1	Effects of molecular weight fractionated humic acid on the transport
2	and retention of quantum dots in porous media
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19 Abstract

Although humic acid (HA) plays an important role in the fate and transport of 20 21 nanoparticles in subsurface environment, the roles of specific fractions of HA on the transport of nanoparticles are still not well understood. In this study, quantum dots 22 (QDs) with carboxyl and amino modification (QD-COOH and QD-NH₂) were used as 23 typical nanoparticles to understand the effects of molecular weight (MW) fractionated 24 humic acid (Mf-HA) on the transport and retention behaviour of nanoparticles. 25 Transport experiments of QDs were performed both in the and presence of 26 pristine- and Mf-HA in both NaCl and CaCl2 sol 27 The M_f-HA had distinct effects on the transport and retention 28 of QDs, which were highly dependent on the MW of M_f-HA. In add the surf te coating of QDs and cation 29 ansport behavior of QDs. In NaCl 30 types also showed significant effects solution, the transport of **O** was dramatically enhanced in the presence of 31 and the hig MW M_f-HA (>100 kDa and 30-100 kDa) could 32 pristine- and M_f-HA enhance the mobility Ds plore significantly than the low MW M_f-HA (10-30 kDa, 33 3-10 kDa, and <3 kDa). The QD-COOH was readily mobile in the sand column and 34 the recovery of injected QD-COOH was significantly higher in the presence of 35 pristine- and Mf-HA. In CaCl₂ solution, the transport of QD-COOH was enhanced in 36 the presence of pristine- and Mf-HA, and the enhancement was significantly 37 correlated with the MW of M_f-HA. However, the transport behavior of QD-NH₂ was 38 not altered by pristine- and Mf-HA. Overall, these findings can improve our 39 understanding of the effects of M_f-HA on the transport and retention of nanoparticles 40

41	in subsurface environment, and suggest that the HA, surface coating and cation types
42	are likely key factors which governing the stability and mobility of nanoparticles in
43	natural environment.
44	Keywords
45	Quantum dots; Transport and fate; Porous media; Humic acid; Molecular weight;
46	Cation type; Surface coating; DLVO theory; Inductively coupled plasma optical
47	emission spectrometer
48	
49	1. Introduction
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existed in environment.¹¹⁻¹³ Furthermore, ENPs will act as a new type of pollutant and
pose a threat to nature environment and human health. Thus, it is important and urgent
to understand the fate and transport of ENPs in environment and evaluate the potential

61 impact of ENPs on environment and human health.

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Numerous researches have been conducted to investigate the transport and

and chemical transformations, including aggregation, adsorption, deposition,

dissolution, and release of toxic ions or reaction with other materials/contaminants

retention of ENPs in porous media through columns packed with quartz sand or glass 63 beads.¹⁴⁻²⁷ Factors such as ENPs properties^{23, 24} (e.g., particle size, shape, preparation 64 methods, concentration, and surface chemistry properties), environmental conditions¹⁴, 65 17, 19, 25, 26 27 (e.g., solution ionic strength and pH, cation type and valence, nature 66 organic matters, surfactant, bacteria and biofilm), and collector physicochemical 67 heterogeneities^{15, 19, 20} (e.g., grain size, type, surface coating, and roughness) have 68 been systematically evaluated the influence on the transport and retention behavior of 69 ENPs in sand column. For example, Torkzaban et al yed a negligible 70 deposition of quantum dots in ultrapure sand, but th 71 nore pronounced in columns packed with goethite-coated sap ⁹ reported that the 72 et al. depth-dependent retention coefficient an solid-phase concentration of 73 k v naximu e decrease of grain size. In general, multi-walled carbon nanotubes increas 74 the solution chemical property is su th as ionic strength and pH, influence the stability 75 changing the surface charge or screening the and mobility of nanonarticles b 76 double layer (EDL).^{28, 29} The stability of nanoparticles interaction of elect 77 depends more on the ionic composition in suspension than ionic strength.¹⁵ In 78 addition, a recent study has found that the co-presence of suspended bacteria could 79 enhance the transport of titanium dioxide nanoparticles through electrosteric and 80 electrostatic effects.²⁷ However, the above discussed studies only considered the 81 individual influence of each environmental factor on ENPs transport. In order to 82 understand the fate and potential influences of ENPs in environment, we must 83 investigate how the transport behaviours of ENPs are affected by the multiple 84

85 environmental factors presented in natural environment.

86	Humic acid (HA), which represents an active and important part of NOM, is
87	ubiquitous in soil and groundwater environment. ³⁰ Previous studies have
88	demonstrated that HA plays an important role on the fate and transport of ENPs. ^{25, 29,}
89	³¹⁻³⁴ Adsorption of HA onto ENPs surface would alter the physicochemical properties
90	of ENPs, and consequently affect the mobility and stability of ENPs in aquatic
91	environment. ^{25, 31} For example, Quevedo et al. ¹⁶ observed that the adsorbed HA on the
92	Al ₂ O ₃ surface caused charge reversal of the collector and then rejused the deposition
93	rates of QDs. Jing et al. ³⁵ found that HA could enhance the notatity of zinc oxide
94	nanoparticles, even at the concentration of HA as lon as 1 mg/L of total organic
95	carbon. Moreover, Chen et al. ³⁶ reported that the aggregation of fullerene
96	nanoparticles was enhanced when Harrod Ca^{2+} Aisted in suspensions, which was due
97	to the bridging between HA Ca ⁺ and Nes. However, as HA consists of various
98	mixtures of organic compound with different sizes of molecular, ³⁷⁻³⁹ bulk HA
99	characteristic may be in afficient delegating for the specific fraction of HA properties
100	and their interaction with nanoparticles. Recent research ⁴⁰ revealed that the molecular
101	weight range of 0.5-2 kDa for humic acid had preferential adsorption ability on
102	carbon nanotubes, while the smallest characterized fraction (MW< 0.4 kDa) could be
103	hardly adsorbed on the carbon nanotubes. Amirbahman et al.41 reported that HA
104	filtered through larger molecular weight cutoff (MWCO) membranes afforded better
105	stability of hematite nanoparticles against deposition. Similar results have been
106	observed when studying the influence of molecular weight fractionated NOM on the

