



Modified linear solvation energy relationships for adsorption of perfluorocarboxylic acids by polystyrene microplastics

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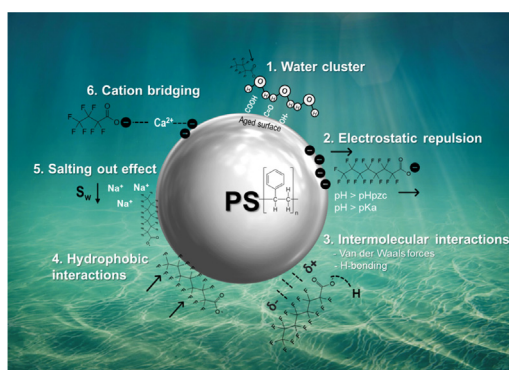
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HIGHLIGHTS

- For the first time, LSER approach was used to predict adsorption of PFAS by MPs.
- Abraham's solvation parameters were corrected to account for ionization of PFCAs.
- The correction improves models' mechanistic interpretation and prediction strength.
- PFAS' MW, MPs' oxidation state, and water type affect adsorption of PFAS by MPs.
- Polarizability and hydrophobicity of PFCAs drive them onto PS MPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics (MPs) could act as vectors of organic pollutants such as *per*- and polyfluoroalkyl substances (PFAS). Therefore, understanding adsorptive interactions are essential steps towards unraveling the fate of PFAS in the natural waters where MPs are ubiquitous. Linear solvation energy relationships (LSER)-based predictive models are utilitarian tools to delineate the complexity of adsorption interactions. However, commonly studied PFAS are in their ionic forms at environmentally relevant conditions and LSER modeling parameters do not account for their ionization. This study aims to develop the first LSER model for the adsorption of PFAS by MPs using a subset of ionizable perfluoroalkyl carboxylic acids (PFCA). The adsorption of twelve PFCAs by polystyrene (PS) MPs was used for model training. The study provided mechanistic insights regarding the impacts of PFCA chain length, PS oxidation state, and water chemistry. Results show that the polarizability and hydrophobicity of anionic PFCA are the most significant contributors to their adsorption by MPs. In contrast, van der Waals interactions between PFCA and water significantly decrease PFCA binding affinity. Overall, LSER is demonstrated as a promising approach for predicting the adsorption of ionizable PFAS by MPs after the correction of Abraham's solute descriptors to account for their ionization.

1. Introduction

Plastics are pragmatic and versatile materials that benefit daily life and industry (Sun et al., 2022; Crawford and Quinn, 2016). Since the 1950s, society's ever-increasing demand for plastics has boosted global

production by >100 times (Plastics Europe, 2021). This massive plastic production has environmental and public health consequences. If the plastic production and waste management remain unchanged, 12 billion tons of plastic waste will be in the environment by 2050 (Ncube et al., 2021; United Nations Environment Programme, 2018). Additionally, plastic debris are exposed to natural weathering processes, which break them down into microplastics (MPs) and make them easier to enter the food chain (Botterell et al., 2019). MPs are complex mixtures

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of polymers and chemical additives, and their hazards may be further exacerbated by the adsorption of synthetic organic compounds (SOC) and pathogens (Rochman et al., 2019; Galloway et al., 2017). Thus, MPs potentially act as vectors for organic pollutants, which can cause severe health implications (Pedà et al., 2016; Rainieri et al., 2018; Bhagat et al., 2022).

Per- and polyfluoroalkyl substances (PFAS) are a class of persistent SOCs. Pollution of natural waters with PFAS is a contemporary environmental crisis overwhelming the public, policy makers, researchers, and practitioners. As a consequence, MPs and PFAS have been detected in aquatic environments originated from numerous point and non-point sources (Sonmez Baghirzade et al., 2021) both individually and in combination (Cheng et al., 2021; Pramanik et al., 2021). Twenty-one PFAS were detected on MPs collected from a river where total PFAS concentrations were >9.1 µg/g (Cheng et al., 2021). Moreover, adsorption of PFAS increases as MPs age and biofilm forms on their surface (Scott et al., 2021). Similarly, MPs preloaded with natural organic matter (NOM) adsorb more PFAS than pristine MPs, due to complex formation between NOM and PFAS (Ateia et al., 2020). These adsorptive interactions can bring about serious health concerns when PFAS-laden MPs are unintentionally ingested by organisms especially if they could desorb in the digestive track (Rainieri et al., 2018; le Bihanic et al., 2020; Sobhani et al., 2021).

