

## Article

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# Dissolved Organic Matter Conformation and Its Interaction with Pyrene As Affected by Water Chemistry and Concentration

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Water chemistry and concentration of dissolved organic matter (DOM) have been reported to affect DOM conformation and binding properties with hydrophobic organic contaminants (HOCs). However, relationship between DOM conformation and its binding properties remains unclear. We designed a multibag equilibration system (MBES) to investigate the variation of carbon-normalized sorption coefficients ( $K_{\text{DOC}}$ ) of pyrene at different DOM concentrations based on an identical free solute concentration at different pHs and in the presence of Al ions. In addition, we studied the conformation of DOM under different conditions via atomic force microscopy (AFM) imaging, dynamic light scattering, and zeta potential measurements. Zeta potential measurements indicated that intra- and intermolecular interaction was facilitated at low pH or with the presence of Al ions, and a more organized molecular aggregate (such as a micelle-like structure) could form, thus, enhancing  $K_{\text{DOC}}$ . As DOM concentration increased, DOM molecular aggregation was promoted in a way reducing  $K_{\text{DOC}}$ . This research is a first attempt to correlate DOM conformation with  $K_{\text{DOC}}$ . Aggregation of DOM molecules resulting from increased zeta potential (less negative) generally led to an increased  $K_{\text{DOC}}$ . Further study in this area will provide valuable information on HOC–DOM interactions, thus, leading to more accurate predictions of  $K_{\text{DOC}}$ .

## Introduction

Dissolved organic matter (DOM) is widely present in the environment and has been proven to be a key factor affecting the behavior of hydrophobic organic contaminants (HOCs) (1). Many studies consistently indicate that water chemistry plays an important role in HOC–DOM interactions. However, the results are often confusing because both negative and positive relationships have been reported between pH or ionic strength and binding coefficients,  $K_{\text{DOC}}$  (2–8). Thus, water chemistry has never been incorporated into HOC fate modeling.

$K_{\text{DOC}}$  was also reported to be different as DOM concentration varied (3, 5, 7, 9, 10). However, most researchers considered DOM concentration of minor environmental significance (5, 7, 9, 11). Experimental designs investigating HOC–DOM interactions were normally based on one initial solute concentration. However, nonlinear HOC–DOM in-

teraction has been recently observed (8, 12–16), which means that  $K_{\text{DOC}}$  is solute-concentration dependent. Then the comparison on  $K_{\text{DOC}}$  is reliable only when the equilibrated aqueous concentration is the same (16), which was generally ignored in the experimental designs for DOM concentration effect on  $K_{\text{DOC}}$ . Therefore, one initial solute concentration experimental design needs to be modified and improved.

DOM has been reported as being long chain amphiphatic molecules (17). The inter- and intramolecular interactions of DOM molecules could lead to a significant change of molecular conformation and consequently affect its environmental functions, such as the interactions with pollutants. Explanations about the influence of water chemistry and DOM concentration on  $K_{\text{DOC}}$  have been proposed based on DOM conformation change (2–5). In this study, conformation change refers to the three-dimensional (3D) structural changes of both single and aggregated molecules because it is extremely difficult (if not possible) to distinguish them for DOM. Several models have been used to describe DOM conformation, such as macromolecules, supermolecules, and micelle or pseudomicelle structures (18). DOM conformation is still a subject of debate. It has been stated that DOM conformation determines its appearance and affects its interaction with HOCs (19). Examination of DOM shape, or conformation, could improve our understanding toward molecular organization of DOM. Because of the newly developed techniques, DOM conformation change can be investigated based on direct observations. For example, atomic force microscopy (AFM), transmission electron microscopy, and dynamic light scattering (DLS) or photo-correlation spectroscopy were all applied to study the conformation of DOM (20, 21). The results showed that the aggregation of DOM was affected greatly by water chemistry, such as pH, ionic strength, and ion valence. Previous studies demonstrated that decreasing pH and increasing ionic strength and ion valence could promote DOM aggregation. However, the influence of these aqueous conditions on the conformation of DOM and its sorption properties was not discussed extensively. As a matter of fact, the conflicting results on water chemistry effect on  $K_{\text{DOC}}$  could be mainly due to the lack of clear relationships between DOM conformation and its sorption characteristics.