aggregation of fullerene,⁴² gold nanoparticles,⁴³ and the photo-reduction of Ag⁺ to 107 silver nanoparticles.⁴⁴ In these studies, the stability of ENPs were considerably 108 enhanced as the adsorbed HA effectively increased electrostatic and/or steric repulsive 109 forces between nanoparticles and nanoparticles. Overall, these findings significantly 110 highlighted the important roles of different HA fractions in the fate and transport of 111 ENPs. Nevertheless, to the best of our knowledge, there is no comprehensive study in 112 investigating the MW fractionated humic acid (Mf-HA) on the transport and retention 113 of ENPs. 114 Quantum dots (QDs), as a kind of ENPs, nown for their 115 distinguished tunable optical properties and l in solar cells, biomedical 116 imaging, luminescent probes, chemical and lighting technologies.^{45,} 117 displ o understand the effects of different ⁴⁶ In this study, we used QDs as a 118 MW of humic acid fractions in the transport and retention of nanoparticles. A series 119 of column experiments with two offerently coated QDs in the presence of mono- or 120 or without pristine- or M_f-HA were performed. 121 divalent electrolyt Additionally, the characteristic of pristine- and M_f-HA, the potential and size of QDs 122 under various conditions were fully investigated. To date, this is the first study on the 123 influence of MW distribution and heterogeneity of HA on the transport and retention 124 of QDs. 125

126 **2. Materials and methods**

127 2.1 Fractionation and characterization of humic acid

Humic Acid (Lot No. 1415936) was obtained from the Sigma-Aldrich (Shanghai,

China). Stock solution (1 g/L) was stirred overnight at room temperature and then 129 filtered through a 0.22 µm pore-size hydrophilic polyvinylidene fluoride (PVDF) 130 membrane to prevent any undissolved HA. The filtrate is referred to as pristine-HA. A 131 series of nominal molecular weight cutoff (MWCO) Amicon Ultra-15 centrifugal 132 filters (with 100, 30, 10, and 3 kDa, respectively) obtained from Millipore (Darmstadt, 133 Germany) were used to fractionate HA. The procedure of fractionating HA followed 134 the protocol reported by Yong et al.⁴⁷ Briefly, all filter units were initially rinsed with 135 deionized (DI) water to remove glycerol thoroughly. Next, t e HA was loaded 136 into the 100 kDa filter and centrifuged at 3737 g for 137 ate was collected without any modification and then further filte e with 30 kDa, 10 kDa, and 138 **6**650 g, 3 kDa filters at centrifuging rates 509 nd 8420 g, respectively. The 139 retentate or filtrate was collected as 140 0 kDa, 30-100 kDa, 10-30 kDa, 3-10 arbon weight percent (wt %) recovery of M_f-HA kDa, and <3 kDa, respective 141 *y*). sub indicating that 9% of HA could be lost onto the filter was 91.0% (SI Tab 142 hing process.48 143 membrane during t

Concentrations of the pristine HA and M_f-HA were quantified as total organic 144 carbon (TOC) with a Shimadzu TOC-V Analyzer. UV-vis spectra spectrophotometric 145 excitation-emission 146 analysis and fluorescence matrices (EEMs) were 147 comprehensively performed for characterizing pristineand M_f-HA. The concentration of HA used to UV-vis and fluorescence spectra analysis was 5 mg/L 148 dissolved organic carbon (prepared in DI water and adjusted to pH 7.0 by 0.1 M HCl 149 and 0.1 M NaOH). UV-vis spectra were measured by a Shimadzu UV-vis NIR 150

Spectrophotometer (UV-3600, Japan). Fluorescence excitation-emission matrices
(EEMs) were performed on Hitachi Fluorescence Spectrophotometer (F-4600, Japan)
with a 1 cm quartz cuvette. Both excitation and emission slit widths were set at 5 nm.
Emission was measured from 280 to 600 nm in 10 nm increments, with excitation
wavelengths in the range of 200 to 450 nm in 10 nm.

156 **2.2 Preparation and characterization of the nanoparticles**

Two types of QDs were used in this study: carboxyl-functionalized CdSe/ZnS 157 QDs (Wu Han Jia Yuan, Catalog No. ne-functionalized Q2525) 158 CdSe/ZnS/PEG ODs (Wu Han Jia Yuan, Catalo 159 Their emission wavelength is 525 nm and particle diameter is The QDs were shipped in 160 borate buffer solution (BBS) at 8 µM. vestigate ne potential effects of humic 161 acid heterogeneity on the transport be 162 Ds, QDs suspensions were prepared by diluting QDs stock solution wit a variety of background solutions (3 mM NaCl or 163 2 mM CaCl₂ in the presence and a sence of pristine- and M_f-HA at pH 7.0). The final 164 ens ons was 5×10^{12} particles/mL. 165 concentration of QD

The electrophoretic mobility (EPM) of QDs was measured by a Zetasizer Nano ZS (Malven Instruments, UK) at a wide range of environmental relevant background solution chemistries. All measurements were conducted in triplicate. Hydrodynamic diameter of the QDs at desired background solution chemistry was assessed by dynamic light scattering (DLS) (ZetaSizer Nano, Malvern) with a 173 ° scattering angle. The size of the particle was also determined by transmission electron microscopy (TEM) under selected conditions. Samples prepared by a small drop of QDs suspension were placed onto copper grid with a carbon backing, following air
dry overnight prior to analysis.¹⁵ The mean sizes of QDs were determined by analysis
of at least three randomly chosen images recorded and each frame more than 30
particles.