Despite the concerns, there are only few studies reporting the adsorption of PFAS by MPs (Bakir et al., 2014; Llorca et al., 2018; Wang et al., 2015). These studies deliver some mechanistic insights into the adsorption process (Llorca et al., 2018); however, given the vast variety of PFAS types, polymer characteristics, and environmental conditions, it is critical to generate systematic knowledge to unravel the adsorptive mechanisms. Conducting laboratory experiments to reveal intermolecular interactions would be expensive, time consuming and laborious, which also prompts the model development. Up till now, one article modeled the adsorption of PFAS by MPs using molecular dynamics simulations techniques and reported that H-bonding, van der Waals forces, and electrostatic interactions contribute to adsorption (Enyoh et al., 2022). Moreover, the partitioning of PFAS to fluid-fluid interfaces was modeled using tools such as quantitative structure-property relationship analysis (Brusseau and van Glubt, 2021; Brusseau, 2019; Lyu et al., 2022) and group-contribution model (Le et al., 2022; Le et al., 2021). Linear solvation energy relationships (LSER), on the other hand, has never been implemented for adsorption of PFAS by MPs. LSER uses a predetermined set of solute properties that are established based on the solvation theory and quantify the molecular interactions of a compound with its surroundings (Apul et al., 2020; Egert and Langowski, 2022). Since the early 1990s, this approach has been used to predict adsorption of a large array of compounds by carbon nanotubes (CNT) (Iijima, 1991), multi-walled CNTs (Hüffer et al., 2014; Apul et al., 2013), single-walled CNTs (Apul, 2014), graphene (Xia et al., 2010), and graphene oxide (Ersan et al., 2019). LSER is pragmatic for predicting the adsorptive interactions of PFAS by MPs as a preliminary tool prior to conducting experimental work (Hüffer et al., 2018; Uber et al., 2019a; Uber et al., 2019b; Xu et al., 2021; Wei et al., 2019). Along with their predictive properties, it can also provide mechanistic insights into molecular level interactions. However, existing LSER methods are limited to neutral compounds and have not attempted to train for ionizable PFAS. Therefore, the objectives of this study are to train the first LSER models for adsorption of ionizable PFAS by MPs and to delineate the impacts of perfluoroalkyl carboxylic acids' (PFCA) molecular weight (MW); water type; and MPs' oxidation state (i.e., presence of carboxylic acid group, -COOH) on adsorption. Despite the limited dataset, this article is the first attempt to predict adsorption of PFAS by MPs, which yielded promising modeling outcomes and provided useful insights for the design of future experimental studies. To provide a preliminary predictive tool and reveal molecular level insights, it is of urgent matter to share the preliminary outcomes of the developed models with researchers in MPs and PFAS literature.

2. Materials and methods

2.1. Collection and corrections for Abraham descriptors

Abraham's LSER approach describes solvation or related activities by the compounds' physicochemical properties. These models provide mechanistic insights because they reveal intermolecular interactions between adsorbents and adsorbates as well as quantifying their relative individual contribution to the adsorption. A typical LSER model that describes the adsorption of neutral organic compounds by using a set of predetermined independent descriptors is shown in Eq. (1):

$$\text{Log } K_d = c + eE + sS + aA + bB + vV \quad (1)$$

where 'log K_d ' is partitioning coefficient between MPs and water under equilibrium conditions. 'E' is the excess molar refraction in units of (cm³ mol⁻¹)/10 representing non-specific van der Waals forces; 'S' is the polarizability/dipolarity parameter, 'A' and 'B' are the hydrogen bond donating and accepting abilities, respectively; and 'V' is the molecular volume or McGowan's volume in units of (cm³ mol⁻¹)/100. Lastly, 'c' is the regression constant, and 'e', 's', 'a', 'b', and 'v' are the fitting coefficients indicating the contribution of each interaction on adsorption (Apul et al., 2020; Xu et al., 2021).

Solvatochromic descriptors for PFAS were obtained from the Helmholtz Centre for Environmental Research (Ulrich et al., 2022). The compounds' SMILES (PubChem, 2022) were inserted into the computational tool to calculate the descriptors. This tool provides descriptors only for the neutral forms of the compounds. However, all PFAS contained in this study, except one (i.e., FOSA, perfluorooctane sulfonamide), exist in almost completely ionized forms in experimental conditions (Table S1). Therefore, collected descriptors were corrected to account for the ionization of PFCA using a set of equations (Text S1 in SI) suggested by Abraham and Acree (2016) for carboxylic acids. In addition, a new descriptor 'J⁻' was introduced to the LSER model as an ionization switch as there are both ionic and neutral PFAS in the dataset. The final form of the model used throughout this study is shown in Eq. (2).

