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Study on the Effects of DOM on the Bioaccumulation of Perfluorinated Acids in *Daphnia magna*

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Abstract: Perfluoroalkyl acids (PFAs), one kind of emerging contaminants, have attracted great attentions in recent years. However, the study about their bioaccumulation mechanism remains scarce. In this research, the bioaccumulation of 6 kinds of PFAs in water flea *Daphnia magna* was studied in the presence of dissolved organic matter (DOM), and the possible interactions between DOM and PFCs were explored by spectra analysis. The results showed that DOM could decrease the bioaccumulation of PFAs at 10 and 20 mg·L⁻¹, and increase the bioaccumulation at 1 mg·L⁻¹. The decrease of BAF was in the range of 11 to 42% and 23 to 77% for FA and HA, respectively. The increase of BAF was in the range of 12 to 44% and 8 to 73% for FA and HA, respectively. The spectrum analysis indicated that the interaction of PFAs and DOM was not due to the bond formation reaction, but the electrostatic attraction.

1. Introduction

Perfluorinated acids (PFAs) is an organofluorine compound with all hydrogens replaced by fluorine on a carbon chain, but the molecule also contains at least one different atom or functional group. PFAs have a wide range of industrial applications [1]. PFAs such as Perfluorooctanesulfonates (PFOS) and perfluorooctanoic acid (PFOA) have been found in water, air and soil, including remote locations such as the Arctic and the Antarctic [2]. PFCs have been found in the aqueous environment ubiquitously in particular. These contaminants have probably been present in the environment and in biota for many years. However, their environmental and biological effects have been realized only recently. PFAs is one kind of persistent organic pollutants, and they are not known to degrade by any natural processes.

Humic substances are one kind of typical dissolved organic matter (DOM), and it including fulvic and humic acids. According to previous studies, about 40-60% of dissolved organic carbon in natural waters was humic substance [3]. The diversity of functional groups of humic substances defines a broad range of interaction with pollutants [4]. The photolysis rates of organic compounds could be increased, and the concentration of pollutants in water could be reduced with the interaction of relatively hydrophobic organic compounds and humic substances [5]. Previous studies have shown that humic substances can distinctly influence bioaccumulation and toxicity of contaminants such as pesticides and chlorinated hydrocarbons in aquatic biota [6]. However, the mechanism of the increase of the bioaccumulation is still unclear. Though some hypothesis has been raised that the increase of bioaccumulation is correlate with the content, types and contact time of humic substances [7], they are still not supported by any real evidence and the mechanism need further research. It's important to



develop methods to measure the sorption of pollutants to humic substances to predict their fate in environment. Studies dealing with the environment behavior of humic substances indicated that the major light-absorbing of these solute in the range of 200 to 800 nm in many natural waters, and spectroscopic techniques is useful in the study of the interaction of DOM and organic pollutant[8].

Humic and fulvic acids are the most abundant components of DOM and widely believed to be representatives of DOM behavior[9]. The goal of this study is to evaluate the effects of humic substances on the bioaccumulation of PFAs by *D. magna*. The spectral analysis was adopted to study the possible mechanism of the binding between humic substances and PFAs.

2. Materials and Methods

2.1 Chemicals

PFAs including PFOS, PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA) and perfluorododecanoic acid (PFDoA) were obtained from Acros Organics (New Jersey, USA). The methanol was purchased from J. T. Baker (chromatography grade, USA). Humic acid (HA) was from Sigma-Aldrich.

2.2 Bioaccumulation experiments

HA and FA was used to study the effects of DOM on the bioaccumulation of PFAs in *D. magna*, and was prepared with the concentration of 1, 10 and 20 mg·L⁻¹ in AFW, respectively. The duration of the bioaccumulation was 21 days. The detailed experiment setting is shown in previous study[10, 11].

