onto the gravel. From the single-step extraction procedure, the recoveries of PFAS ranged between 76.6% and 98.9% (Figure S1). The second extraction step has led to additional recoveries of 2.6% to 21.9% (Figure S1). The third extraction step gave negligible recoveries (within the analysis error). Therefore, for all adsorption experiments, the quartz gravel samples were extracted two times.

2.5. Adsorption of PFAS onto the Surface of Gravel

2.5.1. Influence of Exposure Time

The adsorption experiments were performed using a bulk PFAS solution (at 100 pg/mL) in water (Optima^{TM} LC-MS grade). The concentration of 100 pg/mL was chosen based on values reported in the literature (concentrations ranging from µg/L to ng/L) for environmentally relevant scenarios, including contaminated surface waters. [14,25]. Our goal was to select a concentration that was as low as practically feasible, while remaining above the method LODs to ensure reliable quantification across all target compounds. This approach allowed us to simulate realistic environmental conditions without compromising analytical sensitivity. The beakers containing 37.3 g of quartz gravel (covering the bottom of the beaker) were then filled with 25 mL of the PFAS aqueous solution and stored at room temperature (20 °C) for 1, 3 and 7 days. Aliquots (200 µL) collected from each beaker before and after storing for 1, 3 and 7 days, were transferred (using a pipette) into 10 mL HS vials containing 1 mL of methanol to prevent potential PFAS losses onto the walls of the glass vials during the storage [59]. The solutions in the HS vials were capped and stored at 5 °C until analysis. On the day of analysis, all aqueous samples were spiked with ^{13}C PFAS IS to obtain a concentration 5 pg/mL, followed by addition of 3.8 mL of water to provide 80:20 water:methanol (%, *v*/*v*). The solution in vials was then homogenised by vortex mixing and analysed with the online SPE LC-MS. The experiments were performed in four replicates. The recovery of PFAS in solution after exposure was calculated by comparing the IS corrected chromatographic PFAS peak areas in aqueous solution after exposure (PA_1) with the *PFAS* peak in aqueous solution before exposure (PA_0):

$$PFAS\ Recovery_{exp} = (\frac{PA_1}{PA_0}) \times 100 \quad (1)$$

The percentage of *PFAS* adsorbed to gravel was calculated by comparing the mass of *PFAS* obtained from the surface of gravel after each day of exposure (M_{P1}) with the calculated mass of *PFAS* in the control solution before exposure 0 (M_{w0}):

$$\%\ PFAS\ adsorbed_{exp} = (\frac{Mp_1}{Mw_0}) \times 100 \quad (2)$$

2.5.2. The Influence of Gravel Disturbance on the PFAS Adsorption

A bulk PFAS solution (at 100 pg/mL) in 100% water (Optima^{TM} LC-MS grade) was used for all experiments. 25 mL of the bulk solution was transferred into 250 mL beakers containing quartz gravel and shaken at 125 rpm for 24 h at room temperature (20 °C). Aliquots (200 µL) collected from beakers before and after shaking for 24 h were transferred into a 10 mL HS glass vials. The solutions in the vials were topped up with 1mL methanol and 3.8 mL water and spiked with IS to make 5 pg/mL and analysed with online SPE LC-MS. The experiments were repeated four times. The recovery of *PFAS* in solution after shaking was calculated from the ratio of the IS corrected chromatographic PFAS peak areas after shaking for 24 h (Ps_1) and those before shaking (Ps_0):

$$PFAS\ Recovery_{shak} = (\frac{Ps_1}{PS_0}) \times 100 \quad (3)$$

The percentage of *PFAS* adsorbed to gravel was calculated by comparing the mass of *PFAS* obtained from the surface of gravel with/without shaking for 24 h (Mps_1) with the calculated mass of *PFAS* in the control solution before shaking for 24 h (Mws_0):