$$\text{Log } K_d = c + eE' + sS' + aA' + bB' + vV + j^- J^- \quad (2)$$

2.2. Collection of adsorption descriptors

Partitioning coefficients (K_d) for the adsorption of PFAS by polystyrene (PS) MPs in various water types were collected from Llorca et al. (2018). Modeling efforts did not focus on high density polyethylene (HDPE) MPs in that paper due to the insufficiency of K_d data to train LSER. K_d 's were generated at 20 °C based on 7 days concentrations of compounds that reached adsorption percentage lower than 15 % between day 7 to 50. Database was created for adsorption of 13 PFAS ranging between C₄-C₁₈. Adsorption data for PS MP using 11 PFAS (10 PFCA + FOSA) and 7 PFCA were obtained for seawater and freshwater, respectively. The database for PS-COOH MP was slightly different, containing 10 PFAS (9 PFCA + FOSA) and 9 PFAS (8 PFCA + FOSA) for seawater and freshwater, respectively. The inclusion of neutral FOSA aims to provide the models with ability to differentiate the ionization. Both MPs are virgin (i.e., pristine) and 10 µm in size. Physicochemical properties of freshwater and seawater are given in Table S2. Physicochemical properties and K_d 's of these compounds are listed in Tables S1 and S3, respectively. Additionally, Log K_d values for 13 non-ionizable polycyclic aromatic hydrocarbons (PAH) adsorbed by PS MPs in deionized water was obtained from our earlier review article (Costigan et al., 2022) and listed in Table S4. PAH data was combined with the PFCA dataset for freshwater to demonstrate the importance of descriptor correction on model strength.

2.3. Statistical model development

Multiple linear regressions were conducted by assigning $\text{Log } K_d$ as dependent variable and the modified Abraham solvation descriptors as independent variables using Microsoft Excel. The goodness-of-fit was examined by coefficient of determination (R^2). The predictive precision of the models was quantified by the prediction error sum of squares (PRESS) and the root mean squared error (RMSE). Smaller PRESS and RMSE values indicated a stronger prediction tendency of a model. The multicollinearity of independent variables was quantified by variance inflation factor (VIF). Higher VIF values (>10) indicated severe correlations with one or more of the remaining independent variables. Four modeling scenarios were created to examine the impact of PFCA MW, water type, and PS MPs' oxidation state on the adsorption mechanism. The modeling scenarios are presented in Table S5. Furthermore, one-way ANOVA analysis was performed using Microsoft Excel to show the statistical significance of the predictive improvement achieved after descriptor correction in models containing PAHs and PFCAs.

3. Results and discussion

3.1. Analysis of PFAS adsorption by microplastics

Fig. 1a shows the $\text{Log } K_d$ values for PFAS adsorption with respect to PFAS chain length. First, PFCA with longer carbon chains show higher K_d values, in both water types, ascribed to increasing hydrophobic interactions (Söregård et al., 2020). However, the longest-chain compounds: perfluorohexadecanoic acid (PFHxDA, 16C) and perfluorooctadecanoic acid (PFODA, 18C) disrupt this trend, which can be attributed to semi-micelle formation; or strong binding to dissolved organic carbon in water (Campos Pereira et al., 2018). Second, PFCA adsorb onto MPs more strongly in seawater than in freshwater, regardless of the oxidation state of PS. This can be due to the ionic strength of seawater that enhances the likelihood of adsorption either by decreasing the water solubility of PFCA or developing cation bridges between MPs and PFCA. Unlike PFCA, FOSA's adsorption capacity is not influenced by the water type, which was attributed to its neutral state at the corresponding pH values minimizing the electrostatic interactions. The total organic carbon of seawater is 1.8 folds greater than that of freshwater (Llorca et al., 2018), indicating the adsorption of protonated PFAS is not impacted by NOM competition. Similarly, the adsorption of FOSA on polyethylene (PE) and PS MP is not significantly influenced by ionic strength as it is mainly governed by hydrophobic interactions (Wang et al., 2015). In contrast, PFOS' adsorption

affinity is increased at higher ionic strength, confirming the importance of electrostatic interactions for ionizable PFAS (Wang et al., 2015).