2.3 Spectral properties of DOM and the complex of DOM and PFAs

2.3.1 Binding of DOM and PFAs Humic acid and fulvic acid were chose as the typical DOM. A series content of DOM stock solution were added into 50 ml PP tubes, and then they were diluted to 1, 10 and 20 mg·L⁻¹, respectively. PFOA and PFOS solution were added into these tubes to make sure that each concentration of DOM combined with 0, 1, 5, 10, 20 and 50 µg·L⁻¹ PFAs, respectively. Each concentration gets 3 replications. The measured pH values for these solutions were range from 8.26 to 8.63, and it thought to be no obvious effects on the spectral analysis. The mixed solutions were shaken at 120 rpm in darkness for 72 h. After equilibrium, these solutions were conducted by spectroscopic analysis.

2.3.2 UV/Vis spectra analysis UV/Vis spectra of DOM and DOM-PFAs samples were recorded on a Hewlett–Packard 8453 spectrophotometer in a 1-cm quartz cuvette and scanned from 200 to 800 nm with the interval of 5 nm.

2.4 Extraction and analysis of PFAs

The extraction and analysis of PFAs in daphnia and water refer to previous studies [10]. The recovery rate of PFAs in HA solution was determined use the same extraction and analysis method. A total of 10 ng PFAs standard solution was added in 20 mg/L HA solution and the results indicated that the recovery rate of PFA was range from 82.1% to 98.3%.

3. Results and Discussion

3.1 Effects of DOM on the bioaccumulation of PFAs

As described in our previous study [11], the BAF of PFAs was increased with the increasing perfluoroalkyl chain length under the effects of HA, FA for the carboxylate, and the BAF of sulfonate is higher than the one of carboxylate with the same or longer perfluoroalkyl chain length. For FA, it was enhanced the bioaccumulation of short-chain PFAs (PFOA, PFNA) in *D. magna* when the FA concentration is below 10 mg·L⁻¹ (Figure 1). However, it inhibited the bioaccumulation when the FA concentration reach to 20 mg·L⁻¹; the BAF decreased by 27% and 11% for PFOA and PFNA, respectively.

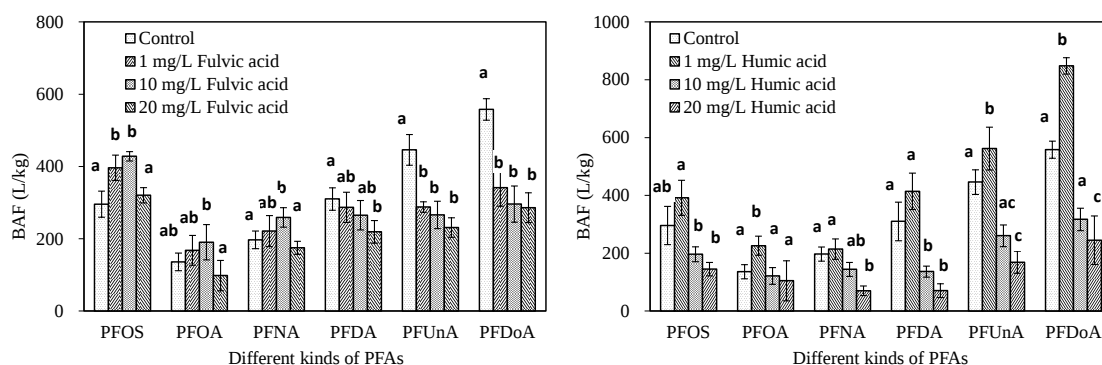


Figure 1. The effects of DOM with different concentrations on the bioaccumulation of PFAs in *D. magna* (different letters means there are significant difference between them ($P < 0.05$) and the groups that have at least one same letter means there are no significant difference between them ($P > 0.05$)).

