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# Adsorption of humic acids to lake sediments: Compositional fractionation, inhibitory effect of phosphate, and implications for lake eutrophication

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GRAPHICAL ABSTRACT

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## HIGHLIGHTS

- Sole and competitive adsorption with phosphate of humic acids (HA) of three sources were studied.
- Adsorption capacity of sediments was highest for HA from algae-dominated lake.
- Carboxyl-containing molecules, proteins and polysaccharides were preferentially adsorbed.
- Inhibition extent of phosphate on HA adsorption was closely related to HA composition.
- Algae-derived organics can promote P mobilization from sediments and enhance internal P loading.

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## ABSTRACT

Humic acid (HA) and phosphate interactions play a vital role in the biogeochemical cycle of carbon and nutrients and thus the trophic state of a lake. The adsorption behavior of HAs to sediments in the absence and presence of phosphate was investigated in this study. Three types of HAs were used, AHA from algae-dominated lake sediments, MHA from macrophyte-dominated lake sediments, and a reference HA (RHA) with terrestrial sources. The adsorption capacity of lake sediments was highest for AHA, which can be explained by that AHA contained more carboxyl-containing molecules, proteinaceous compounds and polysaccharides that were preferentially adsorbed by minerals. Phosphate showed a stronger inhibitory effect on MHA adsorption than on AHA adsorption, suggesting that AHA can more effectively replace phosphate adsorbed to sediments. Our findings show that the functional groups of organic compounds control not only their fractionation and burial but also their ability to replace phosphate in sediments. We propose a novel mechanism to explain the legacy effect of lake eutrophication. That is, as lakes shift from a macrophyte-dominated state to more eutrophic, algaedominated state, increasing algae-derived organic compounds can promote the release of phosphate from sediments, forming a positive feedback loop that sustains internal phosphorus loading and hence lake eutrophication.

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#### 1. Introduction

Although lakes cover less than 4% of Earth's surface (Verpoorter et al., 2014), annual organic carbon (OC) burial in lake sediments could amount to about 25-50% of the OC burial in marine sediments (Dean and Gorham, 1998; Drake et al., 2018). The amount and type of OC buried in sediments are driven by the adsorption or coprecipitation of organic compounds with minerals (Lalonde et al., 2012; Riedel et al., 2013; Sowers et al., 2019). The chemical composition of organic matter (OM) influences its adsorption ability to minerals. Previous studies showed that proteins and carbohydrates enriched with nitrogen and/or oxygen favored the formation of inner-sphere complexes with iron, which facilitated the preservation of highly labile organic compounds in sediments (Henrichs, 1995; Lalonde et al., 2012). Aromatic and carboxylic-containing species were preferentially sorbed to iron (oxyhydr)oxides (Coward et al., 2019; Sowers et al., 2019). The pervasive carbon (C) forms sorbed to soil clay particles included aromatic C, carboxyl C, and polysaccharides (Chen et al., 2014a). These observations suggest that organic compounds with varied functional groups exhibit heterogeneous adsorption characteristics, which could result in compositional fractionation of OM at the water-sediment interface. leading to compositionally distinct compounds between the dissolved. mobile phase (i.e., in the water column) and the sequestered, preserved phase (i.e., in the lake sediment).

Phosphorus (P) is one of the essential nutrients for aquatic biota in lakes, serving as a key moderator for phytoplankton growth and algae bloom. Sediments represent a major pool of P in lakes, and P released from sediments, i.e., internal loading of P, has been considered as a primary factor maintaining lake eutrophication after external loading reduction (Sondergaard et al., 2003). The sequestration of P in sediments occurred mostly through the association with mineral/metal oxide, and this process can compete with the association of OM with minerals (Deng et al., 2019; Luo et al., 2021; Weng et al., 2008). The presence of OM was found to inhibit the sequestration of P by sediments, and the extent of inhibition varied due to the chemical compositions of OM (Du et al., 2019). Similarly, phosphate also competed with organic compounds, such as aromatics, chromophores and acidic groups, for the binding sites on minerals, thereby inhibiting the adsorption and fractionation of OM (Li et al., 2021).

Both OM and P and their interactions are tightly linked to the trophic status of a lake. As nutrient (N or P) loadings increase, shallow lakes shift from a clear state dominated by macrophytes to a turbid state dominated by algae (Scheffer, 2004; Schindler et al., 2008). Algae-derived OM contained more protein-like substances with lower aromaticity than macrophyte-derived OM (Du et al., 2019; Xu et al., 2013; Zhang et al., 2020). Zhang et al. (2020) observed that algae-derived OM and macrophyte-derived OM possessed different characteristics of adsorption onto goethite, varying as a function of molecular size, aromaticity, and functional groups. However, few studies have investigated the interactions between P and OM of diverse origins and compositions during adsorption. This study aimed to answer several questions that remain open. How do the presence and quantity of P influence the amount and compositional fractionation of OM during the adsorption to sediments? Similarly, how do the source and composition of OM influence the adsorption of P to sediments? Addressing this question is crucial to forming an accurate understanding of the sequestration of both P and OC, given that the sources and compositions of natural organic compounds in lakes are heterogeneous and variable.