177 2.3 Adsorption of HA to QDs

Adsorption studies were conducted to confirm the adsorbed amount of HA onto 178 QDs surface at conditions that used in column transport experiments. Immediately 179 after the completion of the QDs suspension preparation, 20 e suspension was 180 added into a clean centrifuge tube. The suspension 181 solutions were stirred for 24 h, then centrifuged 2 h at 8000 rp 0 g) to settle the HA-colloid 182 complex. The HA concentration in super sured by a Shimadzu TOC-V 183 was me Analyzer. The difference between 184 nd final HA concentrations in the aqueous phase was used to cotern ine the adsorbed amount of HA. The results are 185 The complete procedure is provided in the supplementary reported as mg HA 186 Information (SI) 187

188 **2.4 Column transport experiments**

Through column experiments, we firstly studied the individual effect of mono/divalent electrolyte solution (3 mM NaCl or 2 mM CaCl₂) on the transport of QDs, and then investigated the co-influence of pristine- and M_f -HA with mono/divalent electrolyte solution on the transport of QDs. A total of 14 column experiments were conducted following the procedures described by a previous study.⁴⁹ To summarize, a glass chromatography column (1.6 cm i.d ×10 cm length) was wet-packed uniformly with clean sand to avoid introducing air bubbles into the porous media, following mild sonication to achieve maximum packing density. Once packed, the column was equilibrated with at least 10 pore volumes (PVs) of desired background solution (3 mM NaCl or 2 mM CaCl₂ in the presence and absence of pristine- and M_f-HA at pH of 7) in an up-flow mode at a flow rate of 1 mL/min (equivalent to a Darcy velocity of 2.8 m/d).

After equilibrating with background solution, nonreactive tracer tests were used 201 to assess water flow and hydrodynamic dispersion of the pa umn. A pulse (ca. 202 3 PVs) of sodium nitrate (NaNO₃) solution was 203 low rate of 1.0 mL/min into the column, followed by 3 P ground solution injected to 204 replace the tracer solution. The con-205 er in effluent samples was measured by a Shimadzu UV-vis N 206 otometer to obtain the breakthrough curves (BTCs). 207

Once finishing the tracer test, a pulse (ca. 3 PVs) of QDs suspensions with the 208 compositions was introduced into the column 209 same background immediately, and then a pulse of QDs-free background solution (ca. 3 PVs) was 210 injected to elute the unattached QDs. Effluent samples were collected using a fraction 211 collector and an ICP-OES was used to measure the QD concentration. At the end of 212 each experiment, the columns were carefully sectioned into 1.5-cm increments and 213 QDs were extracted from each solid sample and measured to obtain a retention 214 215 profile.

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The concentrations of QDs were determined by an inductively coupled

plasma–optical emission spectrometer (ICP–OES; OptimaTM 7300DV, PerkinElmer,
Inc., Shelton, CT, USA) operated at a RF power of 1,500 W, nebulizer flow of 0.8
L/min, and pump rate of 1.5 mL/min at a wavelength of 214.44nm. The influent and
effluent concentrations of QDs were determined by direction injection into the
ICP-OES without pretreatment. The solid-phase QDs concentration was measured
using ICP-OES after pretreatment (dried at 95 ℃ and digested in 10 mL of nitric acid,
using a microwave-assisted digester). The detailed analytical method of different QDs

concentrations were shown in the study of Yong et al. 20

225 **2.5 Calculation of interaction energy**

In order to better understand the influence 226 ent M_f-HA on the transport and retention behaviour of QDs in under various conditions, 227 med Derjaguin-Landau-Verwey-Overbeek 228 theory were modified by the incorporation of a steric repr term energy when HA coated QDs approach the 229 siv sand surface. 230

, the interaction energy calculations for QDs in electrolytes 231 In the absence were only considered classical DLVO interaction energies, including electrical double 232 layer (EDL) repulsion, van der Waals (VDW) attraction forces. In the presence of HA, 233 the steric repulsion forces including osmotic repulsion (V_{osm}) and elastic-steric 234 repulsion (V_{elas}) force were also considered in the interaction energy calculation. 235 QDs-sand interaction energy was calculated by treating the particle-collector system 236 as a sphere-plate interaction case. Total interaction energy is sum of these forces and 237 steric repulsion forces only considered when HA existed in the QDs suspension. As 238

the coating of particles or the presence of any hydrated ions will prevent surface-surface separation distances to approach x = 0.3 nm,⁵⁰ the interaction forces were intentionally calculated for x > 0.3 nm. This also resulted that the interaction energy profiles structures do not exhibit a primary minimum. The detailed equations used to calculate electrical double layer repulsion (Eq (7) in SI), van der Waals attraction forces (Eq (6) in SI) and steric repulsion energies (Eq (10)-(14) in SI) for QDs-sand are provided in the SI.