$$\%\ PFAS\ adsorbed_{shak} = (\frac{Mps_1}{Mws_0}) \times 100 \quad (4)$$

2.6. Analytical Method

Liquid Chromatography (LC) Q Exactive™ Focus Hybrid Quadrupole-Orbitrap™ MS (Thermo Fisher, Bremen, Germany) was used to analyse the samples. The PFAS analysis was conducted using the online Solid Phase Extraction (SPE) LCMS method adapted from Kourtchev et al. [17] and Folorunsho et al. [12]. The on-line solid phase extraction (SPE) procedure used in this study is described in detail in Kourtchev et al. [17]. In summary, samples were introduced via a 1 mL high-volume injection loop and directed onto a pre-concentration column by the loading pump (Thermo Scientific VF-P10-A), using 0.1% formic acid in water at a flow rate of 1 mL/min. Once the enrichment phase was complete, a 6-port autosampler valve was triggered to initiate the analytical sequence. The elution pump (Thermo Scientific VF-P20-A) then applied a gradient elution using two mobile phases: (A) 2 mM ammonium acetate in 10% methanol, and (B) pure methanol, delivered at a rate of 300 µL/min.

This gradient passed through both the pre-concentration and analytical columns as outlined by Kourtchev et al. [17]. The SPE and analytical columns used were Thermo Scientific™ Hypersil GOLD aQ (20 × 2.1 mm, 12 µm) and Waters® CORTECS C18 (90 Å, 100 × 2.1 mm, 2.7 µm), respectively. The analytical column was maintained at 35 °C throughout the 22-min run time.

2.7. Quality Assurance (QA) and Quality Control (QC)

Several steps were implemented to ensure the reliability and accuracy of the sample analysis. To prevent PFAS accumulation in the Orbitrap LC-MS, the system was continuously flushed overnight using mobile phases A: 2 mM ammonium acetate in water with 10% methanol, and B: 100% methanol at a flow rate of 0.3 mL/min [17] before each batch of analysis. Mass calibration of the Orbitrap MS was performed daily in the negative ionisation mode to ensure mass accuracy within an acceptance limit of ±1 ppm. Prior to analysis of each batch, five system ("zero volume") blanks and three 80:20 (*v*/*v*) water:methanol blanks were analysed to check for potential PFAS accumulation in the system. Additionally, "zero-volume" blanks were analysed between samples and at the end of the sequence to control a potential PFAS carryover. The "zero-volume" blanks and 80:20 water:methanol blanks gave <LOQ values for PFAS.

System suitability tests (SST) were conducted prior to each sample analysis batch to ensure an optimal system performance, by checking the following parameters, i.e., retention time, peak area and height, and chromatographic resolution. Specifically, water:methanol (80:20 *v*/*v*) solutions containing 25 PFAS and 16 [^{13}C] labelled PFAS were prepared (see Section 2.2 of main text for details of the PFAS mix used) on a day of analysis and analysed using an Orbitrap LC-MS. The concentrations of 25 PFAS were at 7.5 pg/mL.

2.8. Statistical Analysis

The data were analysed using one-way ANOVA in Excel (Version 2310) and IBM SPSS (Version 28.0), with results presented in Tables S4 and S5.

The dataset comprised four conditions with four replicates each (total n = 16 observations), meeting the minimal sample size recommended for one-way ANOVA (n > 15) [60]. However, since ANOVA assumes normally distributed residuals, a particularly important consideration with small sample sizes, non-parametric alternatives were also applied. Specifically, the Kruskal–Wallis test, followed by Dunn's post hoc test, was used to assess statistically significant differences ($p < 0.05$).