Here, we evaluated the interaction of OM of different origins (from macrophyte- and algae-dominated lake) with P during their adsorption to lake sediments. We hypothesize that the compositional differences of OM from two typical trophic states of shallow lakes — algae-dominated and macrophyte-dominated — would lead to different adsorption behaviors of OM to lake sediments for both sole adsorption and competitive adsorption with P. We performed adsorption experiments, where humic acids (HAs) extracted from algae-dominated sediments (AHA)

and macrophyte-dominated sediments (MHA) were used to represent dissolved OM (DOM) in the lake water column and untreated sediments were used as the adsorbent. We further included a reference HA (RHA) with a terrestrial source for comparison, as lacustrine DOM contains compounds of both terrestrial and autochthonous origins. To evaluate adsorption behaviors, we established the adsorption isotherms of three HAs, characterized the compositional fractionation of HAs due to adsorption, and quantified the inhibitory effect of phosphate. The composition of HAs was analyzed by combining ultraviolet-visible absorption spectroscopy (UV-Vis), excitation-emission matrix fluorescence coupled with parallel factor analysis (EEM-PARAFAC) and Fouriertransform infrared (FTIR) spectra. Our results provided new insight into the effect of OM compositions on OM-P interactions during adsorption, and how these effects influence the mobilization and sequestration of carbon and phosphorus and their role in the development and recovery of eutrophic lake.

## 2. Materials and methods

## 2.1. Materials

Taihu Lake is a large shallow eutrophic lake located in a highly developed region of eastern China. The lake has a surface area of 2,338 km<sup>2</sup>. The northern region of Taihu Lake is a typical algae-dominated lake zone with frequent cyanobacterial blooms, while the eastern region is a typical macrophyte-dominated lake zone (Zhou et al., 2021b). Two surface sediments were collected in summer 2018, from an algae-dominated lake zone in the north (SedA, 31°26'3" N, 120°11'18" E) and a macrophyte-dominated lake zone in the east (SedM,  $31^{\circ}2'3''$ N, 120°25'47" E), respectively. The sediments were freeze-dried, ground, and homogenized. AHA was extracted from SedA, and MHA was extracted from SedM. The extraction followed a method developed by the International Humic Substance Society (IHSS) for the extraction of humic substances from soils (http://humic-substances.org/isolation-of-ihss-soil-fulvic-and-humic-acids/). HA is only an operationally defined concept and consists of heterogeneous components. A detailed description of the extraction and purification procedure is given in the supplementary materials (Text S1 and Fig. S1). The basic geochemical parameters of the sediments, including the content of organic carbon, P, and metals, are shown in Table S1. The reference HA (RHA) (CAS: 1415-93-6) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Phosphate stock solution was prepared using  $\rm KH_2PO_4$ , and three HA stock solutions were prepared with RHA, AHA and MHA, respectively. The concentrations of phosphate and HAs were expressed in elements P and C, respectively.

## 2.2. Adsorption experiments

Three types of humic acid (RHA, AHA and MHA) and two sediments (SedA and SedM) were used in adsorption experiments, yielding six groups – SedA-RHA, SedA-AHA, SedA-MHA, SedM-RHA, SedM-AHA, and SedM-MHA. In order to evaluate the adsorption process of HAs and P onto lake sediments, sediments used as the adsorbent were not pretreated to remove OC or P to retain the original sediment structure and properties. We evaluated the background concentration of OC and phosphate released from the sediment itself in the experimental system, which was < 5 mg/L for OC and < 0.05 mg/L for phosphate. These values were much lower than those added to the system, indicating that the effects of OC and phosphate from the sediment itself were negligible.

## 2.2.1. Adsorption isotherms of HAs and phosphate

Twenty mL aqueous solutions with a certain concentration of phosphate (0–50 mg/L) or HA (0–100 mg/L) were added into 50-mL centrifuge tubes. The pH of the solution was adjusted to  $7 \pm 0.2$  with 1 M HCl or 1 M NaOH. Subsequently, 0.4 g homogeneous sediment was

placed in the tubes, which were sealed and oscillated at an isothermal shaker at 25 °C and 200 rpm for 24 h. These conditions, such as solid-liquid ratio and the reaction time, were chosen based on preliminary experiments to ensure that the adsorption of HA or phosphate by sediments reaches the state of adsorption equilibrium or saturation. The samples were then centrifuged, and the supernatants were filtered through a 0.45  $\mu$ m cellulose acetate membrane filter. The concentrations of phosphate and HA of filtered supernatants were determined.

#### 2.2.2. HA&P adsorption experiments

To evaluate the simultaneous adsorption of phosphate and HA, twenty mL of aqueous solutions containing both phosphate (0.1, 0.5, 2, 5, 10 and 20 mg/L) and HA (50 mg/L) were added into 50 mL centrifuge tubes. The pH of solutions was adjusted to  $7 \pm 0.2$ , followed by the addition of 0.4 g sediment to each tube. The samples were shaken at 25 °C, 200 rpm for 24 h, and subsequently centrifuged and filtered to obtain the supernatant. A fraction of the supernatant was freeze-dried for FTIR measurement, and the remaining fraction was used for the analysis of phosphate and HA (see 2.3 Analytical methods). Each group of the experiments was performed in triplicate.

