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Unveiling the truth of interactions between microplastics and per- and polyfluoroalkyl substances (PFASs) in wastewater treatment plants: Microplastics as a carrier of PFASs and beyond

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Abstract

Microplastics (MPs) and per- and polyfluoroalkyl substances (PFASs) are ubiquitous contaminants in environments, yet their co-occurrence and interactions remain insufficiently understood. This study aimed to investigate the simultaneous presence and contributions of MPs and PFASs in a wastewater treatment plant (WWTP), shedding light on their correlations across different matrices. Through comprehensive sampling and analysis, we confirmed the concurrent presence of MPs and PFASs and their distinct distribution patterns. Significant correlations ($p < 0.05$) were observed between specific types of MPs and PFASs, suggesting shared sources. Moreover, MPs were identified as carriers of PFASs, with PFASs concentration ranging between 122 and 166 ng/g, predominantly consisting of long-chain perfluorooctanoic acid (PFOA) and short-chain perfluorobutanoic acid (PFBA). Laboratory verification experiment revealed that PFASs could be leached from MPs in aqueous environments, in which commercial MPs exhibited higher leaching potential, with the highest combined concentration of perfluorooctane sulfonate (PFOS), PFOA, and PFBA reaching 10.4 ng/mL. PFOS demonstrated a desorption efficiency exceeding 120% in sorption/desorption experiments, confirming its release from the MPs themselves. These results highlighted the dual roles of MPs as both carriers and sources of PFASs. The identified correlations and contaminant profiles offer a basis for further research into their impacts on ecological health and human exposure pathways. Addressing these concerns requires proactive measures to regulate the production, usage, and disposal of PFAS-containing products and MPs to mitigate environmental contamination effectively.

Keywords: Co-occurrence, Microplastics, PFASs, Recipient, Source, Vector

Synopsis

This study reported the dynamic interactions between MPs and PFASs and verified that MPs can not only serve as carriers of PFASs, but also sources of PFASs.

1. Introduction

Microplastics (MPs), defined as plastic particles ≤5 mm in size, have emerged as a pressing environmental and public health concern due to their widespread detection in various environments, including marine, freshwater and soil ecosystems,[1-3] where they are ingested by various organisms, subsequently infiltrating the food web.[4] Their pervasive presence raises concerns about human exposure and potential health risks,[5] hence, MPs were listed as a category of emerging contaminants.[6] In addition to MPs, per- and polyfluoroalkyl substances (PFASs), a group of organic compounds consisting of at least one fully fluorinated methyl or methylene carbon atom, were also listed as emerging contaminants, due to their widespread use, stability, and environmental persistence, bioaccumulation and toxicity of human and ecosystems.[7] The global production of fluoropolymers exceeds 230,000 tons annually[8] and their release during manufacturing and use poses significant environmental challenges.

MPs and PFASs share several characteristics, such as widespread use, stability, bioaccumulation, and environmental persistence.[9,10] Previous studies have delved into the sorption and adherence mechanisms of PFASs onto MPs, uncovering the vector role of MPs for PFASs.[11,12] The adherence of PFASs to the surfaces of MPs may lead to more severe toxic effects due to their combined exposure,[13,14] and the interaction between them affects the migration and transport of these emerging pollutants in the environment.[15] In addition, due to their exceptional water-oil repellency and robust chemical stability, PFASs are extensively employed as plastic additives, enhancing the performance of plastic products. They are commonly used in the production of raincoat, carpets, food packaging, and non-stick cookware.[8,16,17] Their extensive use and improper disposal lead to their frequent detections in the environment. However, the release of PFASs from environmental MPs remains unclear.

Despite laboratory studies on the sorption mechanisms of PFASs on MPs, real-world data on their co-occurrence and interactions in natural environments remain limited. Although the concurrent presence the two pollutants in stormwater was initially discussed individually,[18] complementary research combined MPs and PFASs is necessary for a comprehensive understanding of their combined impacts and management strategies. Wastewater treatment plants (WWTPs) are significant recipients for domestic and industrial wastewater, making them critical points of study for these pollutants. However, detailed reports on the co-occurrence of MPs and PFASs in WWTPs are scarce. Further to this, understanding the interactions between MPs and PFASs is crucial to comprehending their combined environmental impact and toxicity.[9,10]

Specifically, the study hypothesizes that there is a significant interaction between MPs and PFASs within WWTPs. MPs are known to act as carriers for various contaminants due to their adsorptive properties, and this research aims to demonstrate that MPs can similarly adsorb PFASs as a carrier, facilitating their co-persistence in the treatment process. Further to this, it is hypothesized that MPs can act as a potential source of PFASs leading to secondary pollution. The aim of this research is to investigate the co-occurrence and carrier effect of MPs and PFASs in WWTPs. This study seeks to elucidate the mechanisms of their co-presence and interactions, thereby enhancing the understanding of their environmental behaviors and potential risks.

2. Materials and methods

2.1 Chemicals and reagents

Seventeen PFASs standards and nine mass-labeled internal standards with purities > 98% were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada) (see details in Table S1). The 17 PFASs consist of perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS), and 6:2 chlorinated polyfluorinated ether sulfonic acid (F-53B). Further to this, Methanol (HPLC-grade) was purchased from Merck (Germany). Ammonium acetate (~98%), ammonia solution (NH_4OH, 25%), zinc chloride ($ZnCl_2$) and hydrogen peroxide solution (H_2O_2, 30%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Milli-Q water prepared with a Milli-Q Advantage A10 system (Millipore, Bedford, MA, USA) was used throughout the study. Oasis WAX (6 cc, 150 mg, 30 μm) cartridges were purchased from Waters Co. (Milford, USA). Supelclean ENVI-Carb (250 mg, 100~400 mesh, 3 mL) cartridges were purchased from Supelco Co. (Merck KGaA, Damstadt, Germany). The high-purity nitrogen (99.99%) was purchased from Chuangda Specialty Gas Co., Ltd (Nanjing, China). Finally, the MPs suppliers used in the laboratory verification experiments were provided in the Supporting Information (Table S2).

2.2 WWTP introduction and sample collection

Wastewater samples were obtained from a major WWTP servicing a population equivalent of 0.3 million in Changchun City, a dense population center with significant industrial and commercial activities as a pivotal industrial hub in Northeast China and the capital of Jilin Province. The WWTP processes wastewater from residents through primary, secondary aeration, and tertiary treatment stages. It employs integrated fixed film activated sludge (IFAS) technology with a capacity of 20,000 m^3/day.

Sampling locations included primary treatment, activated sludge biological treatment, secondary sedimentation, and final effluent treatment (Fig. 1). At each sampling point, 1 L volume of samples were collected according to the method mentioned in previous study after appropriate modification,[19] which were collected in a glass bottle for detecting MPs. While 1 L of wastewater and 10 L of activated sludge were collected in polypropylene (PP) bottles for PFASs analysis using stainless-steel containers. Approximately 1 kg of dewatered sludge sample was stored in a stainless-steel container. Sampling day was deliberately selected on a sunny day to ensure a precipitation free period in the preceding week. To prevent cross-contamination, the sampling equipment was rinsed three times with deionized water or methanol between sampling events. All samples were transported to the laboratory and stored at 4°C until analysis.