246 **2.6 Interpretation of nanoparticles transport experiments**

In order to quantitatively compare the transport behavior of 6.05 under different experimental condition, the particle attachment affinency (α) based on colloid filtration theory was calculated following interpression.⁵¹

250
$$\alpha = -\frac{2}{3} \frac{d_c}{(1-\varepsilon)L\eta_0} \ln\left(\frac{C}{C_0}\right)$$
(1)

Where, d_c is the mean maneter of the collector grain, ε is the porosity of packed-bed, L is the nacked-bed length and C/C₀ represents the normalized particle effluent concentration. The value of C/C₀ was determined by numerical integration of the measured particle breakthrough curve for each experiment. η_0 is the single-collector contact efficiency. The value of η_0 was determined using the correlation equation reported by Tufenkije and Elimelech.⁵¹

257 **2.7 Data analysis**

The zeta potential and particle size data were analysed using a One-way ANOVA analysis (Tukey's Honestly Significant Different (HSD)) to identify the statistical differences in measured parameters (HA MW). In additional, a linear regression

- analysis was also performed using average MW for each HA fraction to identify the
- correlation between HA MW and zeta potential or particle size of QDs. Significance
- was set at p<0.05. All tests were performed using the IBM SPSS Statistics version 23
- software package.
- 265 **3. Results and discussion**
- 266 3.1 Chemical characterization of pristine- and Mf-HA

The UV-vis spectra, specific UV absorbance at 280 nm (positively correlated to 267 aromaticity) and E_2 : E_3 (absorbance at 250 and 365 nm) and M_f-HA are 268 presented in Figure 1a-c, respectively. All humic s ated a featureless 269 decrease absorbance with increasing wavelengt 270 of E_2/E_3 was increasing with the decreasing of molecular weight The a sorbances at 280 nm of > 100271 kDa and 30-100 kDa HA fraction than other fractions. These results 272 indicated that the higher MW 273 M_f-HA had more aromatic components and 274 hydrophobic structu

dorescence excitation-emission matrices of pristine-HA 275 Figure 1d-i 276 and Mf-HA. The maximum intensity of the fluorescence peaks was more pronounced for low MW M_f-HA (10-30 kDa, 3-10 kDa and < 3 kDa HA) than high MW M_f-HA (> 277 100 kDa and 30-100 kDa HA). As the humic-like fluorescence is mainly caused by 278 carboxylic groups,⁴² the results demonstrated an abundance of carboxylic functional 279 groups existing in low MW M_f-HA (10-30 kDa, 3-10 kDa, and <3 kDa HA). Previous 280 studies observed similar results that low MW fractionated of NOM had more carboxyl 281 groups while high MW fractions contained more aromatic structures.^{42, 47} 282



3.2 Zeta potentials and tize of QDs in the absence and presence of pristine- and Mr-HA

The ζ potentials and size of QDs measurements were performed with carboxyl and amino modified QDs to gain an insight into the surface potential behavior imparted by each molecular weight HA in the mono- and divalent electrolytes. Figure 2 present the zeta potentials and size of QDs under different solution chemistry conditions. In the absence of HA, the ζ potentials of QD-COOH were more negative in NaCl solution than those in CaCl₂ solution, while QD-NH₂ had more positive

charges in CaCl₂ solution than those in NaCl solution. The aggregation size of QDs in 295 monovalent electrolyte were less than those in divalent electrolyte, which indicated 296 297 the QDs were more stable in monovalent electrolyte than that in divalent electrolyte. In the presence of 3 mg/L pristine- and M_f-HA. The ζ potentials of ODs were 298 more negative relative those in the absence of HA and the aggregation of QDs was 299 inhibited by pristine- and Mf-HA in most conditions. However, the effect of HA MW 300 on the ζ potentials and sizes of two QDs were notably different. In NaCl electrolyte, 301 the ζ potentials of QD-COOH in the presence of M_f-HA was gative relative to 302 those without HA, but the variation in measured & 303 OOH was not significantly correlated with the MW of M_f-H t, the effect of HA MW 304 on the ζ potentials of OD-COOH in Ca significantly correlated with 305 HA MW (SI Table S2). The ζ pot 306 -COOH was more negative in the presence of low MW HA frag 10-30 kDa, 3-10 kDa and < 3 kDa HA) than high 307 ion 30-100 kDa HA). However, the aggregation of 00 kDa an MW HA fraction () 308 yte was inhibited by high MW M_f-HA (> 100 kDa and 309 OD-COOH in di 30-100 kDa HA) more efficiently than by low MW Mf-HA (10-30 kDa, 3-10 kDa and 310 < 3 kDa HA). It is seem to that while low MW HA contained more carboxyl groups 311 (Figure 1) and could impart more negative charges to QDs, it does not contribute to 312 the stability as much as high MW HA. As high MW Mf-HA can impart stronger steric 313 repulsion to QDs than low MW Mf-HA, which resulted in better dispersion of 314 QD-COOH in high MW HA. Interesting, the aggregation of QD-COOH in 315 monovalent electrolyte was slightly enhanced by pristine- and M_f-HA (expect the 316