#### 2.3. Analytical methods

#### 2.3.1. DOC or P concentrations

Dissolved organic carbon (DOC) concentration of HAs was measured on a total organic carbon analyzer (Tekmar Torch, USA). Phosphate concentration was determined using the molybdate blue method on a Lambda 35 UV-Vis spectrophotometer (Perkin Elmer, USA) (Murphy and Riley, 1962). The HA or phosphate adsorption capacity of sediments was calculated as the ratio of the reduced amount of DOC or P in the solution to the associated sediment mass (mg/g).

#### 2.3.2. HA compositions

The absorption spectra of HA were scanned between 200 and 800 nm at 1 nm intervals using a lambda 35 UV-Vis spectrophotometer (Perkin-Elmer, USA). Milli-Q water was run daily as the blank. Several absorbance-based indices were calculated. a254 was the absorption coefficient at 254 nm, and it indicates the abundance of chromophoric OM and aromatic compounds (McKnight et al., 2001; Zhang et al., 2021). SUVA $_{254}$ , calculated as the ratio of absorbance at 254 nm to DOC concentration (unit in  $L \cdot mg^{-1} C \cdot m^{-1}$ ), can be used to estimate the aromaticity of OM. A higher SUVA<sub>254</sub> value indicates a higher degree of aromaticity and humification (Weishaar et al., 2003; Zhou et al., 2016). The spectral slope of  $S_{275-295}$  was calculated as the absolute value of the slope of natural logarithm of absorption spectrum from 275 nm to 295 nm, and  $E_2/E_3$  was calculated as the ratio of  $a_{250}$  to  $a_{365}$ . These two indices have been commonly used to characterize the relative molecular weight of OM, and higher values indicate lower relative molecular weights (Haan and Boer, 1987; Helms et al., 2008).

Fluorescence EEMs were collected using a fluorescence spectrometer (Hitachi F-7000). Excitation (Ex) wavelengths ranged from 200 to 450 nm at 5 nm intervals, and emission (Em) wavelengths were from 250 to 550 nm at 1 nm intervals. Several post-acquisition steps were carried out for correction and standardization: (i) the inner filter effect corrected using the absorption spectra (McKnight et al., 2001); (ii) blank correction by subtracting the EEM spectra of Milli-Q water; and (iii) normalization relative to the area of the Raman peak of Milli-Q water (Du et al., 2016). Humification index (HIX) was calculated by dividing the average fluorescence intensity from 435 to 480 nm by the average from 300 to 480 nm at the excitation of 254 nm (McKnight et al., 2001). A HIX value greater than 4 indicates highly humified OM (Zsolnay et al., 1999).

A PARAFAC model including all HA samples was established using the DOMFluor toolbox in MATLAB R2008a (Stedmon and Bro, 2008). A five-component (C1–C5, in Raman unit, R.U.) model was verified using the split-half analysis and random initialization. The relative abundance of the PARAFAC component (%C1–%C5) was calculated as the fluorescent intensity of each fluorescence component divided by the summed intensities of the five components. The adsorption percentage of the PARAFAC components was calculated as the change in the fluorescent intensity due to adsorption (the initial intensity minus the post-adsorption intensity) divided by the initial intensity, and this parameter (%) was used to measure the adsorption ability of each fluorescence component.

The FTIR spectra were recorded on a Smart iTR Nicolet iS 10 Fourier transform infrared spectrometer (Thermo Nicolet, USA) over the 4000–650 cm<sup>-1</sup> range. The collected FTIR spectra were baseline corrected, smoothed, and transformed to absorbance spectra using the Nicolet OMNIC software (Thermo, USA). The two-dimensional FTIR correlation spectroscopy (2D-FTIR-CoS) analysis was performed using the 2D Shige software (Noda and Ozaki, 2005). The application of synchronous and asynchronous maps revealed the effect of P on HA adsorption. Compared with one-dimensional FTIR spectra, 2D-FTIR-CoS improves the spectral resolution and extends the spectrum to a second dimension and hence allows the deconvolution of overlapping peaks (Noda, 2012; Xu et al., 2013).

#### 2.4. Data analysis

The isotherm data were fitted to the Langmuir model and Freundlich model, which were expressed as Eqs. (1) and (2), respectively:

$$q_{e} = \frac{Q_{m}bC_{e}^{1-c}}{1+bC_{e}^{1-c}}$$
(1)

$$q_e = K_F C_e^{nC_e^{-c}} \tag{2}$$

where  $q_e$  (mg/g) is the adsorption amount of HA, *b*, *c* and n are model parameters,  $C_e$ (mg/L) is the equilibrium concentration of HAs,  $Q_m$  (mg/g) is the maximum adsorption capacity, and  $K_F$  is the Freundlich constant related to adsorption strength.