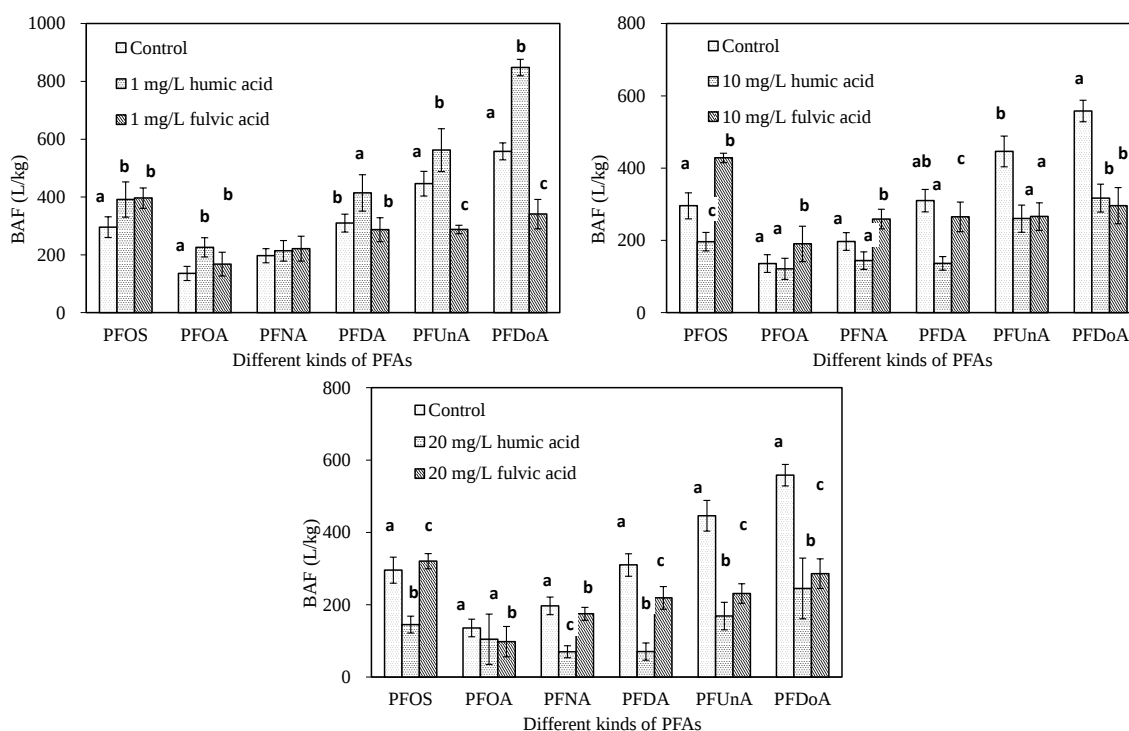


Figure 2. Comparison of BAFs of PFAs between the same concentration of HA and FA (different letters means there are significant difference between them ($P < 0.05$) and the groups that have at least one same letter means there are no significant difference between them ($P > 0.05$)).

It's no doubt that DOM can influence the bioaccumulation of organic chemicals. In commonly, DOM lead to a decrease of the accumulation of these compounds, and it has become generally accepted [12-13]. However, the enhancement of the bioaccumulation of organic compounds due to DOM also has been found in several studies [14].

As shown in Figure 2, at the concentration of $1 \text{ mg} \cdot \text{L}^{-1}$, HA and FA enhanced the bioaccumulation for all kinds of PFAs, while FA only enhanced the short-chain PFAs. When the concentration comes to $10 \text{ mg} \cdot \text{L}^{-1}$, HA decreased the bioaccumulation; however, FA still enhanced the bioaccumulation for short-chain length PFAs, while the decrease of bioaccumulation for the long-chain PFAs was reinforced. The results indicated that, the quantity and types of DOM should be considered when evaluating the bioaccumulation of PFAs in natural aquatic environment. In addition, the functional group of PFAs also should be considered.

3.2 UV/Vis spectroscopic analysis

The UV/Vis spectrum of HA- PFAs and FA-PFAs solutions at different HA/FA concentrations were described in Figur 3. As shown in this figure, UV spectrum of HA and FA was smooth, broad and featureless though the HA/FA concentration was ranged from 1 to 20 mg·L⁻¹. According to Korshin et al., [15], each aromatic chromophore in DOM is expected to have a distinct absorption bands, however, DOM is a complex of many of these chromophore, and for some of them, the absorption bands is at the neighboring wavelength. Thus, the overall spectrum of the DOM represents a superposition of these bands. No new peak was observed after the adding of the different concentration of PFAs (ranged from 5 to 1000 µg·L⁻¹). However, the adding of PFAs to these solutions affect the absorbance of the HA/FA solutions.