Fig. 1b shows the $\text{Log } K_d$ versus octanol water distribution coefficient ($\text{Log } D_{ow}$) of PFCAs. As demonstrated by D_{ow} , longer chain PFCAs are lipophilic (Gagliano et al., 2020). However, Fig. 1b does not include the longest chain PFCAs (13C, 14C, 16C, and 18C) due to a lack of experimental pK_a values in literature, which are required to convert octanol water partition coefficient ($\text{Log } K_{ow}$) to $\text{Log } D_{ow}$. Moderate correlations were observed between $\text{Log } K_d$ and $\text{Log } D_{ow}$ in all of the datasets, which supports that hydrophobic repulsion from water is an important mechanism governing the adsorption of PFCAs with 4C to 12C by MPs. However, PFAS have unique characteristics hampering the capability of single parameters such as D_{ow} or chain length to predict this interaction, especially when the chain length gets longer (Coffin et al., 2021). Compound properties such as D_{ow} or solubility can be useful for modeling SOC partitioning in deionized water, and do not necessarily reflect complex molecular interactions. However, water chemistry plays notable roles in adsorption process in the natural environment (Costigan et al., 2022). Therefore, LSER models containing multiple PFAS identifiers is imperative to develop reliable mechanistic insights for PFAS' interactions with MPs. The traditional LSER models are not designed to predict ionizable compounds. Therefore, this study demonstrates corrections for PFCA descriptors for LSER training in the subsequent sections.

3.2. Investigating the mechanistic impact of descriptor correction on LSER models

A dataset containing PFCAs and non-ionizable PAHs was created to investigate the impact of descriptor correction on the model predictivity. This test was performed using PAHs due to their non-polar and non-ionizable nature making them relatively more straightforward to model with the LSER approach. So that the descriptor correction efforts could focus on PFCAs, and the importance of correction could be better understood without further complexity. Fig. 2 compares models trained by uncorrected and corrected descriptors of PFCA (Table S6) at three different MW cutoffs. All PFCA descriptors were first corrected and then parameter 'J' was assigned to both PFCAs and PAHs. The correction increased adjusted R^2 by 3 % compared to uncorrected models in each MW cutoff, which is a statistically significant increase at 95 % level of significance (Fig. 2a, Table S7). Adjusted R^2 was selected for comparison because the corrected model contains an additional independent variable. PRESS and RMSE values of uncorrected model were 15.02 and 0.87; and those of corrected models were 11.59 and 3.19, respectively. More importantly, the relative significance of parameters remarkably changed after correction (Fig. 2b). Coefficient 'a', indicating the H-bond donating ability, experienced the

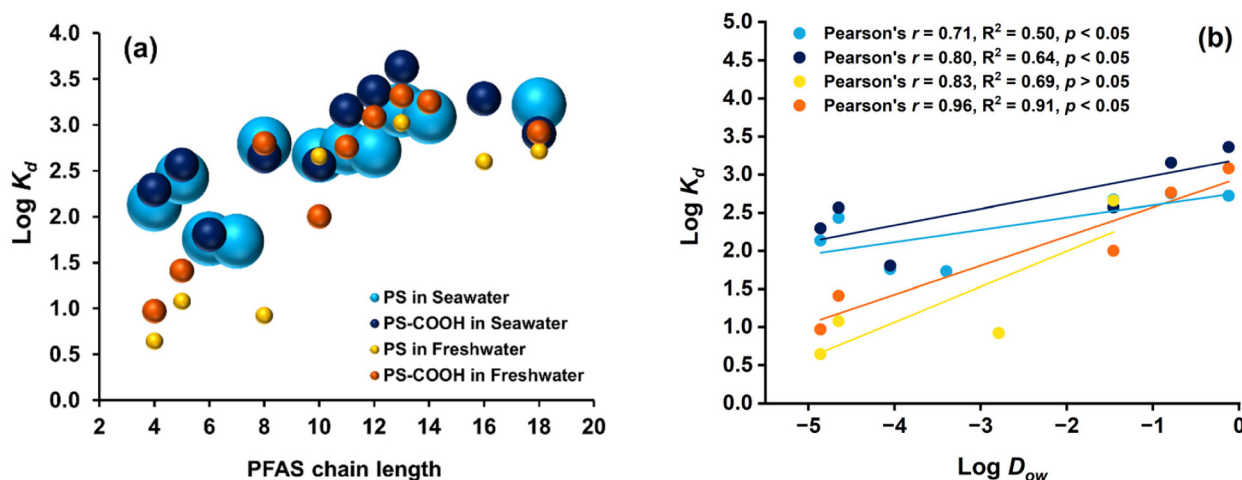


Fig. 1. Partition coefficients ($\text{Log } K_d$) for adsorption of PFCA by PS and PS-COOH MPs in seawater and freshwater with respect to (a) number of C atoms in PFAS chain; and (b) $\text{Log } D_{ow}$. Data from Llorca et al. (2018) and Christensen et al. (2022). Bubble sizes in (a) represent the relative number of data in four different datasets listed. R^2 values of the trendlines related to PS in Seawater, PS-COOH in Seawater, PS in Freshwater and PS-COOH in Freshwater on the panel (b) are 0.50, 0.64, 0.69, and 0.91, respectively.