Statistical analysis was done in SPSS (IBM SPSS Statistics 22.0). Differences in the adsorption parameters among different experiment groups were examined using the analysis of variance (ANOVA) with Tukey's HSD post-hoc test.

#### 3. Results

#### 3.1. Compositional characteristics of HAs

The UV-Vis spectra of RHA, AHA and MHA (DOC concentration = 10 mg/L for all three HAs) showed that the absorbance of 200–800 nm was highest for RHA, followed by AHA and then MHA (Fig. S2). The SUVA<sub>254</sub> and HIX values indicated that the aromaticity was RHA>AHA>MHA (Table 1).  $S_{275-295}$  and  $E_2/E_3$  showed that the RHA and AHA had larger molecular weights than MHA (Table 1).

Four humic-like components (C1, C2, C3, and C5) and one proteinlike component (C4) were identified by the PARAFAC model (Fig. 1 and Table S2). C1 was assigned as high-molecular-weight, terrestrial, humic-like DOM that has been identified as an intermediate product formed during the photochemical degradation of terrestrial substances. C2 was categorized as microbially-derived, humic-like fluorescence that originates from reprocessing of terrestrial OM and has relatively low molecular weights. C3 was identified as a ubiquitous humic-like component, and C5 was assigned as terrestrially-derived, humic-like substances that have been reported in a variety of aquatic environments. C4 was identified as proteinaceous materials that correspond to tryptophan-like substances that are more abundant in algae-derived substances than in plant-derived substances. Humic fluorescence dominated all three HAs - humic-like components (the sum of C1, C2, C3, and C5) of RHA, AHA, and MHA were 97.32%, 78.34%, and 70.24% of total fluorescence, respectively (Table 1).

The FTIR spectra provide information about the functional groups of

## Table 1

Spectral characteristics	of RHA, AHA and MHA.
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HA	$\begin{array}{c} \text{SUVA}_{254} \\ \text{L}{\cdot}\text{mg}^{-1} \ \text{C}{\cdot}\text{m}^{-1} \end{array}$	$S_{275-295} * 1000$	$E_{2}/E_{3}$	HIX	C1 %	C2 %	C3 %	C4 %	C5 %
RHA	7.05	6.71	2.63	11.78	44.42	0.94	12.66	2.68	39.3
AHA	3.48	7.31	2.39	6.05	48.23	8.51	10.18	21.66	11.42
MHA	2.63	7.38	2.86	3.81	34.15	12.97	13.73	29.76	9.39



Fig. 1. EEM contours of the fluorescent components (a-e) and excitation/emission loadings (f-j) of C1-C5 identified using EEM-PARAFAC. (Ex: Excitation; Em: Emission).

three HAs (Fig. 2, Table 2). Twin peaks of AHA and MHA at 2920 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> were assigned to C—H stretching of aliphatic compounds. A strong band at about 1640 cm<sup>-1</sup> of HAs was assigned to aromatic C=C vibrations and the carboxyl function group. A band at 1515 cm<sup>-1</sup> of AHA and MHA was assigned to aromatic C=C stretching of lignin/phenolic backbone, and the 1230 cm<sup>-1</sup> band of AHA and MHA was ascribed to C—O stretching of ethers, carboxyl groups and/or phenolic OH. Two peaks at 1030 and 1080 cm<sup>-1</sup> of AHA and MHA were ascribed to C—O stretching and O—H deformation of polysaccharide structures. At 1640 cm<sup>-1</sup>, RHA had one small peak while AHA and MHA



**Fig. 2.** FTIR spectra of HAs before and after adsorption by sediments (SedA: algae-dominated sediment; SedM: macrophyte-dominated sediment; AHA: algae-derived HA; MHA: macrophyte-derived HA; RHA: reference HA).

#### Table 2

Assignment of the principal descriptive FTIR absorption bands in RHA, AHA and MHA samples. (Table compiled based on Artz et al., 2008).

Wavenumber (cm <sup>-1</sup> )	Assignment	Characterization
2920, 2850	C-H stretching of aliphatic CH <sub>2</sub>	Fats, wax, lipids
1720	C=O stretch of COOH or COOR	Carboxylic acid, aromatic esters
1710-1707	C=O stretch of COOH	Free organic acids
1650–1600	Aromatic C=C stretching and/or asymmetric C-O stretch in COO-	Lignin and other aromatics, or aromatic or aliphatic carboxylates
1550	N-H in plane (amide-II)	Proteinaceous origin
1515-1513	Aromatic C=C stretching	Lignin/phenolic backbone
1426	Symmetric C-O stretch from	Carboxylate/carboxylic
	COO- or OH deformation (COOH)	structures (humic acids)
1450	C-H deformations	Phenolic (lignin) and aliphatic structures
1265-1230	C-O stretching of phenolic	Indicative of lignin backbone
(approximately)	OH and/or arylmethyl ethers	
1136	C-O-C stretching	Polysaccharides <sup>a</sup>
1080–1030	Combination of C-O stretching and O-H	Polysaccharides
	deformation	

<sup>a</sup> (Eusterhues et al., 2011).

had higher peaks, indicating that AHA and MHA may contain more kinds of functional groups, such as carboxyl and phenolic hydroxyl groups. Meanwhile, the peaks at 1030 and 1080 cm<sup>-1</sup> were higher in AHA than in MHA, indicating more abundant polysaccharide structures in AHA.