fraction of > 100 kDa HA). The aggregation of nanoparticles is usually determined by 317 electrostatic and steric repulsion. A previous study⁴⁷ has reported that high MW NOM 318 possibly enhanced the aggregation of PVP-AgNPs through screening the surface 319 coating of PVP thus reducing the steric repulsion, while the zeta potentials of 320 PVP-AgNPs was higher in the presence of high MW NOM. Thus, in this study, 321 although the overcoating or replacement of HA increased the interparticle electrostatic 322 repulsion, it possibly reduced the steric repulsion by screening the surface coating of 323 OD-COOH, which resulted in minor aggregation of QD-CC 324 case. Compared with QD-COOH, The ζ potential 325 he presence of pristine- and Mf-HA were changed strongly stine particles (without 326 HA in suspension). However, HA MW effect on the ζ potentials of 327 on the ζ potentials of QD-NH₂ was QD-NH₂. The effect of each MW fi 328 The aggregation of QD-NH₂ both in mononot significant differences (S **S**3). 329 was inhibited by pristine- and M_f-HA. High MW M_f-HA and divalent electro 330 of QD-NH₂ much better than low MW M_{f} -HA in 331 could inhibit the monovalent electrolyte. It is noted that the effect of each MW fraction of HA on the 332 aggregation size of QD-NH₂ in divalent electrolyte was significant differences (SI 333 Table S3) and the correlations between the aggregation size of QD-NH₂ and HA MW 334 was weakly. In general, the above observed results indicating that while low MW HA 335 imparts more negative charges (contained more carboxyl groups) to QDs in most 336 cases, it does not contribute to the stability as much as high MW HA, likely because 337 of the more important steric effects high-MW has on stability against 338







- 346 **QDs in the sand porous media**
- 347 3.3.1 Effects of pristine- and M_f -HA on the transport and retention of QDs in
- 348 monovalent electrolyte

349 The transport and retention behaviour of QDs in quartz sand both with and
350 without pristine- and M_f-HA in suspensions were first investigated in NaCl solution at

pH 7, and the corresponding breakthrough curves and retention profiles (RPs) are presented in Figures 3 and 4. The data on pristine and > 30 kDa HA coated QDs are shown in (a) and (c) and that < 30 kDa fractions are shown in (b) and (d). The BTCs are plotted as the normalized particle concentration at the column effluent (C/C₀) versus the number of PVs passed through the column. The RPs are given as normalized solid-phase concentration (S/C₀) against column depth.

As shown in Figure 3, very similar breakthrough curves and retention profiles 357 were obtained for QD-COOH in NaCl solution with or v in suspensions. 358 Compared to the transport results, the mobility 359 significant in monovalent electrolyte. Similar observation n previous studies that 360 OD-COOH was highly mobile in the nonovalent electrolyte.^{16, 19, 23} 361 at Interestingly, in the absence of H 362 port of QD-COOH was retarded. **OD-COOH** suspended in 3 Cl appeared in effluent after 1.0 PVs, while the 363 luent was near 100% (SI Table S4). This may be COOH in e 364 mass recovery of Q attachment/detachment to the media when moving 365 attributed to th through column. The retention profile of QD-COOH without HA in suspension 366 revealed a low retention of QD-COOH in sand. This was in good agreement with the 367 DLVO calculation (SI Figure S1) predicated, which indicated sand surface was 368 unfavorable for particle deposition. 369



Figure 3. Effluent breakthrough curve (f_{r} b) and retention profiles (c, d) obtained for QD-COOH transport in quark same to mM NaCl with/without pristine- and M_f-HA at pH 7.0.

370

s of pristine- and M_f-HA on the transport and retention of It is noted that the 374 375 QD-COOH were not significant in NaCl solution. Although the QD-COOH was highly mobile in the sand column, the mass recovery of QD-COOH in effluent was 376 slightly decreased relative to that without HA (SI Table S4). And this decreasing was 377 not related to the MW of HA. Similarly, the retention profiles (Figure 3c and d) and 378 attachment efficiency of QD-COOH (Figure 7) in the presence of pristine- and Mf-HA 379 were higher than those without HA. In an attempt to better explain these observations, 380 the interaction energy between the QDs and sand was calculated at each condition 381

(Table 1). The DLVO energy calculations were modified by the incorporated of a 382 steric repulsion energy (osmotic repulsion and elastic-steric repulsion) when HA 383 coated QDs approach to sand surface. The modified interacting energy profiles for 384 OD-COOH and sand at monovalent electrolyte are presented in SI Figure S2. The 385 modified DLVO interaction energy calculations (SI Figure S2) revealed the presence 386 of a significant repulsive energy barriers (>128 kT) between QDs and sand at all 387 condition, indicating that QDs appeared unlikely to conquer those energy barriers and 388 deposited in primary energy minimum. Previous studies that secondary 389 energy minimum can be an important mechanism 390 e transport of colloid in porous media.^{52,53} As seen in Figure 391 ion energy profiles also showed the existence of a very shallo y minimum at all condition. 392 The calculated value of secondary e im presented in Table 1 showed that 393 the secondary energy minim s deeper in the low MW HA fraction than high 394 e otherw se there would be a relation between mobility and MW HA fraction. B 395 this suggested that the secondary energy minimum 396 MW in the colum was not the mainly mechanism that governed the transport of QD-COOH in this 397 condition.⁵⁴ Moreover, Surface charge heterogeneity could also influence the transport 398 of nanoparticles Previous studies^{54, 55} have also reported that the presence of surface 399 charge heterogeneity in sand could produce local areas of favorable interaction, which 400 could increase colloid attachment even under unfavorable condition. The quartz sand 401 used in this study was thoroughly cleaned to remove surface charge heterogeneity, but 402 nanoscale charge heterogeneities from the sand surfaces cannot be ruled out 403

404 completely. Therefore, a very small amount of QD-COOH deposition in the presence
405 of HA may occur due to the presence of the secondary energy minimum and/or other
406 mechanisms such as surface charge heterogeneities.²²



Figure 4. Effluent breakthrough curve (a, b) and retention profiles (c, d) obtained for

 $QD-NH_2$ transport in quartz sand at 3 mM NaCl with/without pristine- and Mf-HA at

- 411 pH 7.0.