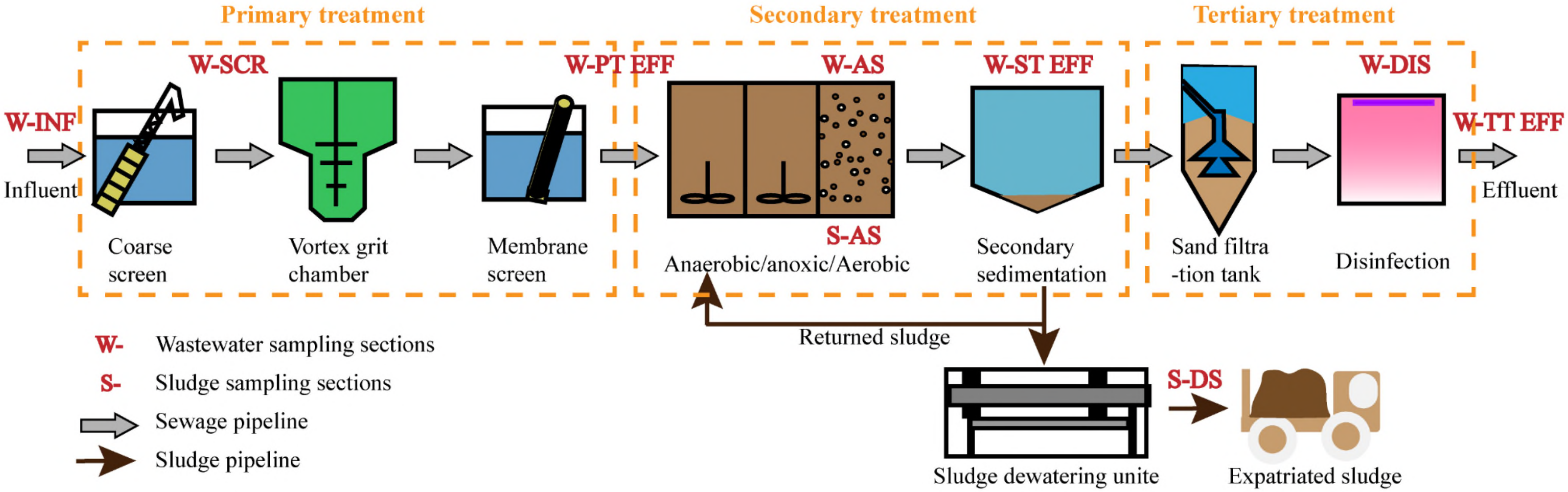

Fig. 1. Schematic diagram of the wastewater treatment processes and the sampling sections of MPs at the WWTP. W-INF: wastewater influent, W-SCR: wastewater effluent after the coarse screen, W-PT EFF: wastewater effluent post primary treatment, W-AS: wastewater in activated sludge, W-ST EFF: wastewater effluent post secondary treatment, W-DIS: wastewater in the disinfection tank, W-TT EFF: wastewater effluent post tertiary treatment, S-AS: activated sludge, and S-DS: dewatered sludge.

2.3 MPs isolations

2.3.1 Isolation of MPs from wastewater samples

The MPs were isolated in accordance with the methodology outlined in the previous study after appropriate modification.[20] Wastewater samples were filtered through a 47 mm diameter stainless steel membrane with 10 μm pores using a vacuum system. The filter containing the captured materials was immersed in 30% H_2O_2, and the materials were transferred to H_2O_2 via ultrasonic treatment (40 kHz), repeated three times to bring the H_2O_2 volume to 200 mL. The digestion step was then conducted for at least 2 h at 75°C, followed by soaking in a 45°C-water bath for at least 96 h until the mixture clarified. The mixture was then filtered through a 10 μm pore sized stainless steel membrane and transferred to a separatory funnel containing 11 M $ZnCl_2$ solution (density ≈ 1.7 g/cm^3). The funnel was sealed, shaken, and left overnight for density-based separation. The supernatant containing any floating particles was filtered again and rinsed with deionized water three times. The obtained membrane was immersed in absolute ethanol for ultrasonic treatment (40 KHz) for at least 30 min. Then, the filtered membrane was removed and rinsed with absolute ethanol for several times, and then the absolute ethanol was concentrated to 200 μL under a gentle stream of high-purity nitrogen.

2.3.2 Isolation of MPs from sludge samples

Dry sludge samples (1 g) were mixed with 100 mL DI water in a glass beaker and stirred for 15 min to ensure even saturation of the sludge. Subsequently, 200 mL of 30% H_2O_2 was slowly added to initiate the digestion reaction. The mixture was heated for a minimum of 6 h at 75°C and then soaked in a 45°C-water bath for 96 h until the solution clarified. All subsequent steps were conducted as per the wastewater samples.

2.4 PFASs Extractions

2.4.1 Extraction of PFASs from wastewater samples

The target PFASs in the wastewater samples were extracted according to our previous study[21] with minor modifications. Wastewater samples were initially filtered using a 0.45 μm glass fiber membrane to remove large particles and biota. Subsequently, 200 mL filtrate was transferred into PP beakers and mass-labeled internal standards were added to ensure a concentration of 5 ng/mL in the final detection sample. Solid phase extraction (SPE) was performed using Oasis weak anion exchange (WAX, 6 cc, 150 mg, 30 μm) SPE cartridges (Waters Corp., Milford, USA). The cartridge was preconditioned sequentially with 5 mL of 0.1% NH_4OH in methanol, 5 mL methanol and 5 mL Milli-Q water at a rate of 1 drop/s. Then, 200 mL of the water samples were loaded into the activated cartridges at the same rate. After concentration, the cartridges were washed with 5 mL of 25 mM ammonium acetate (pH 4), and air-dried until completely dry. The target PFASs retained in the dried cartridges were eluted sequentially with 5 mL methanol and 5 mL 0.1% NH_4OH in methanol. The eluents were collected and concentrated to 1 mL under a gentle stream of high-purity nitrogen, then filtered through a 0.22 μm PP syringe filter (13 mm, Ronghua Scientific, China) into a 1.5 mL vial for subsequent quantification.

2.4.2 Extraction of PFASs from sludge samples

PFAS extraction from sludge samples followed a modified method based on our previous study.[22] Dried activated and dewatered sludge samples (2 g) were placed in 50 mL PP centrifuge tubes and spiked with 5 ng of mass-labelled internal standards. Each sample was digested overnight at 4°C with 2 mL of 100 mM NaOH in acetonitrile (ACN). Prior to extraction, the sludge was sonicated for 30 minutes, then shaken with 20 mL of ACN at 250 rpm for 30 minutes. A mixture of 0.1 mL of 2 M hydrochloric acid (HCl) was added, followed by centrifugation at 1210 g for 15 minutes using a high-speed centrifuge (3H16RI, Herexi, China). The supernatant was transferred to a new 50 mL centrifuge tube.

The extraction process was repeated twice with 10 mL of ACN each time. All supernatants were reduced to 5 mL using a gentle nitrogen gas stream, which were then purified using Supelco ENVI-Carb cartridges (250 mg, 3 mL, Sigma-Aldrich, St. Louis, USA). The cartridges were preconditioned with 3 mL of methanol. The extract concentrates were loaded into the cartridges at a rate of 1 drop/s. The tubes and cartridges were washed with three aliquots of 1 mL methanol three times. All eluates were reduced to 4 mL using a gentle nitrogen gas, and then diluted to 200 mL with Milli-Q water. The diluted elution was then subjected to OASIS WAX-SPE cleanup following the same procedure for wastewater samples. All subsequent steps were conducted as those for wastewater samples.

2.4.3 Extraction of PFASs leaching from L-MPs

To investigate the leaching behaviors of PFASs from MPs, leaching samples (L-MPs, ≥ 1 mm) were collected and characterized. Details of the sampling process and characterization methods were described in Supporting Information (Text S1). After weighing on an analytical balance, MPs were transferred into vials and mass-labeled internal standards were added to ensure a concentration of 5 ng/mL in the final detection sample. The target PFASs were extracted as follows: 15 mL of 0.4% NH_4OH in methanol was added to the vials. The vials were then subjected to 30 min sonication at 60°C to ensure thorough mixing and extraction. Following sonication, the vials were shaken at 250 rpm for an additional 30 minutes to further facilitate the extraction process. After shaking, the contents of each vial were centrifuged at 1210 g for 10 minutes. This step separated the supernatant, which contained the extracted PFASs, from the solid residues. The supernatant was carefully decanted into new tubes to avoid any contamination from the residue. The extraction process was repeated twice to ensure comprehensive extraction of the PFASs from the samples.

The combined supernatants were concentrated to 1 mL using a gentle stream of high-purity nitrogen. This concentration step aimed to increase the detection sensitivity of the subsequent analysis. To purify the concentrated extracts, 40 mg of ENVI-Carb powder (SupelcleanTM, Sigma-Aldrich Co., USA) was used. Finally, the purified extracts were filtered through a 0.22 μm PP syringe filter (13 mm, Ronghua Scientific, China) into 1.5 mL vials. These filtered samples were then ready for detailed analysis using advanced instrumentation to identify and quantify the targeted PFAS compounds.

2.5 Laboratory verification experiment of MPs as a carrier of PFASs

To verify whether MPs can serve as a carrier for PFASs, sorption and desorption experiments were performed using different types of MPs (see details in Table S2).

Specifically, 0.2 g of MPs were added to 10 mL PFASs stock solution consisting of PFBA, PFOA, PFBS, PFOS, F-53B at 100 μg/L in concentration each. The mixture was mechanically agitated at 250 rpm using a thermostatic oscillator (MQL-621R, Minquan Instrument, China) incubated at constant temperature of 25°C for 48 h. Following the completion of the sorption experiment, the supernatant samples were collected and underwent drying. Subsequently, ultra-pure water was introduced into the tubes for the desorption experiment. The bottles were mechanically agitated at 250 rpm at constant temperature of 25°C for 48 h. All aqueous samples were then collected and filtered through 0.22 μm PP filters and stored at 4°C until analysis.