## 3.2. Sole adsorption of humic acids onto the sediments

The adsorption isotherms of HAs (Fig. S3) were fitted well to the Freundlich model and Langmuir model (Table S3). Regardless of the sediment type, the adsorption capacity was highest for AHA and lowest for RHA. Between the two sediment types, the maximum adsorption capacity was higher for SedA (2.30, 3.47 and 2.42 mg/g for RHA, AHA, and MHA, respectively) than for SedM (2.11, 2.39 and 2.17 mg/g, respectively; Table S3). Consistently, the adsorbed amounts of chromophoric OM ( $a_{254}$ ) and fluorescent OM were greater for SedA (Figs. 3b, 3e).

The compositional changes of HAs due to adsorption differed across the HA sources. SUVA<sub>254</sub> of RHA increased after the adsorption by SedA and SedM, whereas SUVA<sub>254</sub> decreased for AHA and exhibited no evident change for MHA (Fig. 3c). All  $S_{275-295}$  values of three HAs increased due to the adsorption to sediments (Fig. 3d). The fluorescence intensity of all five components in AHA and MHA decreased after adsorption (Fig. 3e). In contrast, after RHA adsorption, the fluorescence intensity of C1, C3 and C5 decreased, whereas C2 and C4 increased (Fig. 3e). This observation is due to the low initial abundance of C2 and C4 in RHA (< 4%, Fig. 3f). The control experiment using pure water showed that the sediment itself could release a small amount of C2 (0.31 and 0.52 R.U. from 0.4 g SedA and SedM, respectively) and C4 (0.86 and 0.89 R.U. from 0.4 g SedA and SedM, respectively), which could account for the C2 and C4 increases in RHA.

During the adsorption of AHA and MHA by sediments, the adsorption percentage of the fluorescence components was highest in C1 and second highest in C5 (Fig. S4). This indicates that sediments preferential adsorbed C1 and C5, relative to C2, C3 and C4. RHA also showed similar adsorption characteristics. After adsorption, the relative abundance of C1 in the supernatant of all HAs decreased significantly (P < 0.05), while those of C2, C3 and C4 increased (Fig. 3f). The abundance of C5 in RHA increased slightly after adsorption, while there is no significant change of C5 in AHA and MHA.

To further evaluate compositional changes due to adsorption, we compared the FTIR spectra of HAs before and after adsorption (Fig. 2). The bands at 3600–2700 cm<sup>-1</sup> (O—H and N—H vibrations) were broadened due to adsorption. A reduction in RHA intensity at the 890 cm<sup>-1</sup> band was found after adsorption. The peak intensity of the absorbance bands at 1030 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> decreased greatly after AHA and MHA absorption, indicating the adsorption of polysaccharide structures. Peak intensity of AHA and MHA at bands of 1230 cm<sup>-1</sup>, 1515 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> decreased, indicating the adsorption of phenolic hydroxyl groups, aromatics and carboxyl-containing components, respectively.

#### 3.3. Inhibitory effect of phosphate on humic acid adsorption by sediments

For all three HAs, the amount of HAs adsorbed onto sediments decreased nonlinearly as phosphate concentrations increased, indicating an inhibitory effect of phosphate on HA adsorption (Fig. 4). The adsorption amount of HAs decreased rapidly when equilibrium phosphate concentrations increased from 0 to 2 mg/L and decreased slightly as phosphate exceeded 2 mg/L. The DOC concentration in the aqueous phase can be reasonably predicted by the natural-log transformed phosphate concentration (ln (C<sub>P</sub>)) in the aqueous phase (R<sup>2</sup> > 0.9) (Table S4). The DOC vs. ln (C<sub>P</sub>) regression slope measures the degree of inhibitory effects of phosphate on HA adsorption, and a greater slope shows stronger inhibition. For the adsorption on SedA, the slope for RHA, AHA and MHA were 1.69, 1.04 and 1.96, respectively; for SedM,



**Fig. 3.** Adsorption of HAs by sediments and optical properties of HAs before and after adsorption (SedA: algae-dominated sediment; SedM: macrophyte-dominated sediment; AHA: algae-derived HA; MHA: macrophyte-derived HA; RHA: reference HA). The initial HA concentration was set at 50 mg/L; the letters above the histogram in panels (a) and (b) indicate significant differences, P < 0.05; the black squares represent the initial values of SUVA<sub>254</sub> in panel (c) and  $S_{275-295}$  in panel (d).



Fig. 4. The amount of HAs adsorbed onto sediments as a function of phosphate concentration (SedA: algae-dominated sediment; SedM: macrophyte-dominated sediment; AHA: algae-derived HA; MHA: macrophyte-derived HA; RHA: reference HA).

the slope of RHA, AHA and MHA were 1.46, 1.95 and 1.98, respectively. Therefore, the adsorption of MHA was most strongly inhibited by phosphate for both sediment types.