- 416 **Table 1.** Calculated steric repulsion force, maximum energy barriers, secondary
- 417 minimum depths and distances for QDs interacting with the sand in the

			Steric Φ_m		(kT)	Φ_{\min}	
Electrolyte	Particle	HA type	repulsion	DLVO	Modified	Depth	Distance
			(<i>k</i> T)		DLVO	(k T)	(nm)
	QD-COOH	without HA	/	87.26	/	-0.0047	62
		pristine HA	19.89	123.40	138.77	-0.0044	70
		>100 kDa HA	41.18	105.05	144.27	-0.0039	68
NaCl		30-100 kDa HA	35.10	128.72	155.40	-0.0045	70
		10-30 kDa HA	33.02	97.94	128.24	-0.0049	68
		3-10 kDa HA	32.28	125.76		-0.0048	68
		< 3 kDa HA	24.46	129.20	£ر ¹ 1.	0.0048	70
		without HA	/		\mathbf{X}	/	/
		pristine HA	54.29	30. 9	5.7	-0.0066	62
		>100 kDa HA	113.49	297	81.73	-0.0070	60
NaCl	QD-NH ₂	30-100 kDa HA	107.17	27 26	56.78	-0.0067	60
		10-30 kDa HA	7-, 9	15.97	55.09	-0.0092	54
		3-10 kDa HA	9.	39.04	46.77	-0.0071	62
		< 3 kDa HA	1537	48.00	51.88	-0.0075	64
		without P A		26.14	/	-0.0050	64
		prist [*] e HA	154.45	32.54	154.55	-0.0087	72
	QD-COOH	>1.0 K. II	z12.57	32.43	225.54	-0.0083	72
CaCl ₂		20-100 kDa J A	183.84	26.89	194.62	-0.0067	72
		10-30 kDa-AA	61.97	28.90	74.86	-0.0083	70
	え	-101 Da HA	50.99	40.07	76.68	-0.0118	70
		< 3 kDa HA	50.94	47.68	88.16	-0.0086	74
	QD-NH2	without HA	/	/	/	/	/
		pristine HA	100.51	0.83	45.53	-0.0107	54
		>100 kDa HA	153.08	7.63	81.02	-0.0195	60
CaCl ₂		30-100 kDa HA	149.01	6.30	59.33	-0.0206	60
		10-30 kDa HA	55.30	2.24	12.93	-0.0227	54
		3-10 kDa HA	55.20	8.41	36.36	-0.0181	60
		< 3 kDa HA	54.56	38.94	82.03	-0.0191	70

418 presence/absence of pristine- and M_f -HA in mono- and divalent electrolyte.

419

420 As seen in Figure 4, the transport and retention behavior of QD-NH₂ in the 421 porous media were different with QD-COOH. QD-NH₂ was nearly deposited in the

sand at 3 mM NaCl solution without HA, which was most likely resulted by the 422 strong electrostatic attraction force between positive QD-NH₂ and negative potential 423 424 sand. However, QD-NH₂ suspended in the pristine HA and NaCl was highly mobile in the sand as seen by the high recovery and low retention (Table S4). BTCs of OD 425 reached a peak value of $C/C_0 = 0.74$ after 2 PVs, and 26% of injected QD were 426 retained in the sand. It has been reported that HA could increase particle stability and 427 decrease rates of attachment.^{31, 56, 57} Similar observation showed that HA enhanced the 428 transport of nanoparticles of nTiO₂,⁵² Fullerene (C₆₀).²⁵ In HA can absorb 429 onto particles surface and alter the electrostation 430 increasing the electrostatic repulsive and providing more steri 431 tabilize nanoparticles in the aquatic environment.⁵⁶ 432 433 In the presence of M_f-HA, the n QD-NH₂ in monovalent electrolyte was significantly enhanced. lly, this chanced effect was strongly related to the 434 MW of M_f-HA. High MW M_f-HA enhanced the mobility more significantly than low 435 eper dent effect on the nanoparticle stability by M_f-HA was 436 MW M_f-HA. Such also observed in previous studies.^{42, 47} The injected QDs significantly transported 437 across the column in the presence of high MW HA fraction (>100 and 30-100 kDa 438 HA), while the effluent concentration of QDs was reached a peak value of $C/C_0=0.05$ 439 in the presence of < 3 kDa HA. The retention of QD-NH₂ with low MW HA fraction 440 (30-10 kDa, 3-10 kDa, and < 3 kDa HA) and NaCl in suspensions were higher than 441 those in the presence of high MW HA fraction in suspensions. In addition, the value 442

443 of attachment efficiency of QD-NH₂ was increased with the MW decreasing (Figure