3. Results and Discussion

3.1. PFAS Adsorption onto Gravel Surfaces after Exposure to Contaminated Water

The percentage of PFAS adsorbed onto the surface of riverine quartz gravel from contaminated water after exposure for 1, 3 and 7 days are shown in Figure 1. Regardless of the PFAS functional group, the extent of adsorption onto quartz gravel showed a dependence on the compound's carbon chain length. For instance, among the target compounds, short-chain PFAS, i.e., PFPeA (2.6 ± 0.2%, after 1 day) and medium-chain PFAS, i.e., PFHxA (2.8 ± 0.3% and 1.9 ± 0.2%, after 3 and 7 days, respectively) showed the lowest adsorption onto gravel. Meanwhile, the long-chain PFAS such as PFOS, 9 Cl- PF3ONS, 8:2 FTS, PFDA, showed greater adsorption onto gravel. Several studies have reported an increase in the adsorption of PFAS onto solids with increasing carbon chain length [43,51]. For instance, Chen et al. [43] reported the higher adsorption of long-chain PFAS (PFDA, PFNA and PFOS) onto sediments of the urban reservoir compared to medium-chain PFAS (PFHxS and PFOA). Fabregat-Palau et al. [51] also reported increasing adsorption of PFAS (PFHxA, PFNA, PFOS, PFDoA, PFOA, PFBS, PFBA, and PFHxS) onto soils with increasing carbon chain length. Such observation was attributed to interactions between the hydrophobic moieties of long-chain PFAS and those of the studied solids (soils and sediments) [43,51].

Our results align with findings from other studies which reported that short-chain PFAS may slowly occupy active sites on the surface of adsorbents with large granules than long-chain PFAS [61–63]. Therefore, PFAS may potentially desorb (remobilise) from the surface of gravel into water with time. Additionally, the extent of adsorption to quartz gravel was affected by the PFAS functional group (Figure 1). Among the tested PFAS, PFCA showed the lowest adsorption onto gravel, compared to PFEA, PFSA and FTS homologue (C5–C8) (Table S3). For instance, despite having the same number of carbons, PFOA (C8) had a lower adsorption capacity compared to 9 Cl-PF3ONS (C8), PFOS (C8) and 6:2 FTS (C8). The influence of functional groups on the PFAS adsorption to sediments have been attributed to the smaller size of the carboxylic functional group compared to the sulfonate which results in less hydrophobicity of PFCAs compared to PFSA [35]. The one-way ANOVA results indicated significant difference ($p < 0.05$) between the fractions of PFAS adsorbed onto gravel after exposure for 1, 3 and 7 days except for PFOA, PFNA, PFOS and 9 Cl-PF3ONS (Tables S4 and S5).