The inhibitory effect of phosphate displayed no consistent selectivity for aromaticity or molecular weight. As initial phosphate concentration increased from 0.1 to 20 mg/L, the post-adsorption SUVA<sub>254</sub> of RHA in the aqueous phase decreased gradually from 6.94 to 6.43 for SedA and from 8.13 to 7.54 for SedM (Fig. 5a). In contrast, the SUVA<sub>254</sub> increased for AHA (from 1.97 to 2.26 for SedA and from 2.82 to 2.92 for SedM) and SedA-MHA (from 2.61 to 2.82) but remained largely unchanged for SedM-MHA (Fig. 5b). E<sub>2</sub>/E<sub>3</sub> and S<sub>275-295</sub> remained virtually unchanged for RHA adsorption but decreased for AHA and MHA adsorption (Fig. 5c and d).

The adsorption percentage of the fluorescence components can also be reasonably predicted by the natural-log transformed phosphate concentration (Fig. 6, Table S5). As the phosphate concentration increased, the adsorption percentage of all fluorescent components



Fig. 5. Changes in optical indices of HAs during the adsorption of HAs to lake sediments as a function of phosphate concentration (SedA: algae-dominated sediment; SedM: macrophyte-dominated sediment; AHA: algae-derived HA; MHA: macrophyte-derived HA; RHA: reference HA).

decreased, confirming the inhibitory effect of phosphate on HA adsorption. The only exception was C4 in SedM-RHA group, for which the adsorption percentage of C4 slightly increased with the phosphate concentration. The regression slope of adsorption percentage vs. ln (C<sub>P</sub>) shows that the magnitude of inhibition differed across the five fluorescence components (Fig. 6). The inhibition was strongest on C2, followed by C3 > C5 > C1 > C4 for RHA. For AHA and MHA, the inhibition was strongest for C5, followed by C3 > C2 > C1/C4 (Fig. 6, Table S5).

The synchronous map of 2D-FTIR-CoS showed seven predominant auto-peaks, which were centered at 860, 1030, 1080, 1136, 1426, 1480, and 1640 cm<sup>-1</sup>, respectively (Fig. 7a, c, e, g, Table S6). This pattern revealed that the following bonds or functional groups responded to the presence of phosphate, i.e., aromatic C-H (860 cm<sup>-1</sup>), C—O stretching of polysaccharides (1030, 1080 and 1136 cm<sup>-1</sup>), aromatic C=C (1480 cm<sup>-1</sup>), symmetric C—O stretching from -COOH or -OH (1426 cm<sup>-1</sup>), and aromatic C=C stretching and/or asymmetric C-O stretching in -COOH (1640 cm<sup>-1</sup>). The signs of the cross-peaks according to the synchronous and asynchronous maps are shown in Table S6. According to Noda's rule (Noda, 2012), the sequence of structural changes of HA with the increasing phosphate concentration was in the order of  $1136 \rightarrow 1080/860 \rightarrow 1030 \rightarrow 1480 \rightarrow 1426/1640 \text{ cm}^{-1}$ . Such a sequence suggests that the adsorption of phosphate competed most strongly with adsorption of polysaccharides or aromatics, the whereas carboxyl-containing components were not readily replaced by phosphate.

#### 4. Discussion

#### 4.1. Heterogeneous adsorption behaviors of humic acids by sediments

The three HAs of various origins showed distinct chemical compositions. Overall, the absorption and fluorescence spectroscopy indicate that AHA had higher molecular weights and aromaticity than MHA. In addition, the FTIR data show AHA contained more abundant polysaccharide structures than MHA. Compared to these two HAs, RHA exhibited much higher aromaticity and greater molecular weights but lower relative abundances of carboxyl and phenolic hydroxyl groups and polysaccharide structures. These compositional differences among the three HAs can explain their heterogeneous adsorption behaviors, as discussed below.

In contrast to previous studies suggesting that minerals preferentially adsorb aromatic compounds (Coward et al., 2019; Groeneveld et al., 2020), our data show that aromaticity is not the sole predictor for adsorption. The preferential adsorption of aromatic compounds can explain the decrease in SUVA<sub>254</sub> of AHA after adsorption (Fig. 3c), but it does not explain the increase in SUVA<sub>254</sub> of RHA due to adsorption. Moreover, it does not explain the lesser adsorbed quantities of RHA than AHA, given that RHA had greater aromaticity than AHA. These discrepancies can be explained by our FTIR results, which indicate that carboxyl-containing compounds and polysaccharides also played an important role in HA adsorption. The ligand exchange of carboxylic and hydroxyl groups with metals on the mineral surface is an important pathway for OM adsorption. Polysaccharides have been shown to be critically involved in the ligand exchange of OC with iron (oxyhydro) oxides (Polak et al., 2011; Sowers et al., 2019). The adsorption of polysaccharides is suggested to be facilitated by the formation of inner-sphere surface complexes between the polysaccharide -OH groups and Fe atoms at the mineral surface (Eusterhues et al., 2011; Weisseborn et al., 1995). Furthermore, we observed that the molecular weight of dissolved HAs reduced due to adsorption (Fig. 3d), which suggests the preferential adsorption of high-molecular-weight macromolecules, including polysaccharides. Thus, the higher adsorbed amount of AHA than the other HAs can be attributed to the more abundant