The objectives of this study were (1) to examine the influence of pH, ionic strength, and DOM concentration on its sorption properties using a newly designed method; (2) to investigate the conformation change of DOM under different water chemistry conditions with the aid of AFM and DLS; and (3) to correlate the conformation change of DOM to its sorptive properties.

## Experimental Section

**Chemicals.**  $^{14}\text{C}$  labeled and unlabeled pyrene (PYR) were purchased from Sigma-Aldrich chemical company (St. Louis, Missouri) and were used without further purification. These chemicals were dissolved in methanol separately as stock solutions. All other chemicals and solvents were better than analytical grade. Solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH.

**Preparation of Dissolved Humic Acids.** Commercial Aldrich humic acid (HA) is in sodium salt form, thus it is purified as for Amherst peat HA (12). Briefly, the original particles were dissolved with the aid of NaOH, centrifuged, and filtered. HA was reprecipitated using HCl, and the supernatant was discarded. An aliquot of each purified HA (0.1 g) was dissolved overnight in 2 mL of NaOH (0.5 M) and was mixed with 100 mL of  $\text{NaN}_3$  (200  $\text{mg L}^{-1}$ ) to make a DOM

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solution. NaOH may slightly cause hydrolysis of HA, but hydrolysis would not affect our results because a common DOM solution was used for a given HA. The DOM solution was enclosed in a dialysis membrane (SnakeSkin 3500 Da, Pierce) and was soaked in  $\text{NaN}_3$  solution. The  $\text{NaN}_3$  solution was refreshed everyday for three days. The  $\text{NaN}_3$  solution was then replaced by deionized water and was refreshed everyday for three days. After this procedure, any molecule smaller than 3500 Da and free ions were all discarded. The solution was kept in a refrigerator as a DOM bulk solution and can be stored for one month. This solution was measured using a TOC analyzer (5000A, Shimadzu, Kyoto) for its total organic carbon content. The DOM solution made from Amherst peat HA was noted as PDHA, and that made from Aldrich HA was noted as ADHA. The functional groups and elemental composition of PDHA and ADHA were presented previously (12).

#### Batch Sorption Experiment Using Dialysis Membrane.

The dialysis membrane was soaked in 1 M  $\text{NaHCO}_3$  (30 min) and 1 M  $\text{Na}_2\text{CO}_3$  (30 min), and then washed continuously with running distilled water (30 min). The membrane was tied at one end and placed inside a 40 mL vial. DOM solution and PYR solution were added inside the bag to reach a volume of 25 mL, and deionized water was added to fill the outside of the bag. As previously discussed (16), batch sorption experiment with a fixed DOM concentration and varied solute concentrations is a proper design for investigating the interaction mechanism. Therefore, DOM was made at 20 mg OC  $\text{L}^{-1}$  inside the bag, and PYR was added to reach 5–120  $\mu\text{g L}^{-1}$ . Because water goes through the dialysis bag freely by diffusion, the actual volume of the solution outside the bag was measured at the end of equilibration. The actual DOM concentration inside the bag was recalculated based on the volume measurement. DOM concentration varied less than 5%; thus, this minor DOM concentration change did not affect sorption of PYR. The headspace in the vial was kept minimal by adding the background solution outside of the bag to reduce vapor loss. The vials were sealed using Teflon lined caps immediately after adding solutions in both sides of the bag. The open end of the bag was pressed under the cap, and the bag was thus sealed. After shaking the vials in dark for two days, the caps were released and samples were taken from both sides of the bags for scintillation counting. Preliminary experiments indicated that PYR sorption would reach the equilibrium within 24 h. The sample was mixed with 7 mL of scintillation cocktail, and the DOM concentration in the scintillation counting vial was below 10 mg OC  $\text{L}^{-1}$  to avoid any effect of DOM on PYR measurement (12). PYR concentration outside the bag stands for free solute, whereas concentration inside bag is the sum of free and bound PYR. The concentration of bound PYR was calculated by the concentration difference between both sides and was normalized by DOM concentration (12). All samples, including control (without DOM), were run in duplicate.