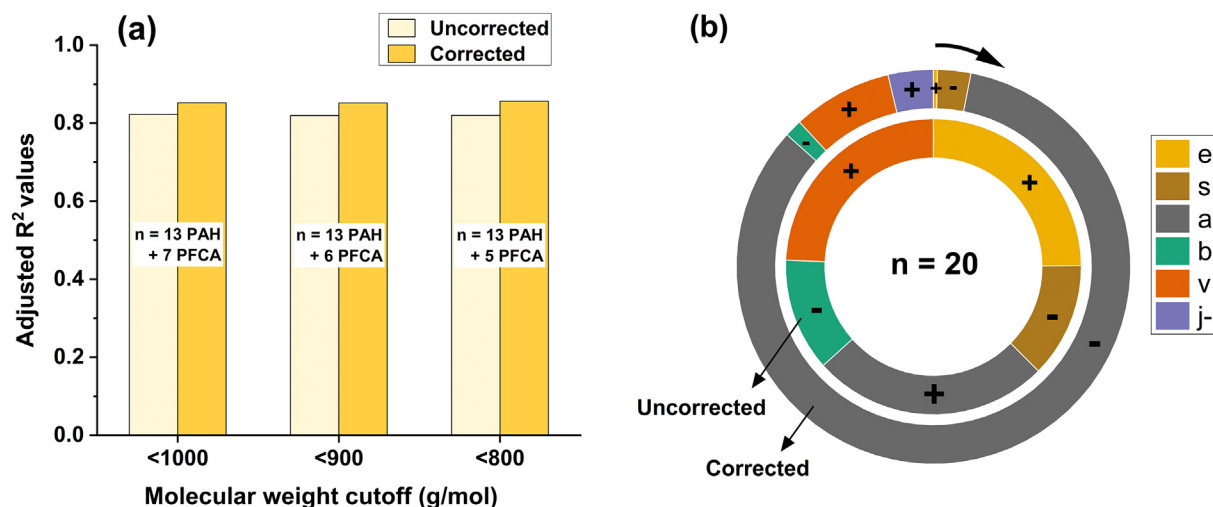


Fig. 2. (a) Adjusted R^2 values of models trained by corrected and uncorrected descriptors at different MW cutoffs. (b) The signs and relative importance of model coefficients for the corrected and uncorrected descriptors ($n = 20$ i.e., 13 PAH and 7 PFCA). Detailed results are provided in Tables S8 and S9. Coefficient 'e' is the excess molar refraction, 's' is the polarizability/dipolarity parameter, 'a' and 'b' are the hydrogen bond donating and accepting abilities, respectively, 'v' is the molecular volume or McGowan's volume, and 'j-' is the ionization switch.

most notable change in both sign and relative importance as the model gained ability to differentiate anionic PFCA from neutral PAHs. This enabled the model to differentiate H-bonding tendencies as the prevailing

factor, which dominated other adsorption mechanisms. The correction of PFCA descriptors improved the model in terms of mechanistic interpretation and slightly increased its prediction strength.