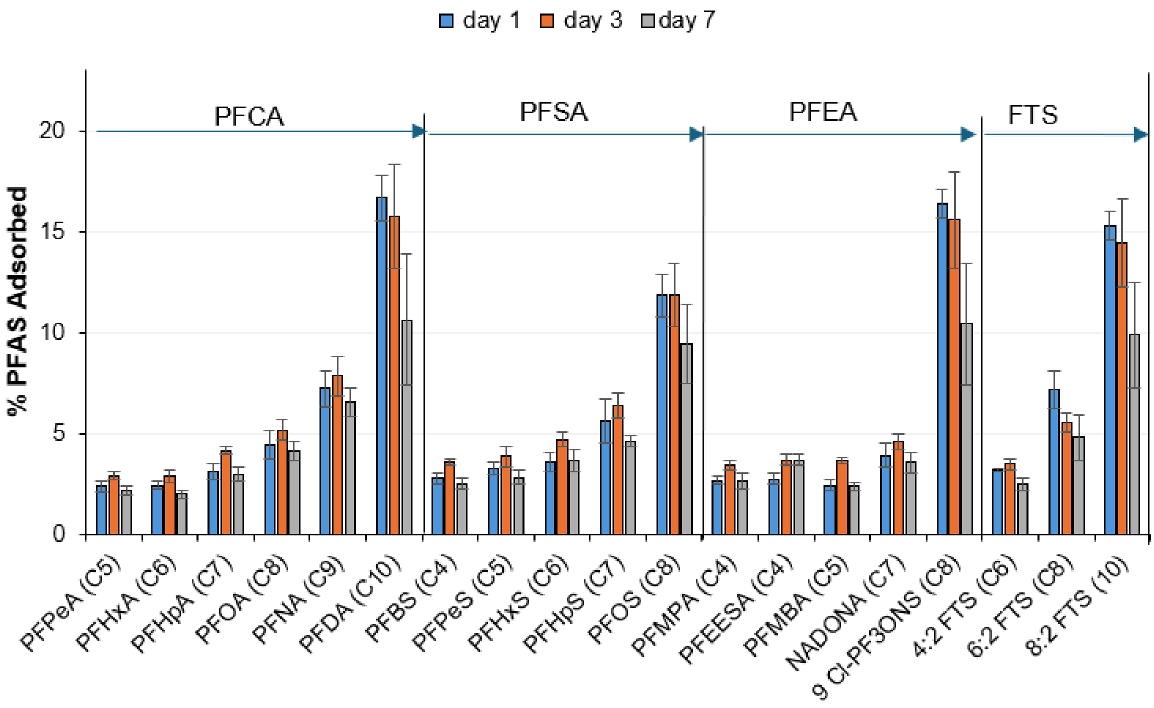

Figure 1. The fraction of PFAS adsorbed onto medium-sized gravel after exposure for 1 (blue bars), 3 (red bars) and 7 days (grey bars) in contaminated water. The error bars correspond to standard deviation values from four experimental replicates.

It should be noted that there was a decrease in the recovery of PFAS, especially long-chain ones, in contaminated water samples after 7-day exposure while those of the short-and medium-chain PFAS remained unchanged (Figure S2). The fraction of long-chain PFAS adsorbed onto the gravel was lower compared to the overall loss of analytes from the PFAS-enriched aqueous solution. This may be due to potential adsorptive competition between the gravel and the glass walls of the containers used to carry out experiments. Although the adsorptive losses of long-chain PFAS to glass have been reported to be lower than other commonly used laboratory materials e.g., polypropylene [57–59], the glass may still possess similar challenges for long-chain PFAS. Therefore, using these materials may not be appropriate for studying long-chain PFAS in highly aqueous solutions over an extended period.

The PFAS partition coefficient (Kd) obtained in our study (Table S6) are consistent with other studies reporting the adsorption of PFAS onto various soil particles of smaller sizes [41,51,64]. For instance, Fabregat-Palau et al. [51] reported Kd values ranging from 2.4 to 21 L/Kg, 2.6 to 38 L/Kg, 11 to 128 L/Kg and 32 to 295 L/Kg for the adsorption of PFHxS, PFOA PFNA and PFOS, respectively, onto soils (clay and silt) with particle sizes < 2 µm. Similarly, Li et al. [65] reported Kd ranges of 1.4–224 L/Kg, 0.1–85 L/Kg, 0.4–6.3 L/Kg for the adsorption of PFOS, PFOA and PFHxS, respectively onto soils. However, the Kd values from our study were 2.7, 13.7, 16.8, 25.0, 25.8, 52.9, 62.9 and 106.1 times greater for 6:2 FTS, PFOS, PFHxA, PFOA, PFHxS, PFBS, PFPeS and PFPeA, respectively, than those determined for AFFF-contaminated soils in the study by Hubert et al. [41], suggesting higher adsorption capacity of the medium quartz gravel used in our study. The lower Kd observed in the study by Hubert et al. [41] is likely due to the size and content of mineral present in the studied soils.

The extent of PFAS adsorption could also potentially be influenced by the mineral composition of the gravel. Solids containing alumina (Al_2O_3) and iron oxide (Fe_2O_3) have been reported to possess more active sites for adsorption than silica (SiO_2) [39,40]. Miao et al. [33] demonstrated that soils with higher content of alumina and iron oxide favoured the adsorption of PFOA compared to those with higher silica content. The quartz gravel used in our study contained a higher percentage of silica (97.5%) compared to alumina (1.3%) and iron oxide (0.2%) (Table S1). This could also potentially explain the difference between our results and those which reported higher adsorption of PFAS. The Kd values determined in our study (Table S6) are consistent with those reported by Zhao et al. [66] for the adsorption of PFBS (0.6 L/Kg), PFHpA (0.6 L/Kg), PFOA (3.4 L/Kg), PFHxS (3.7 L/Kg), PFNA (11.7 L/Kg) and PFOS (24.5 L/Kg) onto aquifer materials with high silica content (89.7%). It should be noted that the degree of PFAS adsorption onto riverine quartz gravel may be impacted by the range of environmental parameters such as water temperature, pH and salinity and PFAS concentrations [34,43], which are outside the scope of this study.