The effect of pH, aluminum ions, and DOM concentration was all investigated using the regular batch sorption experiment (various solute concentration at a fixed DOM concentration), and the sorption isotherms were compared. It should be noted that when the original DOM bulk solution was mixed with ionic strength-adjusted or pH-adjusted background solution, then the pH of solution was always changed because of the replacement of aluminum ions and/or the reaction of hydroxyl groups with hydrogen in DOM. Therefore, to investigate the effect of ions, the pH of DOM solution after the addition of Al was adjusted to  $\text{pH } 7.0 \pm 0.1$ , and the background solution added in both side of the bags had a same ionic strength. When investigating pH influence, the DOM solution was adjusted to pH 4, 7, or 11, and the background solution adding to both sides of the dialysis bags was also adjusted to pH 4, 7, and 11, respectively.

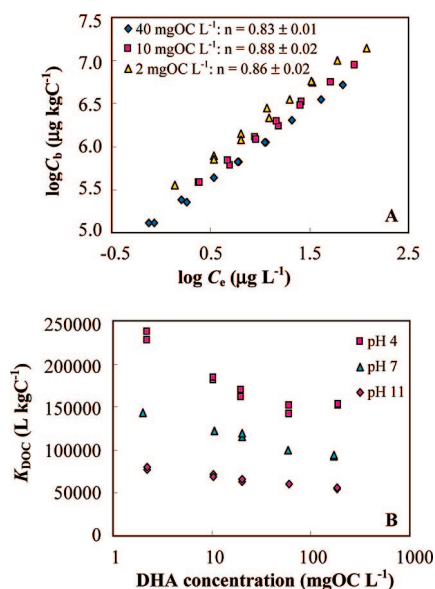
**Multibag Equilibration System (MBES).** The MBES method was developed to compare  $K_{\text{DOC}}$  at a same free-solute concentration (Figure S1, Supporting Information). Briefly, five dialysis bags (20 mL each) containing different DOM concentrations, but with a same water chemistry condition, were tied up at both ends and were placed into one common container (200 mL). PYR solution with the same water chemistry as the DOM solution but no DOM was added outside the bags. The container was sealed immediately with aluminum foil and helical stoppers. After shaking the container in the dark for two days, the samples were taken from both sides of the bags. The weight of each bag was recorded at the end of the experiment to calculate the final concentration of DOM. As in the above batch sorption experiments, the pH and ionic strength of DOM and background solutions were separately adjusted. No precipitation was observed for all the conditions during the equilibration time with continuous shaking (Figure S2, Supporting Information).

**Size Distribution and Zeta Potential Measured by Dynamic Light Scattering.** Dynamic light scattering (DLS) is one of the most effective techniques for the determination of hydrodynamic diameter of colloidal species ranging from long chain polymer to mineral particles (20). The intensity of the light scattered is dependent upon the particle size as well as the number of particles present. Zeta potential is the charge of colloidal materials developed under different solution conditions and can also be determined by DLS using laser Doppler electrophoresis. The setting of the instrument was ascertained by measuring the zeta potential ( $-55 \pm 5$  mV) of the standard latex sample. The samples were put inside a capillary cell and were analyzed on a Malvern Zetasizer (Nano Series, Malvern Instruments). The temperature of the instrument was maintained at  $25 \pm 0.1$  °C during measurement.

**Atomic Force Microscopy (AFM) Study on DOM Conformation.** AFM is a powerful technique for investigating DOM conformation (21). Because muscovite provides an atomically flat plate surface, DOM molecules were coated on muscovite surface and were examined using AFM to investigate the conformation of DOM under different conditions. Briefly, the freshly cleaved muscovite surface was dipped into DOM solution for 20–30 min to allow sorption of DOM molecules. The muscovite samples were then placed into deionized water to remove weakly sorbed particles, followed by air drying. The samples were then analyzed using a tapping mode AFM (TMAFM, Dimension 3100). This procedure avoided the disturbance of DOM solution and washed off free forms of  $\text{Al}^{3+}$  or  $\text{H}^+$ ; thus, the images would represent the DOM conformation as in original solution. The cantilever used in our experiment was tuned in the 0–300 kHz regions using the autotune option. The amplitude set point ( $A_{\text{sp}}$ ) was maintained at 1.2 V for all measurements. The scanning speed was maintained at 1.00 Hz. Height images were obtained and were examined using the NanoScope (6.13 R1).