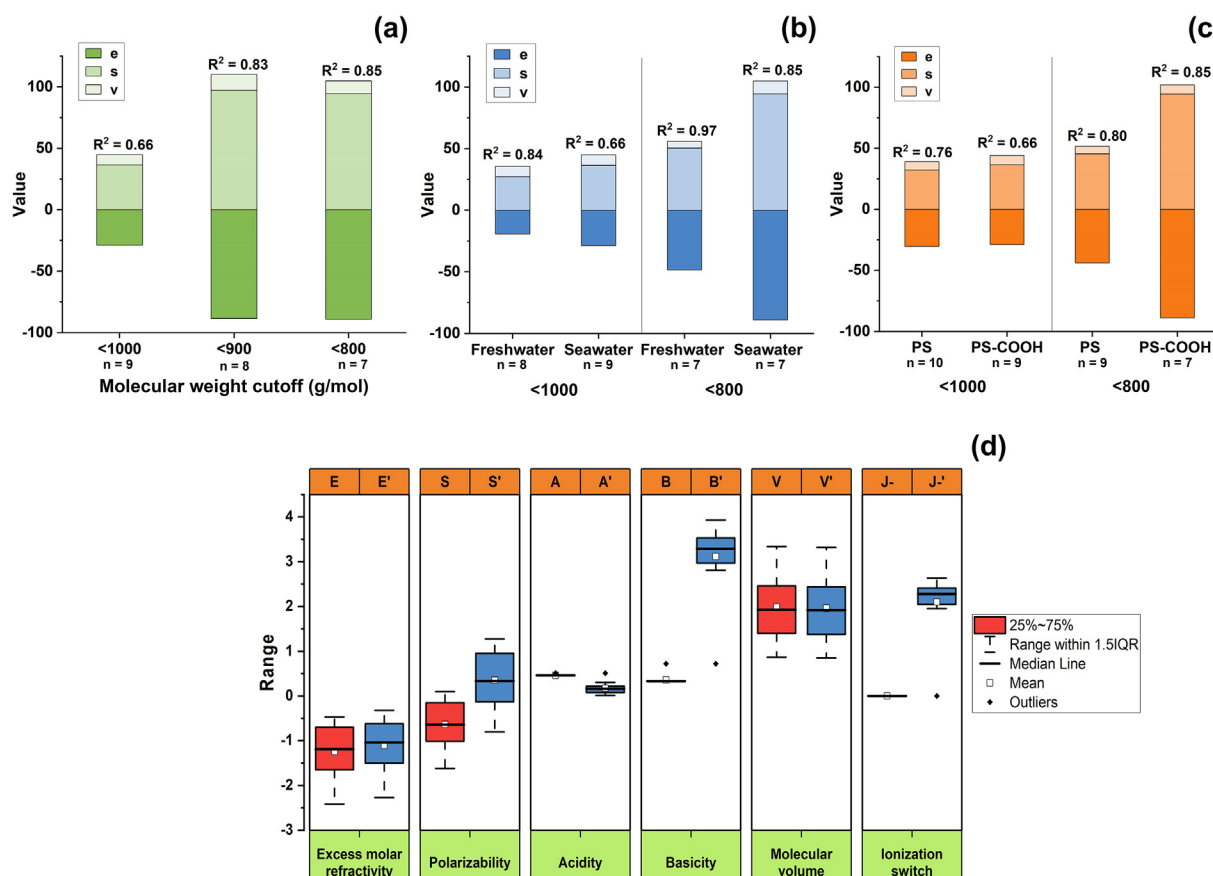


Fig. 3. Regression coefficients for models examining the effect of (a) PFAS' MW cutoff; (b) water type; and (c) PS MPs' oxidation state. Datasets of these models do not include FOA. (Plots for datasets containing FOA are given in Fig. S1). Detailed model results including the coefficients and statistical analyses are provided in Tables S10, S11, S12, and S13. (d) Box and whisker plot for the raw and corrected solvatochromic descriptors. The raw descriptors are given the usual symbols and the corresponding corrected ones are denoted by prime. Data is shown in Table S6. N/A: Not available.

3.3. Corrected LSER for adsorption of PFAS by microplastics

After demonstrating the utility of descriptor correction, models for only PFAS were developed to investigate the mechanisms governing their adsorption onto MPs under varying conditions. Eqs. (3) and (4) show the general forms of the modified LSER models that predicts all scenarios created for PFAS datasets without and with FOSA, respectively. The prime denotes the descriptors that are corrected for model training. It should be noted that the models do not include statistically insignificant parameters.

$$\text{Log } K_d = c - eE' + sS' + vV' \quad (3)$$

$$\text{Log } K_d = c - eE' + sS' - bB' + vV' \quad (4)$$

The results of LSER models (Eq. (3)) are shown in Fig. 3a, b, and c. The relative contribution of each mechanism to adsorption was determined by dividing absolute values of each coefficient by the sum of all coefficients. Dipolar interactions ('S') between MPs and PFCAs are the most significant mechanisms on the adsorption process. This finding affirms the importance of electrostatic forces between the permanent dipoles of PFCAs and MPs. The second most influential factor was 'E', which was negatively correlated indicating that refractive index decreases the adsorption of PFCAs onto MPs because bulk water has higher polarization induction effect on PFCAs than MPs (Uber et al., 2019a). Finally, 'V' was positively correlated with the adsorption, which can be either due to the hydrophobic repulsion of PFCAs demonstrating the greater cavity formation demand of larger molecules in water or non-specific van der Waals attraction between PFCAs and MPs. The LSER model parameters cannot differentiate the two mechanisms, but the model demonstrates that the size of PFCAs is important to predict their partitioning onto MPs. When FOSA was included in the dataset (Eq. (4), Fig. S1), 'B' became negatively correlated with adsorption, which was attributed to FOSA's basicity. The coefficients' order of relative absolute magnitude was the same with the dataset without FOSA (except the 'b' coefficient as the least influential one). The presence of 'b' term in the model indicates that water is a better H-bond donor (Apul et al., 2013) for PFAS than MPs.