In addition, an aqueous leaching experiment was conducted using standard and commercial MPs (see details in Table S2). MPs samples were accurately weighed and added to 20 mL quartz tube tubes, followed by the addition of 10 mL of ultra-pure water to each tube, ensuring that the samples were completely submerged. Previous studies have reported the chemical changes of MPs under UV aging, including carbonyl stretch vibration, which could promote the release of organic matter.[23] Hence, samples were aged via UV condition for 7 days. The aqueous solution was filtered through a 0.22 μm PP filter and stored at 4°C until analysis.

2.6 Analytical Methods

2.6.1 Detection of MPs using laser infrared imaging system

The laser infrared imaging system (8700 LDIR, Chemical Imaging System, Agilent, USA) and optical microscope (OLYMPUS BX51, Japan) were used to identify the MPs.

The 8700 LDIR was operated in attenuated total reflection (ATR) mode, scanning the selected area with a fixed wave number of 1800 cm^{-1} to precisely locate particles. The Agilent Clarity software automatically selected a blank area without particles as the background. Mid-infrared spectra of all particles were obtained within the wave range from 1800 to 975 cm^{-1}. The limit of detection was set as 10 μm. The information on the amount, type and size of the MPs was obtained by automatically comparing the spectra of sample particles to the standard spectra via the Agilent Clarity. MPs were identified based on results with a matching degree exceeding 65% according to previous study.[19]

2.6.2 PFASs analysis

PFASs analysis was conducted using a triple quadrupole high-performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) system (AB SCIEX 5500, USA) operating in negative electrospray ionization (ESI) mode. The UPLC was equipped with an Acquity UPLC C18 column (100 mm × 3.0 mm, 1.7 μm, Waters, USA). The mobile phases consisted of 2 mM ammonium acetate (A) and acetonitrile (B), and a flow rate of 0.3 mL/min, 5 μL of the sample was injected, starting with 80% A and 20% B. The initial conditions were maintained before transitioning to 10% A at 12 min, holding until 15 min, reverting to the initial condition at 16 min, and maintaining equilibrium until 20 min. The column oven was maintained at a constant temperature of 40°C. The following instrument parameters were used: curtain gas (35 psi), collision gas (9 psi), ion spray voltage (-4500 V), temperature (500°C), ion source gas 1 (50 psi), ion source gas 2 (50 psi). PFAS identification and quantification, optimized MS/MS parameters, quantification methods, limits of quantification (LOQ), and limits of detection (LOD) are all detailed in Table S3. The quality assurance and quality control for MPs and PFASs were detailed in Text S2 and the laboratory control spike recovery was shown in Table S4.

2.7 Data analysis

Statistical analysis was performed using the PASW statistics 18 software to examine the normality of the data. And normal P-P plot and Q-Q plot were performed to verify the results, confirming the non-normal distribution. The Spearman rank test was employed to evaluate the relationships between the concentrations of MPs and PFASs, given that the data exhibits non-parametric, ordinal, and monotonic characteristics rather than linear relationships. $p < 0.05$ was recognized as statistically significant. All the data were visualized utilizing Origin 2024 software.

3. Results discussion

3.1 Co-occurrence and correlation of MPs and PFASs in the WWTP

3.1.1 Abundance and compositions of MPs

LDIR was able to efficiently identify a wider range of MPs polymers types (> 10 μm in size) due to the high-resolution imaging and fully automated scanning capability (Fig. 2). The incomplete detection of MPs with sizes of 10-20 μm may lead to underestimation of MP abundance when the size range is large. A total of 21 types of MPs were identified across all samples, with only 4 types, including polyethylene (PE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polyurethane (PU) co-occurring in every sample. PE, PET, and PVC emerged as the predominant polymer types. The total abundance of MPs in W-INF, W-PT EFF, W-ST EFF and W-TT EFF were 2858, 895, 390 and 245 particles/L, respectively (Fig. 2). In contrast, the total abundance of MPs in S-AS and S-DS were 1476 and 3665 particles/g, respectively. The variation in MP accumulation during wastewater treatment processes is potentially influenced by the different retention times associated with these polymer types.

PE, PET, and PVC are the main ingredients of household plastic necessities, such as packaging, toys, home textiles, clothing. For example, PE film serves as a prevalent choice for food packaging materials due to its versatility, cost-effectiveness, and protective properties. And the release of PET fiber from clothes through washing was regarded as an important source of MPs in WWTPs.[19] In addition, polymers contained F, such as polytetrafluoroethylene (PTFE), were identified in this study. It is noted that PTFE has a dual identity, recognized as both a plastic polymer and a perfluorinated compound. Due to its exceptional non-stick characteristics and high-temperature resistance, PTFE is ubiquitously utilized on non-stick pans in daily life. The wide use and diverse characteristics of plastic products may contribute to the distinct distribution profiles of MPs in WWTPs.

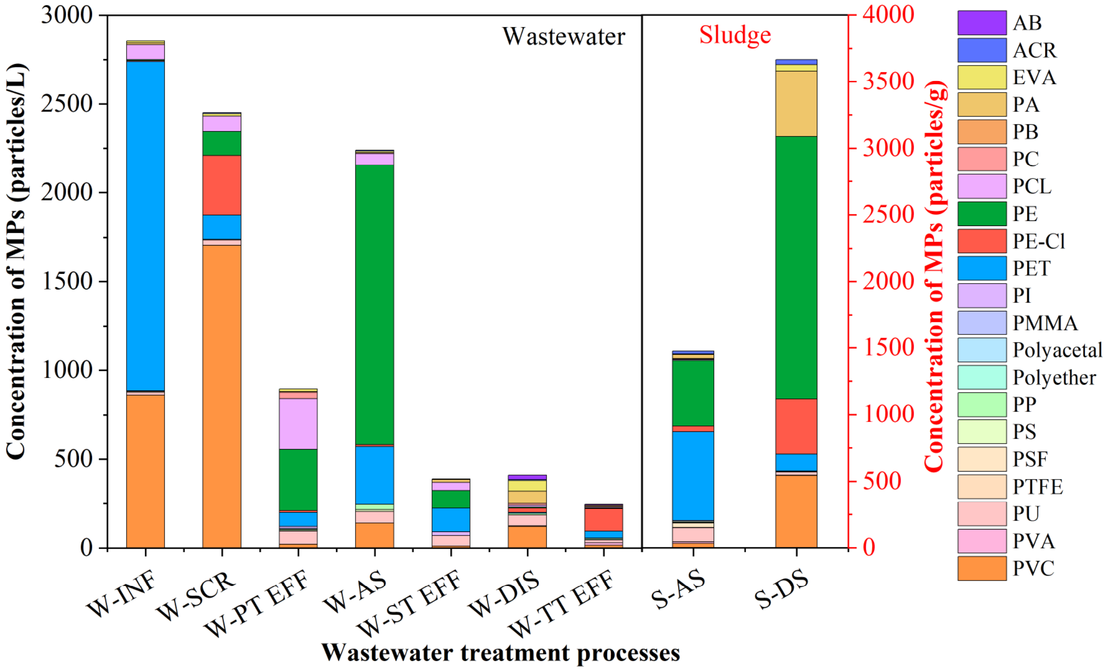

Fig. 2. Abundance of MPs and the accumulated abundance of each type of polymer in wastewater samples and sludge samples in the target WWTP. The designation can be found in the title of Fig. 1. The abbreviation is shown in the Supporting Information (Table S5).

3.1.2 Concentrations and compositions of PFASs

PFASs were detected in all units of the WWTP (Fig. 3). The concentrations of PFASs were 225 ng/L and 68.6 ng/L in the influent and final effluent, respectively, indicating a reduction of 70% in concentration during the wastewater treatment process. There are studies which reported similar trend of PFASs in wastewater treatment with concentrations in influents higher than those in effluents,[24,25] whereas other studies reported observations that PFASs concentrations in influents were lower than those in the effluents.[26,27] In the current study, a significant decrease in PFASs concentration was observed after the physical pretreatment, consistent with the reduction of MPs. We have reported in our previous study that physical processes such as screening during primary treatment, are effective in eliminating MPs.[28] We speculated that the observed reduction in PFASs during primary treatment was probably attributed to their sorption onto suspended particles (e.g., MPs), implying the role of MPs as the carrier of PFASs. In addition, an increasing trend in PFASs concentration was observed during the secondary treatment process and a much higher PFASs concentration was detected in the tank of activated sludge, which was primarily due to the contributions of PFASs precursors microbial transformation[29,30] and the sorption/adhesion behavior of the microbial biofilms in activated sludge.[31] Following the AS treatment, a decreasing trend was observed in the secondary and tertiary treatment processes, different from the previous conclusions that in reduction of PFASs due to the ineffective treatment processes including UV, chlorine disinfection, ozonation and sand filtration.[27,32]