For HA, the adding of PFAs caused the red shift of the HA characteristic peak, and this shift was increased with the increasing PFAs concentration. In other words, PFAs can increase the absorbance of HA solution, and it was increased with the increasing of PFAs concentrations. In addition, the increment was enhanced with the increasing of HA concentration. For FA, the change was similar to HA with the adding of PFAs at different concentrations. The PFAs result in the red shift of FA characteristic peak, and this shift was increased with the increasing PFAs concentration. Relevant research suggested that the redshift of the absorption peak means the transition energy of the electron was reduced and the possibly reason is the increase of the conjugation of the molecular system [16]. Thus, the results indicated that PFAs can enhance the conjugation system of HA and FA.

3.3 Characteristic UV/Vis spectra parameters

Various absorption wavelengths at 254, 280, 365 and 465 nm as well as ratios like A_{250}/A_{365} (E_2/E_3), A_{465}/A_{665} (E_4/E_6) have been cited in literature for the spectral differentiation of the complex solutions of HA-PFAs and FA-PFAs [17].

It's said that light absorbance at 254 nm (A_{254}) correlates well with the traditional comprehensive index of organic matter, such as total organic carbon [2], and the aromaticity of DOM [18]. For FA, The value was increased with the increasing PFAs concentration, it means the PFAs could increase the aromaticity of the FA solution, and it was in accord with the red shift of the spectrum of FA with the adding of PFAs. For HA, there were no obvious trends for the value of A_{254} . Generally speaking, the value of control group is between the low PFAs concentration group (1 and 5 µg·L⁻¹) and the high PFAs concentration group. The reason could be attributed to the complicated composition of HA. The numerous functional groups and chromophores interrupt the effects of PFAs. In addition, the relatively low concentration of PFAs maybe another reason, and it was deduced by the fact that the A_{254} in 50 µg·L⁻¹ group is higher than other groups.

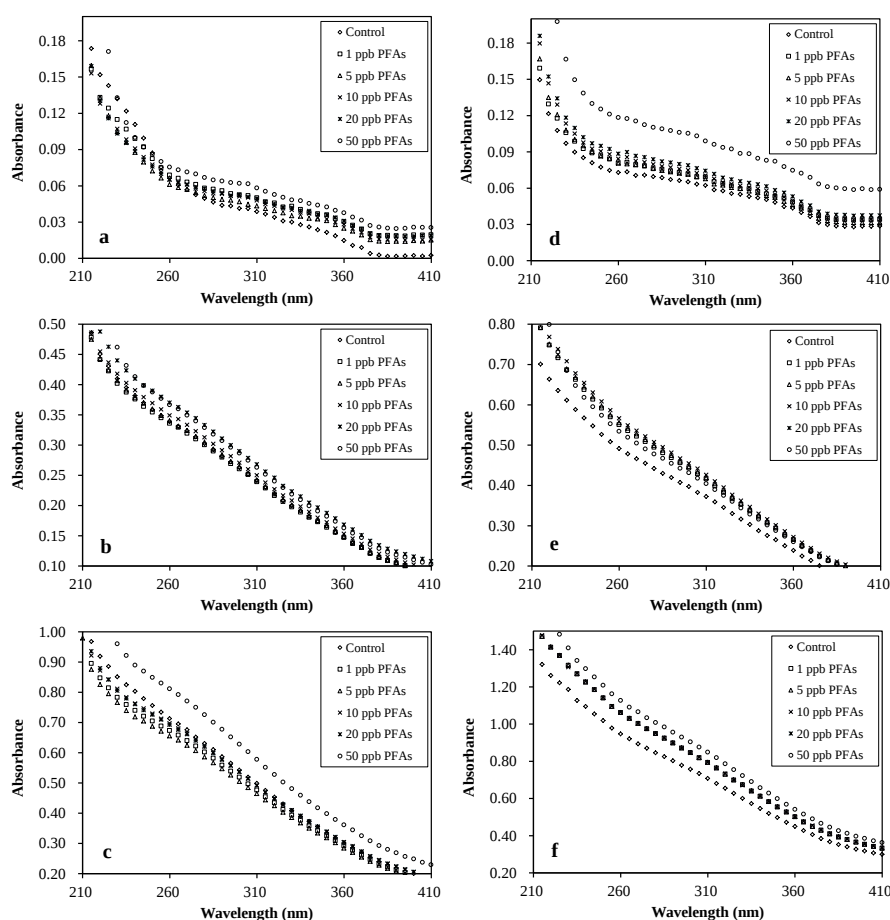


Figure 3. UV/Vis absorptivity of HA- PFAs and FA-PFAs solution in water (the HA concentration is 1, 10 and 20 $\text{mg}\cdot\text{L}^{-1}$ in graph a, b and c, respectively; the FA concentration is 1, 10 and 20 $\text{mg}\cdot\text{L}^{-1}$ in graph d, e and f, respectively)