Fig. 3d shows the uncorrected and corrected descriptors that were used as independent variables to train our models in this study. The outliers showing up after the correction of 'A', 'B', and 'J⁻' belong to FOSA, proving that correction efforts differentiate PFCAs from neutral compounds. The largest change is observed in descriptor 'B', which indicates the conversion from acidic to anionic form. A large and positive 'B' demonstrates that PFCAs are anions with a high H-bond accepting ability. Correspondingly, there is a slight decrease in 'A' since PFCAs are losing their H-donating ability. Similarly, 'J⁻' is a descriptor differentiating PFAS in the dataset depending on their ionization state. On the other hand, the changes in 'E' and 'V' are minimal as only one H⁺ is lost from the molecule with negligible impact on energy requirement for cavity formation. Finally, the value of 'S' increases moderately as the molecules' polarizability increases with a negative ion on the head group of PFCAs. Since all PFCAs have the same functional group (i.e., -COOH) in their structure, their corrected 'A', 'B' and 'J⁻' values are similar across the database with negligible impact on regression ($p > 0.05$). Therefore, they were excluded from the model, resulting in 'E', 'S', and 'V' being the sole governing parameters for the models with the dataset without FOSA. It should be noted that in some cases, keeping insignificant parameters may have a value for capturing underwhelming intermolecular interactions.

3.3.1. Model training for PFCAs with different molecular weight cutoffs

The impact of PFCAs' MW and thus the chain length on LSER models was investigated using datasets with different MW cutoffs. This factor was only possible to be examined for PS-COOH MPs in seawater due to data availability. The results are shown in Fig. 3a (without FOSA) and Fig. S1a (with FOSA). These models trained without FOSA yield $R^2 = 0.66$ (at MW cutoff <1000 g/mol, $n = 9$) and 0.85 (MW cutoff <800 g/mol, $n = 7$). It should be noted that the number of data points and the uniformity

of intermolecular interactions decrease as the MW cutoff decreases. Moreover, as the MW cutoff decreases, coefficient of 'V' decreases, and 'E' increases. Indeed, the 'V' term captures both hydrophobically driven repulsion and size dependent non-specific attraction to MP surface. In this scenario, although 'E' increases, there is an overall decrease in the 'V' meaning that decreasing chain length causes relatively weak hydrophobic interactions. When FOSA is included in the datasets, changes in both R^2 and regression coefficients between MW cutoffs remains similar with the former dataset (Fig. S1a). Consequently, as the PFCAs chain length gets shorter, the importance of hydrophobic interactions decreases, and electrostatic attractions become more predominant.

3.3.2. The effect of water type and polymer's oxidation state

The impact of water type was investigated by comparing the models for PS-COOH in freshwater and seawater. The regression coefficients for datasets with and without FOSA are shown in Figs. 3b and S1b, respectively. The impact of water chemistry differs depending on the MW cutoff. For example, at MW < 1000 g/mol, the relative contribution of 'E' is higher in seawater than in freshwater. A more negative coefficient 'e' can be due to dipolar interactions between PFCAs and ions in seawater, which decreases their adsorption affinity onto MPs. On the other hand, 'V' is more influential in freshwater than in seawater. Again, considering the two terms that 'V' captures, the positive coefficient 'v' is a direct sign for a larger hydrophobicity driven adsorption onto PS-COOH MPs in freshwater. This can be attributed to NOM content of freshwater that covers the MP surface and attracts PFCAs via hydrophobic interactions. The impact of NOM can diminish adsorption in seawater by competing with PFCAs for the surface of MPs. When it is <800 g/mol, the impact of water chemistry on the adsorption mechanism decreases, and the relative importance of parameters becomes almost identical. As a result, NOM content of water can govern the hydrophobic interactions, however its influence is influenced by chain length of PFAS.