Among the 12 PFASs detected in the WWTP, PFOS was the dominant compound, followed by PFBS, PFOA and PFBA. In the current study, the concentrations of PFSAs were much higher than those of PFCAs, which is different than those conclusions observed in different environmental media. For examples, previous studies reported that the PFCAs were dominant and exhibited much higher concentrations than PFSAs in surface water,[33] and groundwater.[34] Despite PFOS/PFOA and their precursors being listed in Annex B of the Stockholm Convention, there exists a list of specified exemptions that permits their large-scale production and almost all historical applications, encompassing their use in carpets, leather, textiles, furniture upholstery, paper and packaging, coatings, and paint additives.[35,36] Consequently, these substances are continuously released into domestic WWTPs. While long-chain PFASs production has significantly reduced over the past two decades due to voluntary industry initiatives (e.g., phased out by 3M in 2000 for PFOA and PFOS) and international regulations (e.g., inclusion in the Stockholm Convention in 2009), the proportional distribution of PFASs detected in this study highlights the prevalence of PFOA and PFOS. The occurrence of short-chain alternatives (e.g., PFBS and PFBA) in different environmental media have been reported extensively in previous studies,[37] and sometimes their usage exceeded the legacy PFOS and PFOA.[38] Recent literature suggests that short-chain PFASs exhibit similar bioaccumulation and persistence characteristics as their long-chain counterparts and pose comparable hazards, as observed in animal studies.[39,40] Interestingly, significant amounts of F-53B, an alternative of PFOS, were detected in the influent and primary treatment effluent, which has been detected in Chinese WWTPs and the environment for mist suppression in metal electroplating applications used in China.[41,42]

PFASs were also detected in activated sludge from the biochemical treatment's aeration tank and in the final dewatered sludge. The concentration of ∑PFASs in activated sludge and dewatered sludge were 76.1 ng/g dry weight (dw) and 61.8 ng/g dw, respectively, and shared a similar multitude. A total of 12 PFASs were detected in sludge samples, among which PFOS and PFOA were the dominant. PFOS was also a major component in the wastewater samples, accounting between17-60% of ∑PFASs. In contrast, PFOA accounted for 25% in the activated sludge, and between 6%-24% in the water samples, indicating higher affinity of PFOA for the solids of the sludge. The long-chain PFOS and PFOA were the dominating compounds in the solid phase, indicating their higher intendency to be sorbed on the solid sludge. Similarly, previous research underscores activated sludge's potential role as a primary repository for PFASs.[31,43] The reuse of biosolids in agricultural lands contributes to the infiltration of PFASs into the environment, emerging as a significant source of PFASs release,[44] thereby emphasizing the criticality of proper sludge disposal in WWTPs. It is noteworthy that partitioning of PFASs to solids increased with the length of alkyl chain, which is consistent with previous studies.[45,46] This is due to the high hydrophobicity of longer C-F chains with hydrophobicity decreasing as the chain length decreases. Given that hydrophobic compounds tend to partition into the activated sludge, hydrophobic partitioning can be considered to be a crucial mechanism affecting sorption and desorption processes of PFASs in sludge and wastewater.

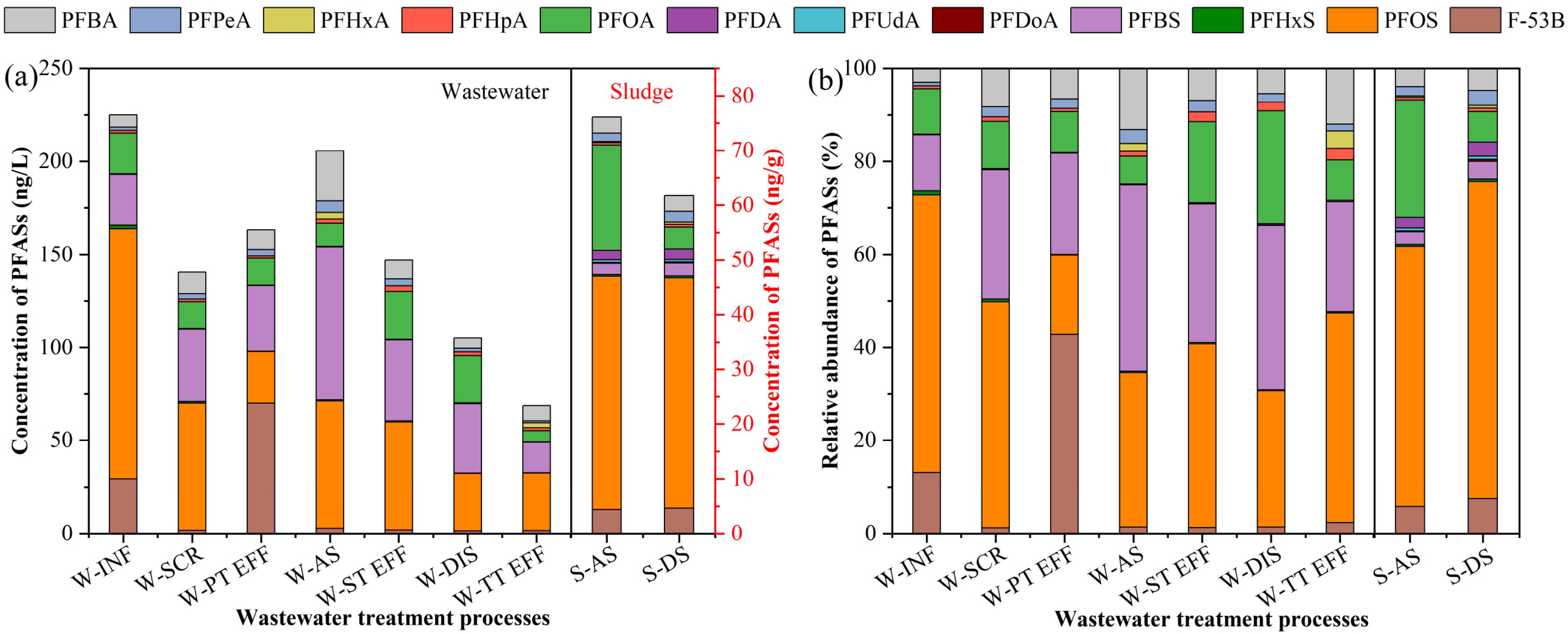

Fig. 3. Concentration (a) and relative abundance (b) of PFASs in different wastewater treatment units. The designation can be found in the title of Fig. 1.

3.1.3 Correlation analysis of PFASs with MPs

A significant positive correlation was found between acrylates (ACR) and PFDA ($p < 0.001$, $r = 0.94$), PET and PFOS ($p < 0.01$, $r = 0.85$), polyamide (PA) and PFDoA ($p < 0.01$, $r = 0.83$), polysulfone (PSF) and PFUdA ($p < 0.01$, $r = 0.82$), and a significant negative correlation was found between PA and PFBA ($p < 0.001$, $r = 0.92$) (Fig. 4). The results of the correlation analysis showed that, for example, as the concentration of PA increased, the concentration of PFDoA also tended to increase, while the concentration of PFBA decreased. The correlation between other substances can also been found in Fig. 4.

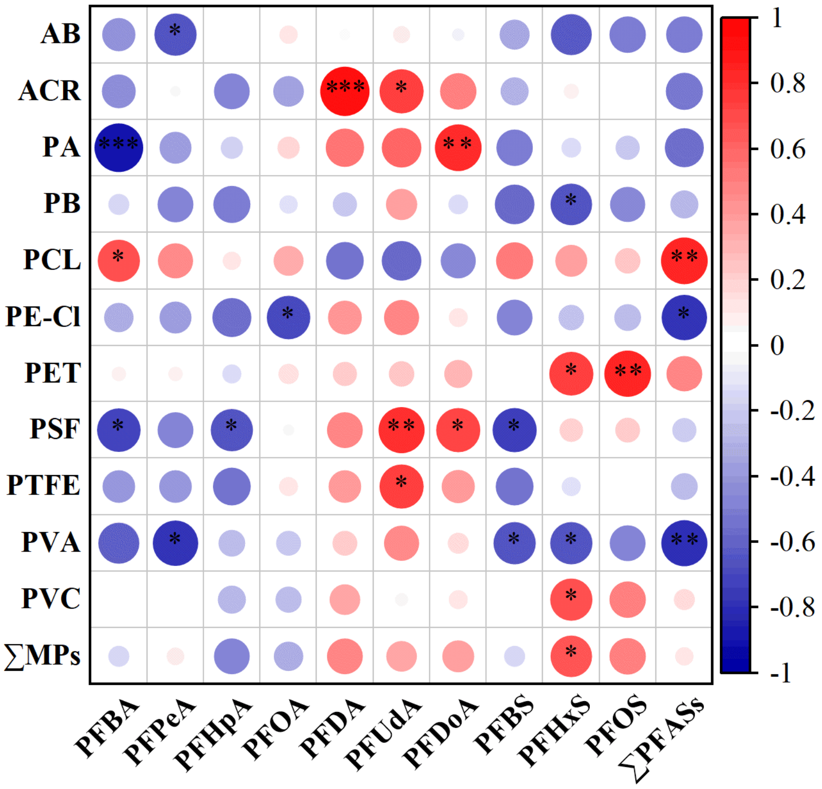

Fig. 4. Spearman rank correlation matrix of PFASs and MPs in WWTP. *** $p \leq 0.001$; ** $0.001 < p \leq 0.01$; * $0.01 < p \leq 0.05$.