## Results and Discussion

**Advantage of MBES Experiment.** Nonlinear sorption resulted in varied sorption coefficients at different free solute concentrations ( $C_f$ ). In traditional single initial solute concentration experiments for HOC–DOM interaction studies, the comparison of  $K_{\text{DOC}}$  was not based on the same free solute concentration. Thus, the difference between  $K_{\text{DOC}}$ s at different DOM concentrations could be underestimated. A detailed demonstration is presented in Figure S3, Supporting Information. In HOC sorption studies on solid particles, single point sorption coefficients were calculated based on Freundlich modeling and were compared at a specific free solute concentrations (13). This concept should also be applied in



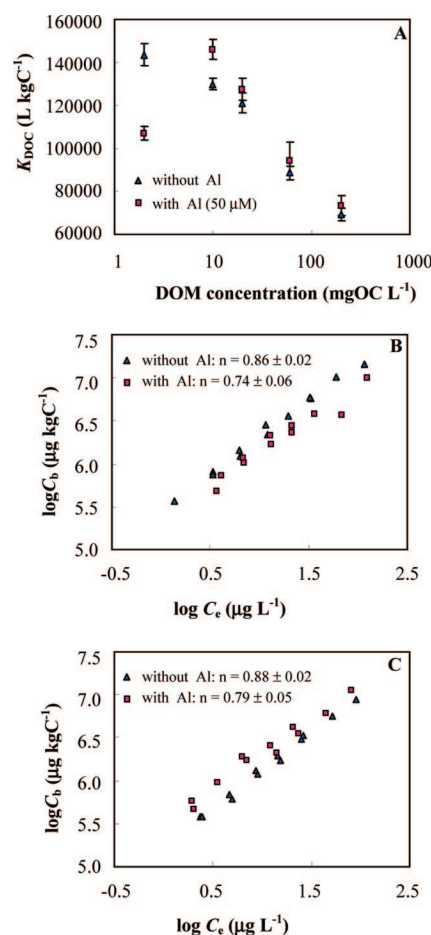
**FIGURE 1.** Effect of ADHA concentration on PYR sorption. Both regular batch sorption study (A) and the MBES experiment (B) showed DOM concentration-dependent sorption. Increasing DOM concentration resulted in decreased sorption, and the trend is more obvious at pH 4 (B). The fitting results of sorption isotherms are presented in Table SI, Supporting Information. The measured free PYR concentration is  $7.5 \mu\text{g L}^{-1}$  in MBES.

HOC–DOM interaction studies. The design of MBES was for this purpose. In our MBES experiment, all dialysis bags containing different concentrations of DOM were soaked in one common container. No matter how much solute bound by DOM of different bags, the free PYR concentration ( $C_f$ ) was always the same for all bags. Therefore, the comparison of  $K_{\text{DOC}}$  at different DOM concentrations is based on an exactly same equilibrated free PYR concentration, and thus is valid and reliable.

**Effect of DOM Concentration on PYR–DOM Interaction.** Decreased PYR binding with increasing DOM concentration was observed in both regular batch and MBES experiments for both ADHA and PDHA (Figures 1 and S4). Consistent with our previous result (12), the nonlinear interaction between DOM and PYR was generally observed. The  $n$  values were not significantly different between different DOM concentrations ( $P < 0.05$ , Figures 1A and S4A).

The effect of DOM concentration on HOC–DOM interaction has been investigated in several studies. Negative relationships between DOM concentration and sorption coefficient were observed (3, 5, 7, 9–11). However, because of large variations, the DOM concentration effect was not obvious, and the conclusion was not convincing (9, 11), or the change of  $K_{\text{DOC}}$  with DOM concentration was considered experimental artifacts (5, 7). However, it should be noted that in these previous studies single initial solute concentration was used often. As discussed earlier, the difference of  $K_{\text{DOC}}$  between different DOM concentrations could be underestimated due to improper experimental design. In both our regular batch and MBES experiments, reduced sorption was observed as DOM concentration increased. The difference was as high as more than 2 times and, thus, could have an impact on HOC fate and bioavailability.