Furthermore, the impact of MP surface oxidation was examined by comparing the model coefficients for PS versus PS-COOH in seawater at different MW cutoffs (i.e., <1000 and <800 g/mol) with FOSA (shown in Fig. 3c) and without FOSA (shown in Fig. S1c). Regardless of having FOSA in datasets, the impact of 'V' is two times greater for PS-COOH than PS, and that of 'E' is smaller for PS-COOH than PS at a MW cutoff <1000 g/mol. Moreover, the relative importance of 'S' is not influenced by the polymer's oxidation state. Considering the 'V' term refers to two different mechanisms mentioned, it can be inferred that the carboxylic acid group of PS MPs enhances the importance of hydrophobic interactions at this cutoff. This could be attributed to the negatively charged surface functional groups repelling the deprotonated PFAS that augments the importance of hydrophobic interactions. When MW cutoff is <800 g/mol, the impact of -COOH on the adsorption process decreases. This can be ascribed to that chain length is more influential factor than the oxidation level of MPs for the studied datasets. Consequently, hydrophobic interactions become more visible for carboxylated PS than plain PS and this difference disappears when PFAS chain length gets shorter. Overall, LSER models show that the interplay between PFAS' MW cutoff, water type and polymer surface have a complex influence on their adsorption by PS MPs. For further decoding of the complex intermolecular interactions, more adsorption data should be generated. Considering that the models were developed using data obtained from a certain size, type, and shape of virgin MPs in this study, outcomes could differ if MPs had different characteristics. Moreover, although the compounds used in this study cover most of PFCAs detected in the environment, perfluoroalkyl sulfonic acids (PFASs) or other PFAS are found in the environment and their addition could improve the LSER model efforts.

4. Environmental implications and overcoming the limitations of LSER modeling for adsorption of PFAS by microplastics

This article introduces LSER modeling for the adsorption of PFCAs by PS and PS-COOH MPs in seawater and freshwater for the first time. Since research on PFAS adsorption onto MPs is at early stages, the lack of data is

a constraint in comprehensive model development for diverse conditions and therefore developed models do not necessarily capture every MP type in various waters. With decreasing cost of analysis and increasing attention to the subject, we anticipate larger published datasets, which will enable the development of more robust models in the near future. Wide applicability of models can be improved by addressing the following three main factors. First, MPs' polymer structure and weathering level can alter the adsorption affinity of PFCA's especially if they have oxygen functional groups that are either in the original polymeric structure or formed after weathering in the environment. In this study, the models developed for PS were tested for HDPE MPs (Table S14) and demonstrated relatively weak predictions. Future studies should focus on producing adsorption data for various MP types and apply the modified LSER modeling approach to overcome this limitation and reveal mechanistic insights. Furthermore, environmental relevance of developed models can be improved by normalizing "Log K_d " values using surface area, and surface oxygen content. This study involved normalizing "Log K_d " values for the model with the largest dataset (Tables S15 and S16). Since the surface area information is available for only one plastic type, surface area-based normalization efforts did not change multiple linear regression results. When adsorption data is produced using different plastics, the impact of surface area will be a determinant.

Second, LSER models were generated for two real water samples, which might have limited their application domain. Even though properties of background solution (i.e., pH, dissolved oxygen, conductivity, and NOM) are known, a diverse set of water conditions need to be tested to reach fundamental level conclusions. Adsorption experiments in synthetic waters mimicking natural conditions with controlled complexities can help to better evaluate the individual impact of each water component. However, it should be noted that the aquatic chemistry conditions to be tested must be environmentally relevant.

Third, PFCA's have carboxylic acid functional groups and the database does not capture other functional groups such as sulfonic acids that are environmentally pertinent. In datasets containing PFCA's only, all compounds have the same functional group, undergoing similar interactions with neighboring molecules. Therefore, different classes of PFAS with different functional groups can enhance the applicability domain of the predictive model. However, extending our models' applicability domain to include PFSA's can only be possible after producing correction equations for descriptors of ionic PFSA's. In this work, in addition to PFCA's-specific models, we added FOSA into the models to improve our understanding of ionic property of PFCA's, without the need for descriptor correction as FOSA exists in its neutral form under experimental conditions. Even though data unavailability limited our attempt, mechanistic explanations were still successfully acquired. For future work, adsorption data can be attributed to semi-micelle formation; or strong binding to dissolved organic carbon in water. Therefore, an extra parameter describing micelle formation potential of PFAS can be added to the equation or " K_d " value can be corrected by the critical micelle concentration of each PFCA.

Developed models have an application domain different than those reported in similar MPs studies, and therefore they are not directly comparable to make conclusive statements using either the model outputs or the predictive precision. However, the predictive strength of our LSER model surpasses that of a group-contribution model (Le et al., 2021), which was developed using air-water surface tension data of PFAS (Table S17). This paper is the first attempt of using LSER approach for ionizable compounds in MPs literature and further studies are needed to make reasonable comparisons.

CRediT authorship contribution statement

M. Dilara Hatinoğlu: Conceptualization, Methodology, Writing – original draft. **François Perreault:** Conceptualization, Writing – review & editing, Project administration, Funding acquisition. **Onur G. Apul:**

Supervision, Conceptualization, Writing – review & editing, Project administration, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Onur Apul reports financial support was provided by National Science Foundation. Francois Perreault reports a relationship with National Science Foundation that includes: funding grants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.160524>.

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