As shown in Fig. 5, ACR, PA, PSF, and PTFE exhibit a higher proportion in sludge compared to wastewater, and similarly, PFDA, PFDoA, and PFUdA are found in a greater proportion in sludge, indicating that they are more likely to accumulate in sludge and be removed through sludge discharge (Fig. 5). Conversely, PFBA and PFHpA are found in higher proportions in wastewater than in sludge, showing a negative correlation with PA and PSF. Our previous study has shown that the sludge acts as a sink for MPs with removal mechanisms being primarily physical sorption or encasement.[28] Similarly, the main removal mechanism of PFASs in WWTPs is physical process, as the degradation of PFASs is challenging[24,47]. Activated sludge is considered a crucial component in trapping and removing these pollutants due to its physical and chemical properties. Overall, these results of this study suggest that the concentrations of MPs and PFASs can be reduced synergistically in WWTPs.

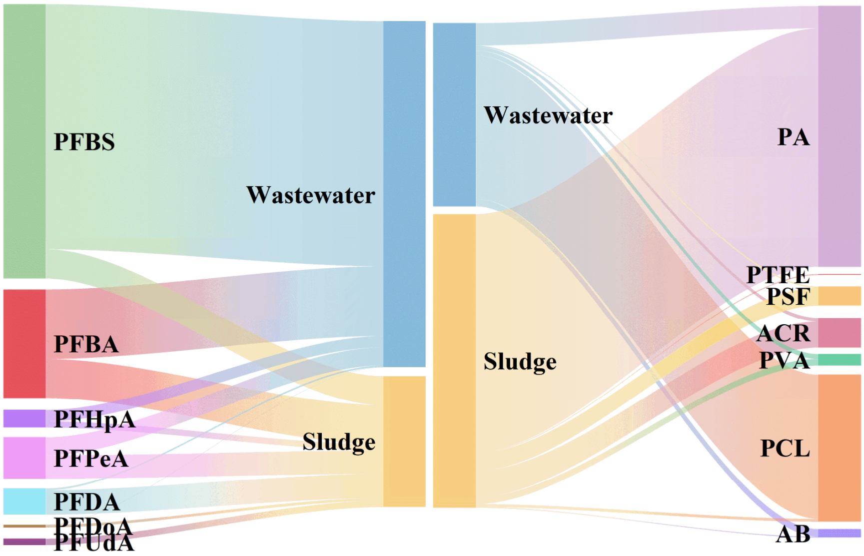

Fig. 5. The relative abundance partitioning in wastewater and sludge of the representative PFASs and MPs.

The observed correlation and co-recognition between MPs and PFASs in environmental samples have sparked speculations about a possible shared fate for these two emerging contaminants. This linkage indicated a complex interaction between MPs and PFASs, as well as the co-existence and translocation in specific ecosystems, known for their similar persistence, bioaccumulation, and potential adverse health effects. The suggestion of a shared fate underscores the need for further research to unravel the mechanisms behind this association. The carrier effect of MPs for PFASs also underscore the importance of considering the multifaceted challenges posed by the two emerging pollutants, emphasizing the urgent need for stringent controls on products containing both PFASs and MPs.

3.2 Validation of contributions of MPs to PFASs in wastewater

Eleven PFASs were detected and quantified in the extract from MPs, which were used to calculate the PFASs mass in MPs, resulting in the PFASs concentration in MPs ranging from 122 to 166 ng/g (Fig. 6). Notably, PFOA, PFBA, PFOS, PFBS, and F-53B were dominant across multiple environmental matrices (wastewater and sludge), as well as onto MPs. The concentrations and compositions of PFASs associated with MPs were generally mirrored those in wastewater and sludge, suggesting a correlation between the presence of PFASs and MPs. Previous studies have shown that consumer plastic products often contain high levels of PFOA. For example, Gremmel et al.[48] found that hat PFOA was the most prevalent among 23 PFASs extracted from outdoor jackets and similar results were observed in clothing by Lang et al.[49] High levels of PFOA were also detected in food packaging materials and baking paper.[50,51] Even jackets labeled as having fluorine-free impregnation contained 20 ng/m^2 PFOA.[48] Additionally, despite the phase-out of PFOA by 3M, previous studies reported that its levels have not declined as expected, with the percentage of linear isomer PFOA increasing, indicating ongoing production of fluorinated chemicals.[35,52]

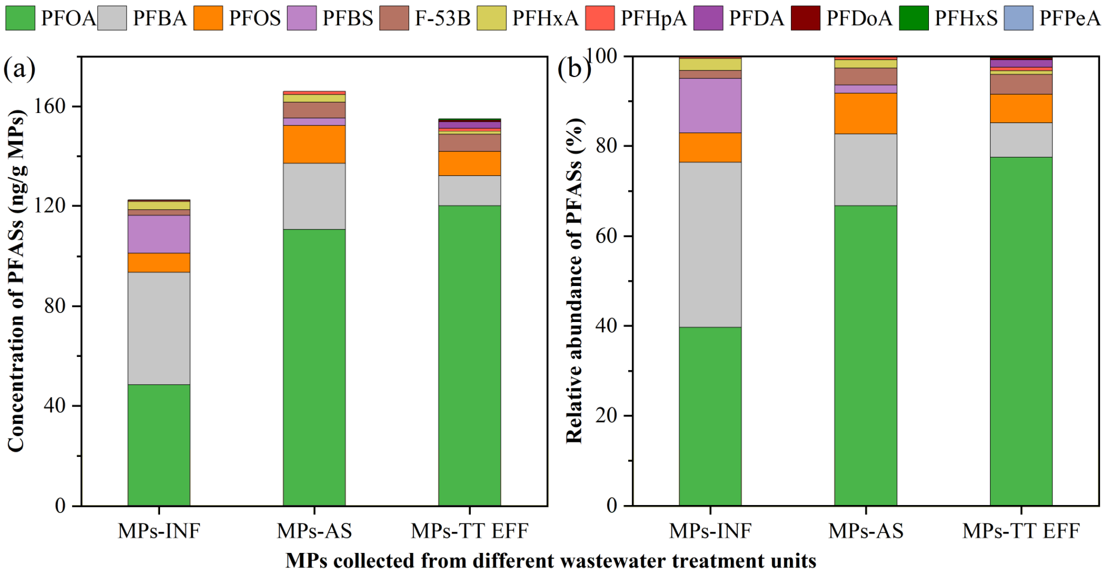

Fig. 6. Concentrations (a) and relative abundance (b) of PFASs associated with MPs.

Short-chain PFASs have been introduced as alternatives to long-chain PFASs. For instance, PFBS has replaced PFOS in the ScotchGard formulas, and PFBA has been introduced as an alternative to PFOA.[53,54] This change accounts for the high relative abundance of short-chain PFASs. Additionally, even perfluorinated polymers such as PVF and PFTE can contribute to PFASs contamination. Interestingly, fluorinated chemicals have also been found in nonfluorinated polymers. PFASs are used in various applications, including mold release agents in plastic production. However, due to variations in manufacturing processes and a lack of detailed information on the specific processes used for our samples, it remains unclear whether the detected PFASs originated from the manufacturing process itself or were absorbed from other sources during shipping, handling, and storage. Evidence suggests that both fluoropolymers and nonfluorinated polymers can contain PFASs. Overall, these preliminary findings highlight the need for a better understanding of small-molecule PFASs originating from various polymer materials, including their use in textiles, electronics, and food packaging.

3.3 Verification of MPs serving as a carrier for PFASs

The results of MPs aqueous leaching revealed that MPs could release PFASs into aqueous environments (Fig. 7(a)). The dominant PFAS compound released was PFOS, followed by PFOA. A small amount of PFBA (0.224 ng/mL) was released by PVC-Coat, while no PFBS and F-53B were detected in the aqueous solutions. PVC-Coat exhibited the highest leaching capacity, with the combined concentrations of PFOS, PFOA, and PFBA reaching10.4 ng/mL. PE-Glove also showed substantial leaching for PFOS and PFOA, further supporting the finding that commercial MPs, potentially due to surface treatments or additives, were more prone to releasing PFASs. Commercial MPs showed higher leaching concentrations, indicating they may be more of a source compared to the virgin MPs. The leaching behavior highlighted the potential of MPs to serve as sources of PFASs, which could contribute to PFASs contamination.