**Effect of pH and the Presence of Al on PYR–DOM Interaction.** Both regular batch and MBES experiments were conducted to investigate the influence of pH and ionic strength on PYR–DOM binding. Promoted PYR–DOM binding with decreased pH was observed using MBES (Figures 1B and S4B) as in the regular batch experiment previously reported (12). After the addition of Al ( $50 \mu\text{M}$ ),  $K_{\text{DOC}}$  decreased

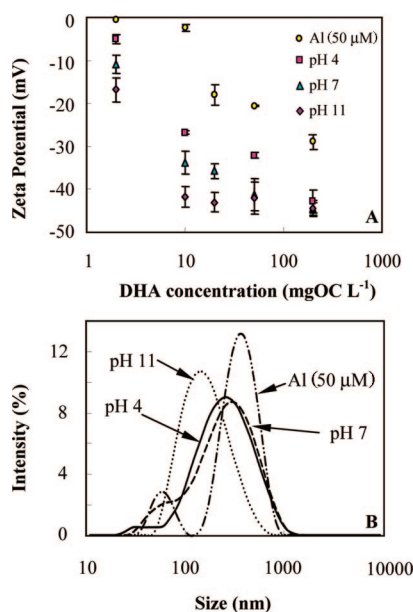


**FIGURE 2.** Effect of Al ( $50 \mu\text{M}$ ) on PYR sorption by ADHA. Addition of Al resulted in both an increase and a decrease of  $K_{\text{DOC}}$  depending on DOM concentration in the MBES system (A). Bars stand for standard error for four replications. The decreased and increased sorption after addition of Al was also observed in regular batch experiments at DOM concentrations of 2 (B) and 10  $\text{mg L}^{-1}$  (C), respectively. The fitting results of sorption isotherms are presented in Table SI.

at a DOM concentration of  $2 \text{ mg OC L}^{-1}$ , increased at  $10 \text{ mg OC L}^{-1}$ , and showed an increased trend but did not significantly change at higher DOM concentrations (Figure 2A). Regular batch experiments also showed that the addition of Al increased and decreased sorption at DOM concentration of 2 and  $10 \text{ mg OC L}^{-1}$ , respectively (Figure 2, panels B and C). Similar phenomenon was observed for PDHA (Figure S5, Supporting Information).

The influence of ionic strength and pH on HOC–DOM interactions has attracted research interest for decades. However, no consistent results have been obtained. Both positive (2, 3) and negative (4, 5) relationships between pH and  $K_{\text{DOC}}$  have been reported. Ionic strength is an even more complicated factor. Opposite trends of the ionic strength effect on  $K_{\text{DOC}}$  (such as negative (2, 6) and positive (7) relationships) was observed. In addition, different trends in one research were reported depending on pH values (22) or ion species (23). Based on the observation of  $K_{\text{DOC}}$  variation, Lee et al. (24) proposed a three-stage variation model to describe DOM conformation change with increasing ionic strength, namely, variation of HA structural configuration, HA aggregation, and salting-out effect. However, if they used ions that easily cause DOM precipitation, such as Fe and Al, a fourth stage, as precipitation, could be included. The salting-out effect has been applied to explain the enhanced HOC sorption after the addition of ions (5). However, the enhanced HOC sorption is not because of HOC–DOM interactions but





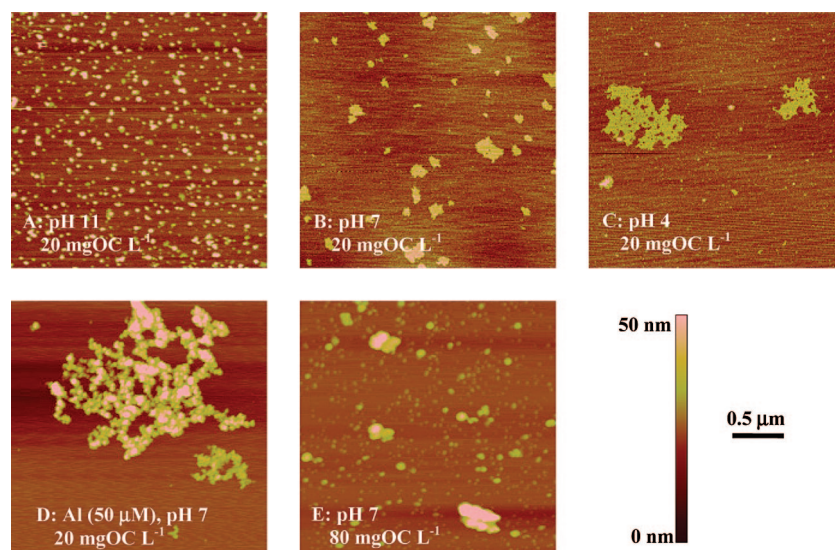
**FIGURE 3.** Zeta potential vs DOM concentration at different pHs (A) and typical intensity-based particle size distribution at a DOM concentration of 20 mg C L<sup>-1</sup> under different conditions (B). Zeta potential decreases as DOM concentration increases. At lower DOM concentrations, zeta potential showed a trend of pH 4 > pH 7 > pH 11. The addition of Al resulted in a significant increase of zeta potential. At pH 11, particle size distribution was log-normal distributed, with the peak appearing at 140 nm. The major peak shifted to 255 and 295 nm for pH 4 and 7, respectively, indicating a generally increasing molecular size. A small peak at 30–50 nm could also be noticed at pH 4 and 7, indicating the existence of molecules with reduced size compared to those at pH 11. Bimodal distribution was observed after the addition of Al. Data of replicate experiments are presented in the Supporting Information (Figures S7–S10).