444	7). These observations indicated that high MW HA fraction could enhance the
445	mobility of QD-NH ₂ in monovalent electrolyte more efficiently than low MW HA.
446	Compared with QD-COOH, the influence on the transport of $QD-NH_2$ was more
447	efficient with the same MW Mf-HA, indicating that the role of surface coating of
448	particles is also important in the transport behaviour of nanoparticles. Adsorption
449	studies revealed that the adsorbed amount of HA onto QD-NH2 surface increased with
450	the increasing of HA MW (SI Table S5). The adsorbed HA on nanoparticles surface
451	could impart more electrostatic force and steric repulsion force or particles. Table 1
452	showed that the steric repulsion energy in high MW Mr Areas signer than in low
453	MW M_f -HA fraction, and the height of the energy barry in high MW HA fractions (>
454	100 kDa and 30-100 kDa HA) were higher then that in low MW HA fractions (10-30
455	kDa, 3-10 kDa and < 3 kDa HA) after incomparing the steric repulsion energy into
456	DLVO calculations. These results indicated that high adsorption and strong steric
457	repulsion ⁴⁷ of high MW M _f -HA ould explain the aforementioned MW-dependent
458	effect (high MW H4 in nion could enhance the mobility of QD-NH ₂ in monovalent
459	electrolyte more efficiently than low MW HA). Furthermore, the modified DLVO
460	interaction energy profiles (SI Figure S3) showed that the secondary energy minimum
461	in the low MW HA fraction (10-30 kDa, 3-10 kDa and < 3 kDa HA) were deeper than
462	in high MW HA fractions (> 100 kDa and 30-100 kDa HA). It is suggesting that
463	secondary minimum is likely an important mechanism for the obtained transport
464	behavior of QD-NH ₂ . Nonetheless, how the component (the composition of each MW
465	fraction of HA) interacted with the surface coating of nanoparticles in this enhanced

transport is still not well clarified. Further study should investigate how specific



467 component influences the transport and fate of nanoparticles.

472 3.3.2 Effects of pristine- and M_f -HA on the transport and retention of QDs in the 473 divalent electrolyte

The transport and retention behavior of QDs was also studied in divalent electrolytes. Figures 5 and 6 showed the observed BTCs and RPs of QD-COOH and QD-NH₂, respectively. Compared with Figure 3a, QD-COOH was significantly deposited in the sand at 2 mM CaCl₂. Other studies^{19, 22} which investigated the

transport and retention of QDs have also reported relatively high deposition rates on 478 sand. DLVO calculations (SI Figure S1) suggested the presence of a high energy 479 barrier (26.14 kT) and a deep secondary energy minimum (-0.0050 kT) between 480 OD-COOH and sand. This suggested an higher energy barrier against OD-COOH 481 deposition in the primary energy minimum, while QD-COOH can be captured in the 482 secondary energy wells.⁵⁸ Moreover, it has been reported that the divalent cations 483 could decrease the surface potential through screening particle charge and form 484 divalent cation (Ca²⁺) bridging between the negatively QDs and the 485 negatively charged sand surfaces.⁵⁹ Thus, the sig 486 of QDs in the presence of Ca²⁺ is likely due to the formatio ging between QDs and 487 surface and the secondary energy minin 488

489 Furthermore, Figure 5a also sh he pristine- and M_f-HA had distinct effects on the transport and ren of QE-COOH in divalent electrolyte. All of the 490 of QDs in the sand column. In the presence of pristine HA, HA enhanced the me 491 pic y increased to a maximum peak value and then slowly 492 the BTCs of QD decreased. Moreover, the BTCs of QD-COOH were nearly coincided with that of 493 nonreactive tracer. Similar BTCs shapes were also observed in the presence of Mf-HA. 494 Compared with the monovalent electrolyte, the transport of QD-COOH in divalent 495 electrolyte was more sensitive to the changes in MW of Mf-HA. All of the Mf-HA 496 enhanced the mobility of QDs in the sand column and high MW HA fraction (>100 497 kDa, 30-100 kDa HA) facilitated the transport of QDs in CaCl₂ solution more 498 significantly than lower MW HA fraction (3-10 kDa, and <3 kDa HA). Moreover, the 499

retention profile of QD-COOH with M_f-HA in suspension was lower than that without 500 HA, while the shapes of retention profiles of QD-COOH with HA in suspensions were 501 502 similar with those without HA in suspensions. This result suggested that the presence of HA in OD-COOH suspensions may not change the deposition mechanisms of 503 QD-COOH in the sand under divalent electrolyte.⁶⁰ However, these observations 504 were in good agreement with the modified DLVO interaction energy profiles (SI 505 Figure S4) predicated. The height of the energy barrier in high MW HA fractions (> 506 100 kDa and 30-100 kDa HA) were higher than in low MW tions (10-30 kDa, 507 3-10 kDa and < 3 kDa HA), while the secondary en 508 is deeper in the low MW HA fraction than high MW HA frac 509 lition, the secondary energy - 10 kĎa HA minimum is less deep for 3 kDa than for this was also reflected in the 510 transport behavior of QD-COOH 511 These results suggested that the secondary energy minimum an insportant mechanism for QDs transport. 512 studies also revealed that the amount of adsorbed HA onto Moreover, adsorption 513 ghe in the presence of high MW HA than those in low MW 514 **QD-COOH** surface HA (SI Table S5). This preferential adsorption of high MW NOM was also observed 515 on mineral solid surface by ¹³C-nuclear magnetic resonance and size exclusion 516 chromatography analysis.^{61, 62} The adsorption of HA could provide additional 517 electrostatic repulsion and steric repulsion, and the steric repulsion provided by high 518 MW was stronger than that provided by low MW HA fractions, which results in the 519 higher recovery of QDs in the presence of higher MW M_f-HA. 520



Figure 6. Effluent breakthrough curve (a, l/) which retention profiles (c, d) obtained for
QD-NH₂ transport in quartz sind a 3 mM CaCl₂ with/without pristine- and M_f-HA at
pH 7.0.