Furthermore, the sorption/desorption verification results revealed that most the long-chain PFASs such as PFOS, F-53B and PFOA exhibited high sorption percentage (Fig. 7(b)), which was in agreement with the previous studies that indicated higher sorption of MPs for long-chain PFASs.[55,56] Short-chain PFASs such as PFBA and PFBS had lower sorption across all MPs, likely due to their reduced hydrophobicity and molecular size. These results indicated that MPs could serve as sorbent for PFASs, especially long-chain PFOS and F-53B. PFOS exhibited a desorption efficiency of 126% and 124%

from PE-Standard and PE-Caps (Fig. 7(c)), suggesting that in addition to full desorption from MPs, further release occurred. This result verified that PFOS was released directly from the MPs themselves, as demonstrated in Fig. 7(a). The consistently high desorption efficiency of PFOS across all MP types, particularly PE, highlighted its release potential, which may be attributed to residual PFASs or fluorinated compounds from manufacturing processes. PE-Caps also demonstrated high desorption efficiency for F-53B and PFBS, probably due to surface modifications or inherent properties of commercial MPs that promote desorption. PTFE-Standard showed significantly lower desorption efficiency for most PFASs, suggesting that PTFE acted as a more persistent sorbent for PFASs in aquatic environments. These results emphasized the role of MPs as a carrier for PFASs with sorption and desorption behavior in the environment.

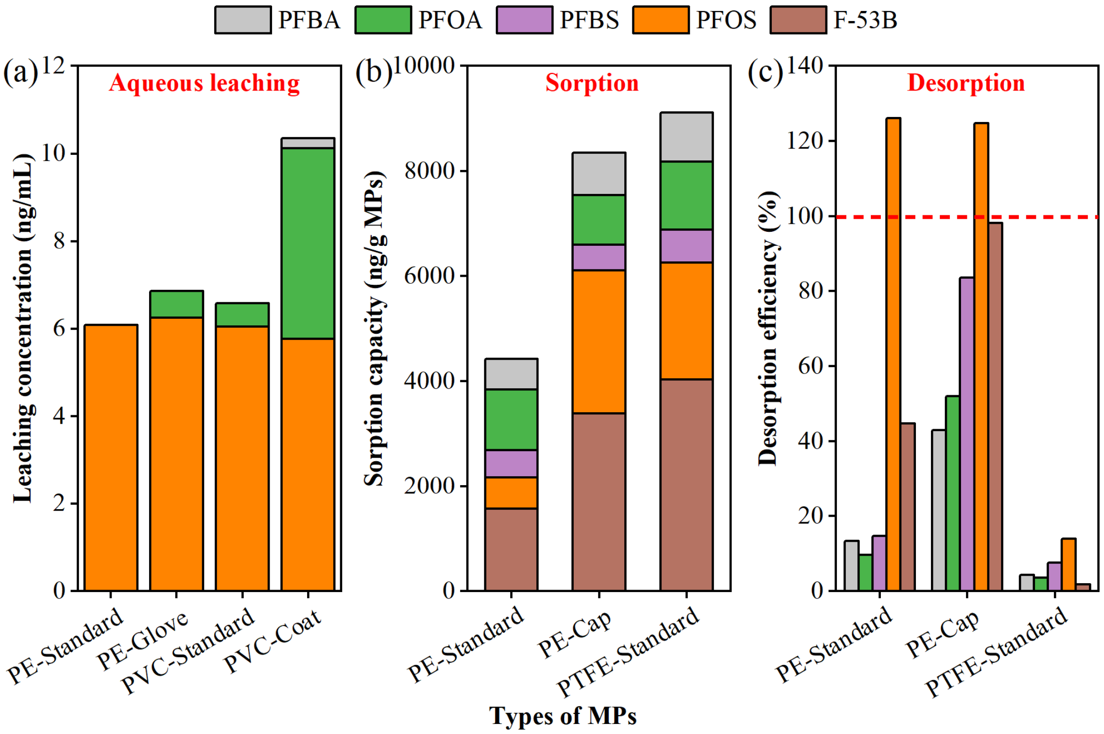

Fig. 7. PFASs sorption onto different representative MPs and desorption of PFASs from MPs. The designation can be found in Table S2.

MPs carry PFASs both by incorporating additives during production and by sorbing contaminants from the environment. Simultaneously, they can release PFASs into the environment through desorption or intrinsic leaching. The observed leaching in both standard and commercial MPs emphasized the potential for PFASs contamination in aquatic environments. These findings revealed the dual roles of MPs as both carriers and sources of PFASs, providing crucial insights into the dynamic behavior of the two emerging pollutants. The interactions between MPs and PFASs would contribute to the long-term persistence in ecosystems, posing potential environmental risk.

4. Environmental implications

Our study provides insights into the co-occurrence and interactions of MPs and PFASs in the environment. Notably, MPs were identified as carriers of PFASs, with measured concentrations ranging from 122 to 166 ng/g for target PFASs, highlighting their significance as environmental contamination pathways. Furthermore, MPs act as a potential source of PFASs, which is manifested in the disposal and leaching of perfluorinated polymers, additives from plastic products, and environmental sorption/desorption processes. Additionally, our findings highlight a strong correlation between MPs and PFASs, evident in their synergistic removal mechanisms within WWTPs and their simultaneous detection in environmental samples. Variations in PFASs and MPs concentrations highlight economic implications for WWTP operations, emphasizing the urgent need for stringent controls on products containing PFASs and MPs. Overall, this study advances our understanding of the environmental behaviors and fate of MPs and PFASs, advocating for regulatory measures to curb their pervasive contamination. Proactive steps are crucial to mitigate the environmental impact of these persistent pollutants and protect both environmental and human health.

Credit author contribution statement

Min Ma: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Frederic Coulon:** Writing – review & editing, Funding acquisition. **Zhiwen Tang:** Writing – review & editing, Conceptualization. **Zhiyuan Hu:** Validation, Investigation. **Ye Bi:** Resources, Investigation. **Mingxin Huo:** Supervision, Methodology. **Xin Song:** Writing – review & editing, Data curation, Supervision, Methodology, Funding acquisition, Conceptualization.

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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Supporting Information Available

This information is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ali, M.; Xu, D.; Yang, X.; Hu, J. Microplastics and PAHs mixed contamination: An in-depth review on the sources, co-occurrence, and fate in marine ecosystems. *Water Res.* **2024**, *257*, 121622. DOI: 10.1016/j.watres.2024.121622.

(2) Talbot, R.; Chang, H. Microplastics in freshwater: A global review of factors affecting spatial and temporal variations. *Environ. Pollut.* **2022**, *292*, 118393. DOI: 10.1016/j.envpol.2021.118393.

(3) Shi, W.; Wu, N.; Zhang, Z.; Liu, Y.; Chen, J.; Li, J. A global review on the abundance and threats of microplastics in soils to terrestrial ecosystem and human health. *Sci. Total Environ.* **2024**, *912*, 169469. DOI: 10.1016/j.scitotenv.2023.169469.

(4) Habumugisha, T.; Zhang, Z. X.; Uwizewe, C.; Yan, C. Z.; Ndayishimiye, J. C.; Rehman, A.; Zhang, X. Toxicological review of micro- and nano-plastics in aquatic environments: Risks to ecosystems, food web dynamics and human health. *Ecotoxicol. Environ. Saf.* **2024**, *278*, 116426. DOI: 10.1016/j.ecoenv.2024.116426.

(5) Barboza, L. G. A.; Vethaak, A. D.; Lavorante, B. R. B. O.; Lundebye, A. K.; Guilhermino, L. Marine microplastic debris: An emerging issue for food security, food safety and human health. *Mar. Pollut. Bull.* **2018**, *133*, 336-348. DOI: 10.1016/j.marpolbul.2018.05.047.

(6) MEEPRC. Action plan for new pollutants control. China, M. o. E. a. E. o. t. P. s. R. o., Ed.; Beijing, 2022.

(7) Evich, M. G.; Davis, M. J. B.; McCord, J. P.; Acrey, B.; Awkerman, J. A.; Knappe, D. R. U.; Lindstrom, A. B.; Speth, T. F.; Tebes-Stevens, C.; Strynar, M. J.; Wang, Z.; Weber, E. J.; Henderson, W. M.; Washington, J. W. Per- and polyfluoroalkyl substances in the environment. *Science* **2022**, *375* (6580), 9065. DOI: 10.1126/science.abg9065 (acccessed 2024/07/07).