is due to reduced HOC solubility. In this study, the ionic concentration was low (50 μM) and was not high enough for salting-out of PYR to take place (Figure S6, Supporting Information). In addition, the reduction of  $K_{\text{DOC}}$  at 2 mg OC L<sup>-1</sup> in the presence of Al could not be explained by salting-out. Therefore, the variation of  $K_{\text{DOC}}$  with the change of water chemistry should have arisen from the conformation change of DOM molecules.

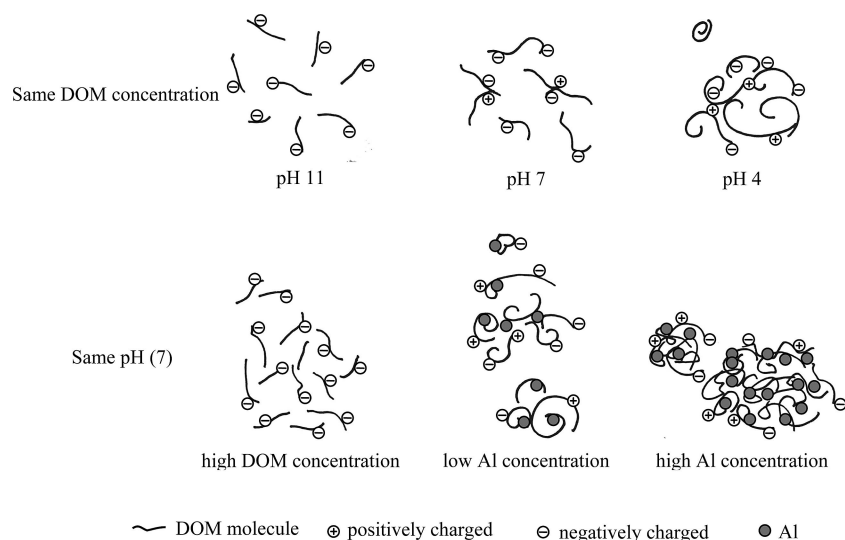
Explanations on  $K_{\text{DOC}}$  variation based on DOM conformation change have been provided in several studies. For example, the positive relationship between pH and  $K_{\text{DOC}}$  was due to the decurling (3) or loose structure (2) at alkaline pH that makes the sorption sites more available to HOCs, whereas the decreased sorption with increasing pH was mostly attributed to the increased polarity of DOM molecules due to the deprotonation of functional groups (4, 5). These explanations for opposite results all seem to be consistent with DOM molecular conformation change at different pHs (25). However, none of these were based on any direct conformation observation. Thus, the explanations tend to be speculative. On the other hand, the DOM molecular conformation studies are seldom coupled with HOC–DOM interaction results. Therefore, DOM conformation was studied in this work along with PYR sorption experiment.