3.2. PFAS Sorption onto Gravel after Shaking for 24 h

The fraction of PFAS adsorbed onto medium-sized quartz from contaminated solution after and without shaking for 24 h are shown in Figure 2. The results show a trend of the adsorption of studied PFAS with increasing carbon-chain length, after shaking (up to 12.5 ± 1.7%) and without shaking (up to 16.7 ± 1.1%). Moreover, the extent of adsorption was found to be affected by the PFAS functional group. Among the tested PFAS, PFCA showed the lowest adsorption onto gravel, compared to PFEA, PFSA and FTS homologue (C5-C8) (Table S7). No statistical differences were observed between the fractions of PFAS adsorbed onto gravel after shaking and without shaking for 24 h ($p > 0.05$) except for 9 Cl-PF3OUdS, 8:2 FTS, PFDA ($p < 0.05$) (Table S8).

Lower adsorption losses of 9 Cl-PF3OUdS, 8:2 FTS and PFDA onto gravel was observed after shaking which can potentially be explained by agitation disrupting the adsorption equilibrium [67]. Shaking can lead to enhanced desorption of adsorbed molecules or prevent the effective attachment of adsorbates to the adsorbent by creating a more dynamic environment [68,69]. In our study, sample shaking may have hindered the formation of stable PFAS-gravel interactions, which are typically favoured under static conditions (without shaking), where molecules have more time to settle and interact with the surface of gravel.

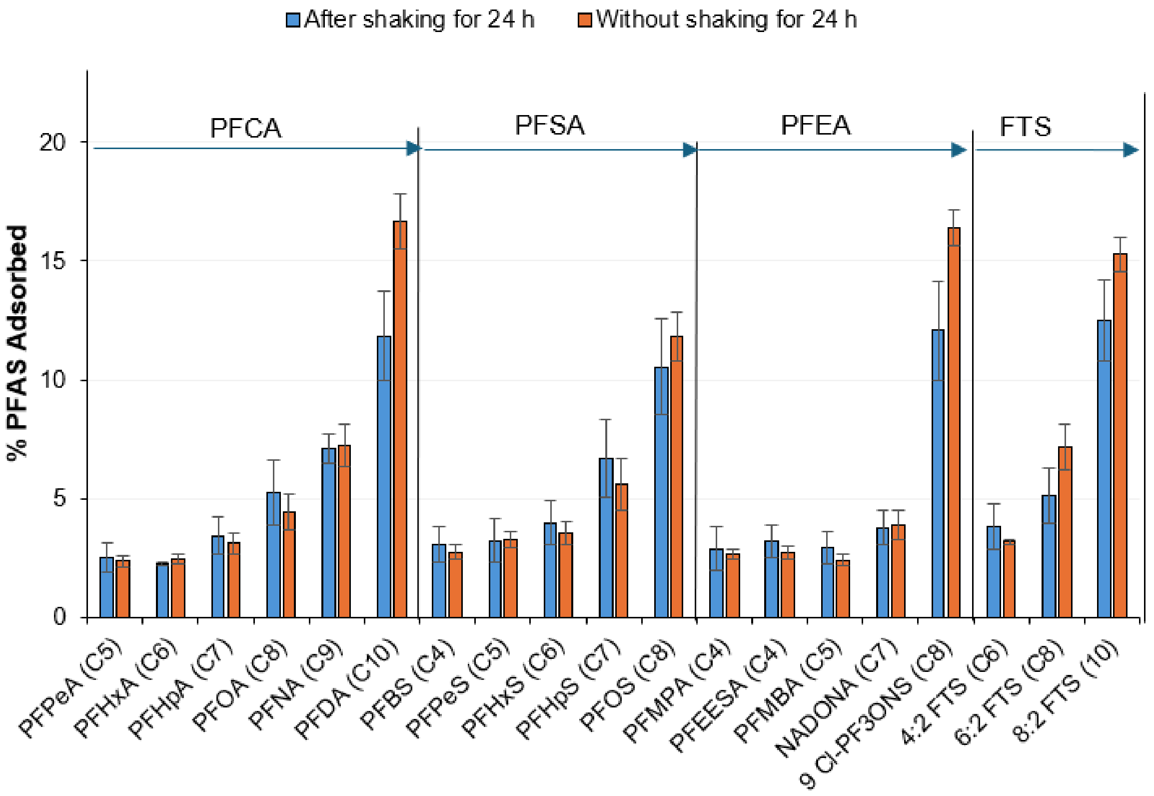

Figure 2. The fraction PFAS adsorbed (%) onto the surface of gravel after shaking (blue bars) and without shaking (red bars) for 24 h. The error bars correspond to standard deviation values from four experimental replicates.