(8) Glüge, J.; Scheringer, M.; Cousins, I. T.; DeWitt, J. C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C. A.; Trier, X.; Wang, Z. Y. An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science-Processes & Impacts* **2020**, *22* (12), 2345-2373. DOI: 10.1039/d0em00291g.

(9) Dai, Y.; Zhao, J.; Sun, C.; Li, D.; Liu, X.; Wang, Z.; Yue, T.; Xing, B. Interaction and combined toxicity of microplastics and per- and polyfluoroalkyl substances in aquatic environment. *Frontiers of Environmental Science & Engineering* **2022**, *16* (10), 136. DOI: 10.1007/s11783-022-1571-2.

(10) Kang, P.; Zhao, Y.; Zuo, C.; Cai, Y.; Shen, C.; Ji, B.; Wei, T. The unheeded inherent connections and overlap between microplastics and poly- and perfluoroalkyl substances: A comprehensive review. *Sci. Total Environ.* **2023**, *878*, 163028. DOI: 10.1016/j.scitotenv.2023.163028.

(11) Salawu, O. A.; Olivares, C. I.; Adeleye, A. S. Adsorption of PFAS onto secondary microplastics: A mechanistic study. *J. Hazard. Mater.* **2024**, *470*, 134185. DOI: 10.1016/j.jhazmat.2024.134185.

(12) Yu, F.; Wu, J. P.; Wang, H. Y. Z.; Bao, Y. Z.; Xing, H. Y.; Ye, W. P.; Li, X. H.; Huang, M. H. Interaction of microplastics with perfluoroalkyl and polyfluoroalkyl substances in water: A review of the fate, mechanisms and toxicity. *Sci. Total Environ.* **2024**, *948*, 175000. DOI: 10.1016/j.scitotenv.2024.175000.

(13) Zhao, Z.; Zheng, X.; Han, Z.; Yang, S.; Zhang, H.; Lin, T.; Zhou, C. Response mechanisms of Chlorella sorokiniana to microplastics and PFOA stress: Photosynthesis, oxidative stress, extracellular polymeric substances and antioxidant system. *Chemosphere* **2023**, *323*, 138256. DOI: 10.1016/j.chemosphere.2023.138256.

(14) Yang, H.; Lai, H.; Huang, J.; Sun, L.; Mennigen, J. A.; Wang, Q.; Liu, Y.; Jin, Y.; Tu, W. Polystyrene

microplastics decrease F–53B bioaccumulation but induce inflammatory stress in larval zebrafish. *Chemosphere* **2020**, *255*, 127040. DOI: 10.1016/j.chemosphere.2020.127040.

(15) Bere, K.; Xiong, X.; Sáringer, S.; Douglas, G.; Szilagyi, I. Microplastics as an adsorption and transport medium for per- and polyfluoroalkyl substances in aquatic systems: Polystyrene and undecafluorohexanoic acid interactions. *J. Mol. Liq.* **2023**, *384*, 122285. DOI: 10.1016/j.molliq.2023.122285.

(16) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40* (1), 32-44. DOI: 10.1021/es0512475.

(17) Luo, Y. L.; Gibson, C. T.; Chuah, C.; Tang, Y. H.; Naidu, R.; Fang, C. Raman imaging for the identification of Teflon microplastics and nanoplastics released from non-stick cookware. *Sci. Total Environ.* **2022**, *851*, 158293. DOI: 10.1016/j.scitotenv.2022.158293.

(18) Pramanik, B. K.; Roychand, R.; Monira, S.; Bhuiyan, M.; Jegatheesan, V. Fate of road-dust associated microplastics and per- and polyfluorinated substances in stormwater. *Process Saf. Environ. Prot.* **2020**, *144*, 236-241. DOI: 10.1016/j.psep.2020.07.020.

(19) Tian, Y. J.; Chen, Z.; Zhang, J. Y.; Wang, Z. Z. F.; Zhu, Y. J.; Wang, P.; Zhang, T.; Pu, J.; Sun, H. W.; Wang, L. An innovative evaluation method based on polymer mass detection to evaluate the contribution of microfibers from laundry process to municipal wastewater. *J. Hazard. Mater.* **2021**, *407*, 124861. DOI: 10.1016/j.jhazmat.2020.124861.

(20) Fan, Y. F.; Zheng, J. L.; Deng, L. G.; Rao, W. X.; Zhang, Q. J.; Liu, T.; Qian, X. Spatiotemporal dynamics of microplastics in an urban river network area. *Water Res.* **2022**, *212*, 118116. DOI: 10.1016/J.Watres.2022.118116.

(21) Tang, Z. W.; Song, X.; Xu, M. M.; Yao, J.; Ali, M.; Wang, Q.; Zeng, J.; Ding, X. Y.; Wang, C. J.; Zhang, Z. X.; Liu, X. Effects of co-occurrence of PFASs and chlorinated aliphatic hydrocarbons on microbial communities in groundwater: A field study. *J. Hazard. Mater.* **2022**, *435*, 128969. DOI: 10.1016/j.jhazmat.2022.128969.

(22) Xu, C.; Song, X.; Liu, Z. Y.; Ding, X. Y.; Chen, H.; Ding, D. Occurrence, source apportionment, plant bioaccumulation and human exposure of legacy and emerging per- and polyfluoroalkyl substances in soil and plant leaves near a landfill in China. *Sci. Total Environ.* **2021**, *776*, 145731. DOI: 10.1016/j.scitotenv.2021.145731.

(23) Suhrhoff, T. J.; Scholz-Böttcher, B. M. Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics - A lab experiment. *Mar. Pollut. Bull.* **2016**, *102* (1), 84-94. DOI: 10.1016/j.marpolbul.2015.11.054.

(24) Pan, C. G.; Liu, Y. S.; Ying, G. G. Perfluoroalkyl substances (PFASs) in wastewater treatment plants and drinking water treatment plants: Removal efficiency and exposure risk. *Water Res.* **2016**, *106*, 562-570. DOI: 10.1016/j.watres.2016.10.045.

(25) Kibambe, M. G.; Momba, M. N. B.; Daso, A. P.; Coetzee, M. A. A. Evaluation of the efficiency of selected wastewater treatment processes in removing selected perfluoroalkyl substances (PFASs). *J. Environ. Manage.* **2020**, *255*, 109945. DOI: 10.1016/j.jenvman.2019.109945.

(26) Coggan, T. L.; Moodie, D.; Kolobaric, A.; Szabo, D.; Shimeta, J.; Crosbie, N. D.; Lee, E.; Fernandes, M.; Clarke, B. O. An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). *Heliyon* **2019**, *5* (8), e02316. DOI: 10.1016/j.heliyon.2019.e02316.

(27) Kim, J.; Xin, X.; Mamo, B. T.; Hawkins, G. L.; Li, K.; Chen, Y.; Huang, Q.; Huang, C.-H. Occurrence and Fate of Ultrashort-Chain and Other Per- and Polyfluoroalkyl Substances (PFAS) in Wastewater

Treatment Plants. *ACS ES&T Water* **2022**, *2* (8), 1380-1390. DOI: 10.1021/acsestwater.2c00135.

(28) Ma, M.; Huo, M. X.; Coulon, F.; Ali, M.; Tang, Z. W.; Liu, X.; Ying, Z.; Wang, B.; Song, X. Understanding microplastic presence in different wastewater treatment processes: Removal efficiency and source identification. *Sci. Total Environ.* **2024**, *929*, 172680. DOI: 10.1016/j.scitotenv.2024.172680.

(29) Li, Y. J.; Bräunig, J.; Angelica, G. C.; Thai, P. K.; Mueller, J. F.; Yuan, Z. G. Formation and partitioning behaviour of perfluoroalkyl acids (PFAAs) in waste activated sludge during anaerobic digestion. *Water Res.* **2021**, *189*, 116583. DOI: 10.1016/j.watres.2020.116583.

(30) Chen, H.; Peng, H.; Yang, M.; Hu, J.; Zhang, Y. Detection, Occurrence, and Fate of Fluorotelomer Alcohols in Municipal Wastewater Treatment Plants. *Environ. Sci. Technol.* **2017**, *51* (16), 8953-8961. DOI: 10.1021/acs.est.7b00315.

(31) Gobelius, L.; Glimstedt, L.; Olsson, J.; Wiberg, K.; Ahrens, L. Mass flow of per- and polyfluoroalkyl substances (PFAS) in a Swedish municipal wastewater network and wastewater treatment plant. *Chemosphere* **2023**, *336*, 139182. DOI: 10.1016/j.chemosphere.2023.139182.