**Fig. 6.** The adsorption percentages of PARAFAC components as a function of logarithmically-transformed phosphate concentration (C<sub>p</sub>: concentration of equilibrium phosphate in mg/L. SedA: algae-dominated sediment; SedM: macrophyte-dominated sediment; AHA: algae-derived HA; MHA: macrophyte-derived HA; RHA: reference HA).



**Fig. 7.** Synchronous (a, c, e, and g) and asynchronous (b, d, f, h) 2D correlation maps generated from the 800 cm<sup>-1</sup> to1750 cm<sup>-1</sup> for the FTIR of AHA and MHA after adsorption by sediments as a function of phosphate concentration (SedA: algae-dominated sediment; SedM: macrophyte-dominated sediment; AHA: algae-derived HA; MHA: macrophyte-derived HA; RHA: reference HA). The red and blue colors represent positive and negative correlations, respectively. Deeper color intensity suggested a stronger positive or negative correlation.(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

polysaccharides and carboxyl-containing compounds in AHA (Fig. 2). Our results show that proxies for aromaticity, such as SUVA<sub>254</sub>, are inadequate to depict the adsorption characteristics of OM, because carboxylic and hydroxyl groups can be more important than aromaticity in controlling the quantity of HAs adsorbed to sediments.

The heterogeneous adsorption behaviors of the five fluorescence components can be linked to their different chemical properties and initial abundances (fluorescent intensity). Generally, C1 (humic-like, photochemical degradation product of terrestrial OM) showed the strongest adsorption among the five components (Fig. 3e and S4), likely due to the larger molecular size of C1 (as evidenced by the longer emission wavelength). These large-sized molecules likely have abundant aromatic or carboxylic groups that can be adsorbed through  $\pi$ - $\pi$  interaction or ligand exchange (Lee et al., 2015; Qin et al., 2015). In addition, the adsorbed quantity of adsorbate is directly proportional to its initial concentration in a certain concentration range (Zhang et al., 2020). C1 was the most abundant component, and this high abundance can enhance its ability to compete with other PARAFAC components for adsorption. Protein-like C4 (tryptophan-like component) was more effectively adsorbed than C3 (humic-like DOM from terrestrial sources) and C2 (microbially produced humic-like DOM) in the groups of SedM-AHA, SedM-MHA and SedA-AHA (Fig. S4), suggesting the adsorption of proteinaceous compounds onto the sediments. This is consistent with the previous studies showing that proteins can be adsorbed onto iron minerals via the mechanisms of ligand exchange and electrostatic adsorption (Pan et al., 2020; Zhang et al., 2020).

The adsorption and fractionation of OM can lead to changes in the composition and bioavailability of OM in water. Proteinaceous compounds or polysaccharides are usually more readily available for microbial degradation than humic compounds (Lu et al., 2021; Zhou et al., 2021a). The preferential adsorption of the two kinds of compounds can reduce the bioavailability of organic materials in the water column but enhance the bioavailability and mineralization process of OM buried at the surface sediments, resulting in changes in microbial communities and processes that drive carbon and nutrient cycling. Further efforts are warranted to investigate changes in the bioavailability and burial of OM

due to adsorption and how these changes impact element cycling and energy flow at the ecosystem level.

#### 4.2. Competition between HAs and phosphate during adsorption

We observed the inhibitory effect of phosphate on HA adsorption, which suggests a competitive adsorption mechanism. This is consistent with previous observations that phosphate inhibited the adsorption of some DOM fractions (e.g., aromatics) during the co-adsorption of phosphate and DOM onto minerals (Li et al., 2021; Luo et al., 2021; Weng et al., 2008). The competition can be explained by that phosphate, via electrostatic adsorption and ligand exchange, occupies the adsorption site that otherwise will be occupied by organic compounds. Furthermore, adsorbed phosphate can reduce the positive charge on the sediment surface, thereby reducing the adsorption capacity of sediments to the negatively charged OM (Zhang and Zhang, 2010).