For some kinds of pollutants, such as phenolic substances, aniline derivatives and benzoic acids, the π - π^* electron transitions occur when the wavelength is 280 nm [19, 20]. According to Weishaaret al., [21], the absorbance at 280 nm is well correlated with the molecular weight of organic matters. Thus, the molar absorbance at 280 nm may reflect the change of DOM before and after the binding of PFAs in molecular levels. As shown in Figure 4, the absorbance of different concentrations of HA and FA at the wavelength of 280 nm were well correlated with the PFAs concentration, and the correlation coefficients were range from 0.65 to 0.98. we can deduced that PFAs was bond to HA and FA, and these kinds of bond enlarged the molecular weight of HA/FA.

E_2/E_3 is the absorbance ratios measured at the wavelength of 250 and 365 nm, and similar to A_{254} , it could correlate with the molecular size and aromaticity [22]. As shown in Table 1, besides the control group, the values were decreased with the increasing PFAs concentrations for each HA/FA concentration group. However, there were no significant differences between them ($P > 0.05$). For HA, the values of E_2/E_3 in 1 $\text{mg}\cdot\text{L}^{-1}$ group were higher than 10 and 20 $\text{mg}\cdot\text{L}^{-1}$ group, and they were close to each other for the latter two groups. For FA, the value in 1 $\text{mg}\cdot\text{L}^{-1}$ group were lower than 10 and 20 $\text{mg}\cdot\text{L}^{-1}$ group and, like HA, they were close to each other for the latter two groups.

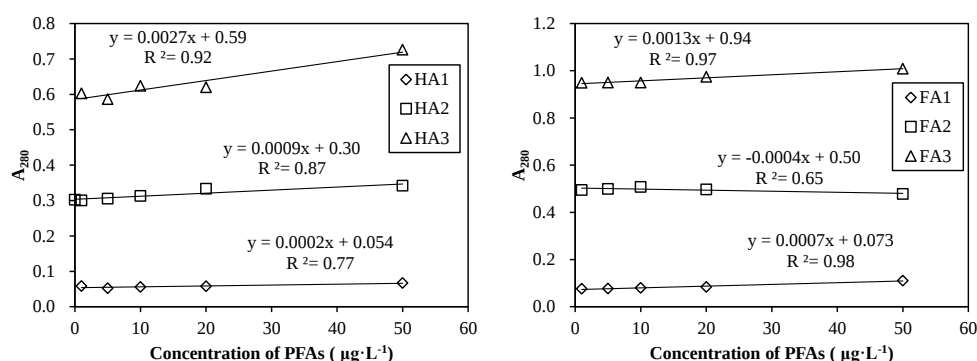


Figure 4. Absorbance of different concentration of humic acid and fulvic acid at the wavelength of 280 nm as the function of PFAs concentration (HA1, HA2 and HA3 represent the humic acid at 1, 10 and 20 $\text{mg}\cdot\text{L}^{-1}$, respectively, and the same to the FA1, FA2 and FA3)

4. Conclusions

In conclusion, the results indicated that, the bioaccumulation of PFAs by *D. magnacould* significantly affect by HA and FA. They could decrease the bioaccumulation of PFAs at 10 and 20 $\text{mg}\cdot\text{L}^{-1}$, and increase the bioaccumulation at 1 $\text{mg}\cdot\text{L}^{-1}$. The decrease of BAF was in the range of 11 to 42% and 23 to 77%, while the increase of BAF was in the range of 12 to 44% and 8 to 73% for FA and HA, respectively. The spectrum analysis indicated that the interaction of PFAs and DOM was not due to the bond formation reaction, but the electrostatic attraction.

Acknowledgements

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