4. Conclusions

The adsorption of 19 PFAS, including perfluoro-carboxylic acids (PFCA, C4–C10), perfluoro-sulfonic acids (PFSA, C4–C8), PFEA (C4–C8), and FTS (C6–C10), onto medium-sized quartz gravel was examined following exposure to a contaminated solution for 1, 3, and 7 days, with additional mechanical disturbance (i.e., shaking).Our results indicate that the level of PFAS adsorption to medium-sized gravel is dependent on the carbon chain length and functional group of the analyte. Long-chain PFAS, including new-generation 9 Cl-PF3ONS and 8:2 FTS, adsorbed to the greatest extent onto the gravel, while PFCAs showed the lowest adsorption capacity compared to other functional groups with corresponding carbon chain length. Our results suggest that PFAS may adsorb to medium-sized quartz gravel in contaminated water within 24 h. The disturbance (i.e., shaking) of gravel and contaminated water showed no statistically significant difference in the extent of adsorption for most PFAS onto gravel, except for a few long-chain PFAS namely 9 Cl-PF3OUdS, 8:2 FTS and PFDA. This potentially suggests that relevant processes in natural aquatic systems such as tidal flows or mechanical disturbances, may likely influence the adsorption of these long-chain PFAS onto the surface of medium-sized quartz gravel.

To the best of our knowledge, this is the first study that investigates the adsorption of new-generation PFAS onto riverine medium-sized quartz gravel. It provides relevant information for the early evaluation of short-, medium- and long-chain PFAS in contaminated water. These findings contribute to understanding PFAS mobility in aquatic environments, supporting efforts to monitor PFAS in surface waters and predict their short- and long-term environmental impacts.

Supplementary Materials

The additional data and information can be downloaded at: https://media.sciltp.com/articles/others/2508221400495125/ECCS-1324-supplementary_revised.pdf. Figure S1: PFAS recoveries after first, second and third filter extraction steps. Figure S2: Amount of PFAS (%) in solutions after exposure for 1, 3 and 7 days in contaminated water. Figure S3: Amount of PFAS (%) in the aqueous solutions after shaking, and without shaking for 24 h. Table S1: Chemical composition of quartz pebbles used in our study. Table S2: PFAS analytes and corresponding isotopically labelled standards. Table S3: Non-parametric statistical comparison between adsorption of different PFAS functional groups onto gravels after exposure (up to 7 days). Table S4: Statistical comparison of the amount of PFAS (%) adsorbed to pebbles after exposure for 1, 3 and 7 days. Table S5: Nonparametric statistical comparison of amount of PFAS (%) adsorbed to pebbles after exposure for 1, 3 and 7 days. Table S6: Partition Coefficient for PFAS adsorption to quartz aggregates after exposure for 1, 3 and 7 days. Table S7: Non-parametric statistical comparison for PFAS adsorption onto aggregates after shaking and without shaking for 24 h. Table S8: Statistical comparison of the amount of PFAS (%) adsorbed to pebbles after exposure with shaking and without shaking for 24 h.

Author Contributions

O.F.: conceptualisation, methodology, investigation, resources, data curation, writing—review & editing, visualisation. A.B.: co-conceptualisation, resources, review & editing, co-supervision. I.K.: conceptualisation, methodology, resources, writing—review & editing, supervision, project administration. All authors have read and agreed to the published version of the manuscript.

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Data Availability and Statistical Reporting

Data will be available upon request. The statistical analysis results are provided in the SI.

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Conflict of Interest Disclosure

The authors declare 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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