**Conformation of DOM Under Different Conditions.** Zeta potential decreased with increasing DOM concentration at a specific pH, and decreased zeta potential was observed with increasing pH at a fixed DOM concentration (Figure 3A). However, at a DOM concentration of 200 mg OC L<sup>-1</sup>, the difference of zeta potentials between different pHs was not obvious. The addition of Al (50 μM) increased zeta potential (less negatively) significantly at all DOM concentrations (Figure 3A). Zeta potential is the index for the charge of colloids, and higher negative charges indicate higher electronic double layer potential of the colloidal DOM molecules. Because DOM molecules have structures with various functional groups, molecular repulsion and attraction could take place for both inter- and intramolecules. These interactions were shown in DLS results. Particle sizes had a log-normal distribution at pH 11 with the peak centered at 140 nm (Figure 3B). The major peak shifted to 255 and 295 nm for pH 4 and 7, respectively, indicating a generally increasing molecular size. Interestingly, a small peak at 30–50 nm could also be seen at pH 4 and 7, indicating the existence of molecules with decreased size compared to those at pH 11. The small-size molecules became clearer after the addition of Al, and a bimodal distribution was observed (Figure 3B).

DOM is a mixture of molecules with various functional groups. At pH 11, most functional groups, such as carboxylic and phenolic acid groups, were completely ionized. Therefore, the molecules are dispersed because of electrostatic repulsion (as shown by the lower zeta potentials, Figure 3A). In this system, the DOM solution is relatively uniform, and



**FIGURE 4.** AFM images showing different DOM conformations under various conditions. Aggregation increased significantly from (A) to (C) as pH decreased from 11 to 4. Sponge-like aggregates were observed for DOM at pH 4 (C) and with the presence of Al (D). Aggregates were also observed at high DOM concentration (E).



**FIGURE 5. Schematic diagram of DOM conformation under different conditions, highlighting the change of zeta potential. At alkaline pH, low zeta potential (i.e., more negative) results in inter- and intramolecular repulsion. The molecules are dispersed and stretched. As pH decreases, zeta potential increases and electrostatic repulsive force decreases. The introduced Al not only increases zeta potential, but also functions as bridging ions. Therefore, even larger aggregates are observed. Well-organized small particles resulting from self-curling (i.e., intrainteraction) could also be observed. However, as Al load further increases, the cross-linking and the size of aggregates further increase, and consequently, DOM precipitates out.**

DLS measurement always showed a low polydispersity index, indicating a relatively stable conformation of DOM molecules or increased colloidal stability. However, at pH 4 and 7, as zeta potential increased (became less negative), the repulsion between molecules decreased, and aggregation took place between molecules. Hence, the particle sizes increased. But as for individual molecules, self-curling reduced apparent molecular size. Addition of Al enhanced the zeta potential closer to 0 mV, under which aggregation and self-curling extensively occurred, and a clear bimodal distribution indicated both inter- and intramolecular interactions. In our results, the particle size difference at pH 4, pH 7, and with the presence of Al was not significant, probably because of the disturbance of DOM solution during the sampling and measuring procedure.

Using AFM, significant aggregation was observed at pH 4 or in the presence of Al (Figure 4, panels C and D). Sponge-like structure was observed for these conditions, indicating formation of big aggregates of DOM molecules. Furthermore, the molecules with smaller apparent size than that at pH 11 were also seen in these images. The image at pH 11 showed uniform small particles, which indicates a relatively uniform DOM solution (Figure 4A). Therefore, AFM images are consistent with DLS measurements, providing further information for aggregate size and 3D structures of DOM.

Reduced particle size at decreased pH or increased ionic strength was reported in other studies (26), but with emphasis on self-curling of DOM molecules. However, aggregation between DOM molecules should also occur because of the decreased repulsion at decreased pH or increased ionic strength, as indicated by our zeta potential measurements. We observed both increased and decreased particle size (i.e., bimodal distribution) at decreased pH or increased ionic strength, and consistent results were obtained using different techniques.

Aggregated particles were also observed as DOM concentrations increased (Figure 4E). The same phenomenon was reported by other researchers (27, 28). Although zeta potential was very low for high DOM concentration solutions, DOM molecules could aggregate because of the reduced free space for their movement and decreased intermolecular distance.