We also found that the presence of phosphate altered the compositional fractionation process of HAs during the adsorption to sediments. Aromaticity (SUVA<sub>254</sub>) and molecular weight (S<sub>275-295</sub>, E<sub>2/E<sub>3</sub>) displayed</sub> opposite changes between the sole HA adsorption and the co-adsorption of HA&P (Fig. 3 & 5). These patterns overall suggest that phosphate competes better than some fractions of HA onto the sediments, thus inhibiting the adsorption of the molecules that would have been immobilized in the absence of phosphate. Carboxyl-group associated compounds were more resistant to phosphate replacement than polysaccharides and aromatics (Fig. 7 and Table S6), likely because those carboxyl groups combine with minerals through ligand exchange to form inner-sphere complexes, a stronger interaction than the weak outer-sphere complexes associated with the adsorption of aromatics via electrostatic or  $\pi$ - $\pi$  interactions (Chen et al., 2014b; Henneberry et al., 2012; Lee et al., 2015; Oren and Chefetz, 2012). Our findings demonstrate that chemical compositions of organic molecules influence their selective adsorption and the level of 'resistance' to the inhibitory effects of phosphate, which together can lead to the compositional fractionation at the water-sediment interface during the adsorption process. This process alters the mineralization and burial of OM of various degrees of



#### Algae-dominated lake



**Fig. 8.** A conceptual model describing the competitive adsorption between phosphate and OM in macrophyte-dominated and eutrophic, algae-dominated lakes. The model shows that more organic compounds produced in eutrophic lakes can mobilize P from the sediment, which sustains the internal loading of P and establishes a novel mechanism for the legacy effect of lake eutrophication. Yellow arrows indicate the phosphorus fluxes, and orange arrows indicate the OM fluxes. The arrow thickness denotes the magnitude of fluxes.(For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

bioavailability. For example, P loading in lakes can compete with polysaccharides for the adsorption and elevate the quantities of polysaccharides in the water column, which can enhance microbial activities and fuel the carbon and nutrient cycling, given that polysaccharides are an active substrate for microbial metabolism.

Our finding that algae-derived and macrophytes-derived organics showed different abilities in competing with phosphate for adsorption has important implications for the mobilization and sequestration of P in lakes. AHA competed better with phosphate than MHA, as evidenced by the weaker inhibitory effect of phosphate on AHA adsorption (Fig. 4, Table S4). This observation suggests that algae-derived organic substances are more likely to promote the desorption and release of phosphate from sediments through the competitive adsorption mechanism. We propose a conceptual framework describing a positive feedback mechanism where eutrophication and P mobilization reinforce each other through OM source switching (Fig. 8). In macrophyte-dominated lakes, macrophyte-derived organics compete weakly with phosphate for adsorption, limiting their ability to mobilize phosphate adsorbed to sediments. In contrast, for eutrophic lakes where algae dominate, algaederived OM containing abundant polysaccharides and proteinaceous compounds can be readily adsorbed to the sediment and hence trigger the release of phosphate from the sediment to the overlying water. This process can sustain a high phosphorus level in eutrophic lakes, further stimulating algal blooms and the generation of algae-derived OM. Such a positive feedback loop may serve as an essential pathway contributing to the internal P loading in lakes but has not been previously recognized. Eutrophic lakes can maintain a high internal P loading on the time scale of several decades despite a rigorous control of external P loading (Sondergaard et al., 2003). Our findings provide a novel explanation for the long-observed legacy effect of lake eutrophication.

#### 5. Conclusions

Our results revealed that sediments preferentially adsorb macromolecular polysaccharides and carboxyl groups containing compounds, resulting in the compositional fractionation of OM between the aqueous and solid phases. Algae-derived HA adsorption capacity of sediments was greater than those associated with macrophyte-derived HA or terrestrial-derived HA. This difference can be linked to the higher contents of polysaccharides, proteinaceous and carboxyl-containing compounds in algae-derived HA. The presence of phosphate significantly inhibited the adsorption of OM by sediments, with polysaccharides and aromatics being more readily replaced by phosphate than carboxylcontaining components. These findings show that sole and competitive adsorption can significantly change the chemical composition and thus biogeochemical roles of OM in the water column and sediment of a lake. Compared to macrophyte-derived HA or terrestrial-derived HA, algaederived HA competed better with phosphate for adsorption, demonstrating more substantial potential in replacing and mobilizing phosphate adsorbed to sediment surfaces. Based on this result, we propose a conceptual model by which eutrophication and internal P loading reinforce each other through OM source switching. This model establishes a novel mechanism to explain the widely observed legacy effects of lake eutrophication.

## CRediT authorship contribution statement

ShuaiLong Wen: Investigation; Formal analysis; Writing – original draft. YueHan Lu: Writing – review & editing. ChunYan Luo: Investigation. ShiLin An: Investigation. JiaRu Dai: Investigation. ZhengWen Liu: Resources. JiCheng Zhong: Resources. YingXun Du: Conceptualization; Supervision; Writing – review & editing.

## Novelty statement

Our results show that the functional groups of organic compounds control not only their water-sediment fractionation and burial of organic matter but also their ability to replace and mobilize phosphate in sediments. The adsorption capacity of lake sediments was higher for humic acid from algae-dominated lakes (AHA) than that from macrophyte dominated lakes (MHA). The inhibitory effect of phosphate on the adsorption of AHA is weaker than that on MHA. **Based on these findings, we propose a novel mechanism to explain the legacy effect of lake eutrophication.** Eutrophic lakes produce more organic compounds that can mobilize P from sediments, which can generate a positive feedback loop to eutrophication.

#### 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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#### Appendix A. Supporting information

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