(32) Liu, T.; Hu, L. X.; Han, Y.; Xiao, S.; Dong, L. L.; Yang, Y. Y.; Liu, Y. S.; Zhao, J. L.; Ying, G. G. Non-target discovery and risk prediction of per- and polyfluoroalkyl substances (PFAS) and transformation products in wastewater treatment systems. *J. Hazard. Mater.* **2024**, *476*, 135081. DOI: 10.1016/j.jhazmat.2024.135081.

(33) Llewellyn, M. J.; Griffin, E. K.; Caspar, R. J.; Timshina, A. S.; Bowden, J. A.; Miller, C. J.; Baker, B. B.; Baker, T. R. Identification and quantification of novel per- and polyfluoroalkyl substances (PFAS) contamination in a Great Lakes urban-dominated watershed. *Sci. Total Environ.* **2024**, *941*, 173325. DOI: https://doi.org/10.1016/j.scitotenv.2024.173325.

(34) Wei, C.; Wang, Q.; Song, X.; Chen, X.; Fan, R.; Ding, D.; Liu, Y. Distribution, source identification and health risk assessment of PFASs and two PFOS alternatives in groundwater from non-industrial areas. *Ecotoxicol. Environ. Saf.* **2018**, *152*, 141-150. DOI: https://doi.org/10.1016/j.ecoenv.2018.01.039.

(35) Zhu, Y. C.; Ro, A.; Bartell, S. M. Household low pile carpet usage was associated with increased serum PFAS concentrations in 2005-2006. *Environ. Res.* **2021**, *195*, 110758. DOI: 10.1016/j.envres.2021.110758.

(36) UNEP. The 9 new POPs: An introduction to the nine chemicals added to the stockholm convention by the conference of the parties at its fourth meeting, 2009. Programme, U. N. E., Ed.; 2010.

(37) Li, F.; Duan, J.; Tian, S. T.; Ji, H. D.; Zhu, Y. M.; Wei, Z. S.; Zhao, D. Y. Short-chain per- and polyfluoroalkyl substances in aquatic systems: Occurrence, impacts and treatment. *Chem. Eng. J.* **2020**, *380*. DOI: ARTN 122506
10.1016/j.cej.2019.122506.

(38) Brendel, S.; Fetter, É.; Staude, C.; Vierke, L.; Biegel-Engler, A. Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH. *Environmental Sciences Europe* **2018**, *30*, 9. DOI: 10.1186/s12302-018-0134-4.

(39) Ateia, M.; Maroli, A.; Tharayil, N.; Karanfil, T. The overlooked short- and ultrashort-chain poly- and perfluorinated substances: A review. *Chemosphere* **2019**, *220*, 866-882. DOI: 10.1016/j.chemosphere.2018.12.186.

(40) Sunderland, E. M.; Hu, X. D. C.; Dassuncao, C.; Tokranov, A. K.; Wagner, C. C.; Allen, J. G. A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and

present understanding of health effects. *Journal of Exposure Science and Environmental Epidemiology* **2019**, *29* (2), 131-147. DOI: 10.1038/s41370-018-0094-1.

(41) Wang, S. W.; Huang, J.; Yang, Y.; Hui, Y. M.; Ge, Y. X.; Larssen, T.; Yu, G.; Deng, S. B.; Wang, B.; Harman, C. First Report of a Chinese PFOS Alternative Overlooked for 30 Years: Its Toxicity, Persistence, and Presence in the Environment. *Environ. Sci. Technol.* **2013**, *47* (18), 10163-10170. DOI: 10.1021/es401525n.

(42) Ruan, T.; Lin, Y. F.; Wang, T.; Liu, R. Z.; Jiang, G. B. Identification of Novel Polyfluorinated Ether Sulfonates as PFOS Alternatives in Municipal Sewage Sludge in China. *Environ. Sci. Technol.* **2015**, *49* (11), 6519-6527. DOI: 10.1021/acs.est.5b01010.

(43) Fredriksson, F.; Eriksson, U.; Kärrman, A.; Yeung, L. W. Y. Per- and polyfluoroalkyl substances (PFAS) in sludge from wastewater treatment plants in Sweden — First findings of novel fluorinated copolymers in Europe including temporal analysis. *Sci. Total Environ.* **2022**, *846*, 157406. DOI: 10.1016/j.scitotenv.2022.157406.

(44) Zhou, T.; Li, X.; Liu, H.; Dong, S. M.; Zhang, Z. H.; Wang, Z. Y.; Li, J. B.; Nghiem, L. D.; Khan, S. J.; Wang, Q. L. Occurrence, fate, and remediation for per-and polyfluoroalkyl substances (PFAS) in sewage sludge: A comprehensive review. *J. Hazard. Mater.* **2024**, *466*, 133637. DOI: 10.1016/j.jhazmat.2024.133637.

(45) Arvaniti, O. S.; Ventouri, E. I.; Stasinakis, A. S.; Thomaidis, N. S. Occurrence of different classes of perfluorinated compounds in Greek wastewater treatment plants and determination of their solid-water distribution coefficients. *J. Hazard. Mater.* **2012**, *239*, 24-31. DOI: 10.1016/j.jhazmat.2012.02.015.

(46) Arvaniti, O. S.; Andersen, H. R.; Thomaidis, N. S.; Stasinakis, A. S. Sorption of Perfluorinated Compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment. *Chemosphere* **2014**, *111*, 405-411. DOI: 10.1016/j.chemosphere.2014.03.087.

(47) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014**, *50*, 318-340. DOI: 10.1016/j.watres.2013.10.045.

(48) Gremmel, C.; Frömel, T.; Knepper, T. P. Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets. *Chemosphere* **2016**, *160*, 173-180. DOI: 10.1016/j.chemosphere.2016.06.043.

(49) Lang, J. R.; Allred, B. M.; Peaslee, G. F.; Field, J. A.; Barlaz, M. A. Release of Per- and Polyfluoroalkyl Substances (PFASs) from Carpet and Clothing in Model Anaerobic Landfill Reactors. *Environ. Sci. Technol.* **2016**, *50* (10), 5024-5032. DOI: 10.1021/acs.est.5b06237.

(50) Shoeib, T.; Hassan, Y.; Rauert, C.; Harner, T. Poly- and perfluoroalkyl substances (PFASs) in indoor dust and food packaging materials in Egypt: Trends in developed and developing countries. *Chemosphere* **2016**, *144*, 1573-1581. DOI: 10.1016/j.chemosphere.2015.08.066.

(51) Kotthoff, M.; Müller, J.; Jürling, H.; Schlummer, M.; Fiedler, D. Perfluoroalkyl and polyfluoroalkyl substances in consumer products. *Environmental Science and Pollution Research* **2015**, *22* (19), 14546-14559. DOI: 10.1007/s11356-015-4202-7.

(52) Gebbink, W. A.; Glynn, A.; Berger, U. Temporal changes (1997-2012) of perfluoroalkyl acids and selected precursors (including isomers) in Swedish human serum. *Environ. Pollut.* **2015**, *199*, 166-173, Article. DOI: 10.1016/j.envpol.2015.01.024 (acccessed 2015-04-01).

(53) Eschauzier, C.; Haftka, J.; Stuyfzand, P. J.; de Voogt, P. Perfluorinated Compounds in Infiltrated

River Rhine Water and Infiltrated Rainwater in Coastal Dunes. *Environ. Sci. Technol.* **2010**, *44* (19), 7450-7455. DOI: 10.1021/es100471z.

(54) Liu, S. Y.; Yang, R. J.; Yin, N. Y.; Faiola, F. The short-chain perfluorinated compounds PFBS, PFHxS, PFBA and PFHxA, disrupt human mesenchymal stem cell self-renewal and adipogenic differentiation. *Journal of Environmental Sciences* **2020**, *88*, 187-199. DOI: 10.1016/j.jes.2019.08.016.

(55) Enyoh, C. E.; Wang, Q.; Wang, W.; Chowdhury, T.; Rabin, M. H.; Islam, R.; Yue, G.; Yichun, L.; Xiao, K. Sorption of Per- and Polyfluoroalkyl Substances (PFAS) using Polyethylene (PE) microplastics as adsorbent: Grand Canonical Monte Carlo and Molecular Dynamics (GCMC-MD) studies. *Int. J. Environ. Anal. Chem.* **2022**, 1-17. DOI: 10.1080/03067319.2022.2070016.

(56) Llorca, M.; Schirinzi, G.; Martinez, M.; Barcelo, D.; Farre, M. Adsorption of perfluoroalkyl substances on microplastics under environmental conditions. *Environ. Pollut.* **2018**, *235*, 680-691. DOI: 10.1016/j.envpol.2017.12.075.

Unveiling the truth of interactions between microplastics and per- and polyfluoroalkyl substances (PFASs) in wastewater treatment plants: microplastics as a carrier of PFASs and beyond

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https://doi.org/10.1021/acs.est.4c08898