521

 L_2 a background electrolyte, the mobility of QD-NH₂ was 525 In contrast, not significantly influenced by the pristine- and M_f-HA. QD-NH₂ was completely 526 deposited on the sand at most conditions. Specially, the transport of QD-NH₂ was 527 slightly enhanced by the pristine HA and <3kDa HA fraction, but the enhancement 528 was negligible. The retained concentration of QD-NH₂ decreased significantly with 529 the increasing transport distance in the presence of pristine- and Mf-HA. Moreover, 530 the shapes of retained profiles for QD-NH2 were similar under all examined 531 conditions, indicating that the deposition mechanism was similar in divalent 532

electrolyte. Although the adsorption of HA changed the chemical properties of 533 QD-NH₂ and enhanced the electrostatic repulsion and between QD-NH₂ and sand, the 534 presence of Ca²⁺ could also form cation bridging between HA and sand or HA and 535 HA. Modified DLVO interaction energy calculation (SI Figure S5) predicted the 536 presence of >12 kT primary energy maximum and a deeper secondary energy 537 minimum in the presence of HA. In addition, the height of energy barrier in the 538 presence of < 3 kDa was higher than in other MW HA and the depth of secondary 539 energy minimum in pristine HA was less than other condi may be result a 540 little amount of QD-NH2 moving through the colu 541 on of < 3 kDa HA or pristine HA existed in the suspensions that the depth of secondary 542 energy minimum in this condition (QD in divalent electrolyte with or 543 saspended without pristine and M_f-HA) were 544 n other conditions that have been examined in this study. This agge ted that the QD-NH₂ much more likely deposited 545 y energy minimum. The significant deposition of in the prim in the secondary than 546 IA maybe account for the lower energy barriers and 547 $QD-NH_2$ in the pr deeper secondary energy minimum. 548

In a word, these results for the M_f-HA on the transport and retention of COOHand NH₂-QD in mono- and divalent electrolyte indicated that the coating agent, cation type and the M_f-HA have a great influence on the transport of QDs in sand. Generally, high MW M_f-HA could enhance the mobility of QDs more obviously than low MW M_f-HA. This MW-dependent effect was ascribed to the amount of adsorbed HA on QDs surface was higher in the presence of high MW M_f-HA than that in the presence of low MW HA fraction, and the steric repulsion from high MW M_{f} -HA was stronger than that of low MW M_{f} -HA. However, HA cannot govern the transport behaviors of QDs in some conditions. Solution chemistry and particle coating (e.g. carboxyl and amino) were also important for the transport and fate of nanoparticles reported by previous studies. The difference transport behaviors for QDs in porous media also suggested the important of cation type and particle coating on the transport of QDs in environment.



566 Understanding the transport and fate of ENPs in saturated sand column is 567 important to evaluate the potential risk of these materials to environmental and human 568 health. In this study, well-controlled column experiments were conducted using two 569 QDs with different surface functionalizes. The results showed that coating of QDs has 570 a distinguishing effect on the transport and retention of QDs in both pristine HA and 571 M_f-HA. Those findings emphasize that nanoparticles with various coatings will

behave differently even under the same condition. In addition, the results also showed 572 that the different MW of HA fraction play different role in the transport of QDs. 573 574 Pristine- and Mf-HA enhanced the transport of carboxyl coated QD and amino coated OD in divalent electrolyte and monovalent electrolyte, respectively, and high MW HA 575 fraction enhanced the transport of QDs more significantly than low MW HA fraction. 576 Nevertheless, the transport of carboxyl coated QD in monovalent electrolyte 577 decreased slightly in the presence of pristine- and M_f-HA. The transport of amino 578 coated QD was not much different in the absence and of pristine- and 579 Mf-HA. This molecular-dependent effect on the mole 580 als that different fractions of HA from the natural environment much distinguishing effects 581 on nanoparticles transport and fate. As the W compo ent of various source of HA is 582 583 much unlike and physical or chemical ald also alter the MW distribution of urther **dudies** investigating the effect of MW HA from identical source, 584 A on the transport and fate of nanoparticles are composition of different soured I 585 ver, in order to further thoroughly understand the 586 highly recommen influence of HA on the transport and fate of nanomaterial, the effects of pH and 587 concentration of M_f-HA should be also investigated in future. 588

- 589 **Conflicts of interest**
- 590 There are no conflicts of interest to declare.
- 591 Acknowlegements

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715 List of figures

- **Figure 1.** (a) UV-vis spectra, (b) the quotient of absorbance values at 250 nm and 365
- nm (E_2/E_3), (c) the absorbance values at 280 nm for pristine- and M_f-HA, and (d-i)
- Fluorescence EEMs of visitive-HA and M_f -HA.

Figure 2. Zeta potentials (a and c) and particle size (b and d) of QDs in the absence

- and presence of pristine- and M_f-HA in 3 mM NaCl or 2 mM CaCl₂ solutions.
- **Figure 3**. Effluent breakthrough curve (a, b) and retention profiles (c, d) obtained for
- 722 QD-COOH transport in quartz sand at 3 mM NaCl with/without pristine- and M_f-HA
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- 729 at pH 7.0.
- **Figure 6.** Effluent breakthrough curve (a, b) and retention profiles (c, d) obtained for
- 731 QD-NH₂ transport in quartz sand at 3 mM CaCl₂ with/without pristine- and M_f -HA at
- 732 pH 7.0.



738

How the molecular weight fractionated humic acid affects the transport and retention

740 of quantum dots in porous media?