**Implication for HOC—DOM Interactions from Molecular Conformation.** Al has been proven to be a very effective

coagulant for DOM (29), because Al could neutralize negative charges and reduce the double layer thickness and repulsion between DOM molecules. In addition, Al could form a bridge between DOM molecules, thereby promoting aggregation. After investigating the fate of applied Al in a model humic substance, Kazpard et al. (30) concluded that, at low Al concentrations, hydrated Al selectively bound with hydroxylic and phenolic groups, whereas at high Al concentrations, hydrated Al could bind with other functional groups. Thus, cross-linking between DOM molecules could be substantially enhanced, molecular volume decreased, and the density of the aggregates increased, which can subsequently cause precipitation. They also characterized the hydrophobic microenvironment of the humic substance using polarity sensitive fluorescence of PYR. They observed a decreased polarity of humic substance solution after the addition of Al; however, further addition of Al increased its polarity, consistent with our results on the effect of Al on  $K_{\text{DOC}}$  at different DOM concentrations. In both our regular batch and MBES experiments, decreased  $K_{\text{DOC}}$  was observed at low DOM concentration after adding Al. Although Al concentration was always 50  $\mu\text{M}$ , the organic carbon-based loading of Al was higher for low DOM concentration solution than that of high DOM concentration. Therefore, a more compact form of aggregates could be formed; hence,  $K_{\text{DOC}}$  decreased due to low availability of binding sites.

Generally speaking, the aggregation of DOM increased with decreasing pH, increasing ionic strength and DOM concentration in this study. However, the binding coefficient did not follow the same order. The  $K_{\text{DOC}}$  was found to increase with decreasing pH, with increasing ionic strength, and with decreasing DOM concentration. It could be clearly noticed that in our DOM conformation study the aggregation coupled with an increase of zeta potential generally enhanced PYR sorption, whereas the aggregation coupled with a decrease or without a change of zeta potential decreased PYR sorption. This phenomenon indicates that the reduction of repulsion led to the aggregation in which hydrophobic regions were assembled together. Therefore, sorption was enhanced (12). However, the increase of DOM concentration resulted in a decrease of free space for the movement of DOM molecules

and aggregated in a way the sorption was decreased, probably due to the reduced numbers of binding sites on a carbon basis.

Figure 5 is a schematic illustration for DOM conformation change regarding its sorption with HOCs. The formation of the hydrophobic region is the key factor affecting HOC–DOM interactions, and zeta potential plays a very important role in the formation of the hydrophobic region during DOM aggregation. At alkaline pH, low zeta potential (i.e., more negative) results in inter- and intramolecular repulsion. The molecules are dispersed and stretched out. In this case, a limited hydrophobic region could be formed, and thus, the sorption coefficient ( $K_{\text{DOC}}$ ) with HOC is low. As pH decreases, zeta potential increases, and electrostatic repulsive force decreases. The introduced Al not only increases zeta potential, but also functions as bridging ions. Therefore, even bigger aggregates are observed. Well-organized small particles resulting from self-curling could also be observed. The self-curling of and aggregation between DOM molecules form large hydrophobic regions. Consequently, the sorption increases. However, as Al load further increases, the cross-linking and the size of aggregates further grow, and consequently, DOM will precipitate out.

It is well-known that  $K_{\text{DOC}}$  varied with the change of water chemistry and DOM origin, and no general method could be employed to predict it. This study demonstrates that  $K_{\text{DOC}}$  change could be explained by DOM conformation change. Therefore, it is possible to combine sorption and conformation results. Furthermore, research in this area is important for understanding HOC–DOM interaction mechanisms and for developing models to more accurately predict  $K_{\text{DOC}}$  and the fate of HOCs in the environment.

## Acknowledgments

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## Supporting Information Available

Fitting results of the isotherms from regular batch sorption experiment (Table S1); multibag equilibration system (MBES) experimental design (Figure S1); appearance of DOM solution with the presence of Al (50  $\mu\text{M}$ ) used in this study (Figure S2);  $K_{\text{DOC}}$  comparison based on different experimental designs (Figure S3); effect of PDHA concentration on PYR sorption (Figure S4); effect of Al (50  $\mu\text{M}$ ) on PYR sorption on PDHA (Figure S5); effect of the Al ions (50  $\mu\text{M}$ ) on PYR analysis (Figure S6); intensity-based particle size distribution of 20 mg OC L<sup>-1</sup> ADHA at pH 4, 7, and 11, measured by dynamic light scattering of ADHA concentrations of 20, 50, and 200 mg OC L<sup>-1</sup> (Figures S7–S9, respectively), and in the presence of 50  $\mu\text{M}$  Al (Figure S10). These materials are available free of charge via the Internet at <http://pubs.ac.org>.

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