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# 1 **Stabilization of fragmental polystyrene nanoplastic by natural organic matter:**

## 2 **Insight into mechanisms**

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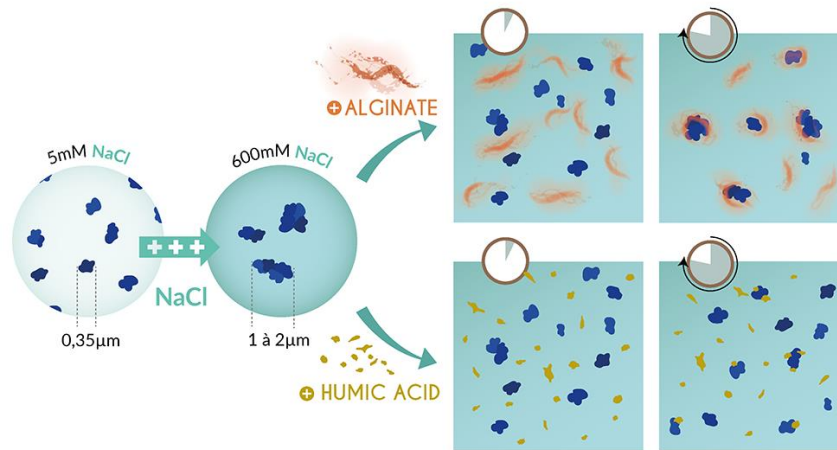
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## 12 **ABSTRACT**

13 The increasing amount of plastic debris in the environment and its disintegration into  
14 submicrometric particles is a cause for concern. Due to the colloidal nature of nanoplastics, their  
15 environmental fate should be investigated separately from that of microplastics. Abiotic factors greatly  
16 influence nanoplastics' stability. This will affect its residence time in the hydrosphere. So, we  
17 investigated the behavior of two different nanoplastic models (with different sizes and shapes) regarding  
18 ionic strength, pH, and varying concentrations of two natural organic matters: humic acid and sodium  
19 alginate. The results demonstrate that both natural organic matters enhanced the aqueous stability of  
20 nanoplastics over time at high ionic strengths. Depending on the organic matter's nature, different  
21 stabilizing mechanisms were revealed using dynamic light scattering and asymmetrical flow field flow  
22 fractionation coupled to static light scattering. Humic acid provides electrostatic repulsion between  
23 particles, and some larger humic acid molecules provide a steric hindrance. Sodium alginate sorbs onto  
24 and bridges separate particles and small aggregates of nanoplastics. The covered particles are stabilized  
25 by steric hindrance. The results highlight the importance of considering natural organic matters'  
26 properties when assessing nanoplastics behavior in the environment.



27

28 **KEYWORDS**

29 Plastic debris, Environmental fate, Aggregation, Ionic strength, Morphology

30

31 **SYNOPSIS**

32 Mechanisms of nanoplastic stabilization will depend on the composition of the natural organic  
 33 matter.

34

## 35 INTRODUCTION

36 As the use of plastic-based materials increases, plastic waste in the environment increases  
37 proportionally<sup>1,2</sup>. These last five years, it was demonstrated that plastic debris could persist as  
38 nanoplastic (< 1 $\mu$ m) before eventual mineralization of the polymer<sup>3-5</sup>. Environmental sampling of  
39 plastic debris at the ocean surface, coupled to numerical modeling, suggests that a substantial part of all  
40 the plastic debris is composed of nanoplastics<sup>6-8</sup>. Since nanoplastics are an emerging contaminant, their  
41 environmental fate should be better described. While airborne transport of microplastics is increasingly  
42 coming under scrutiny<sup>9,10</sup>, water remains the environmental compartment where most plastic debris is  
43 found<sup>11,12</sup> and where oxidative and hydrolytic conditions are favorable to plastic degradation<sup>13-16</sup>. As  
44 such, it is crucial to understand the behavior of nanoplastics in aqueous systems.

45 To describe a colloidal material's environmental fate in aqueous systems, successive and  
46 complementary approaches consist of modeling simple environmental systems in the lab, using these  
47 results to establish numerical simulations, and, finally, confronting these simulations with the analysis  
48 of environmental samples<sup>17</sup>. Based on this approach, experimental systems describing nanoplastics' fate  
49 have emerged<sup>18</sup>, especially concerning porous media<sup>19-21</sup> and water<sup>22,23</sup>. Nanoplastics' stability in water  
50 is generally determined by measuring changes in their size and sedimentation rates. Using this approach,  
51 the stability of nanoplastics has been assessed in natural waters<sup>23-33</sup>, in deionized water with various  
52 ionic compositions, ionic strengths, and pHs<sup>21,22,25,31,34-40</sup>, in the presence of NOM and suspended  
53 sediments<sup>22,23,27,31,33,34,36,38-41</sup> and in the presence of extracellular polymeric substances (EPS)<sup>37,42</sup>. Most  
54 studies have used polystyrene (PS) latex spheres, which are perfectly smooth, spherical, and  
55 monodisperse in size. Recently, the stability of more environmentally relevant models, such as aged  
56 polystyrene (PS) latex spheres, laser-ablated PS, or fragmental PET, has been studied<sup>37,39,43,44</sup>.

57 While these studies allow the emergence of global trends concerning nanoplastic stability, they also  
58 have inconsistent conclusions. For example, nanoplastic models have been observed to be both stable  
59 and unstable in artificial seawater<sup>33,45</sup>, and in the presence of iron<sup>23,34</sup>. Such discrepancies can be  
60 explained first by the physical and chemical properties of the nanoplastics models used (size, shape,  
61 surface functionalization, composition, purity, etc.), which are known to strongly affect the behavior of

62 colloidal materials. Additionally, nanoplastics are strongly sensitive to the media's properties (type,  
63 concentration, and speciation of electrolytes, nature of the organic matter, pH). Indeed, according to the  
64 relative concentration of spherical PS nanoplastic models, NOM, and cations, opposite behaviors have  
65 been observed<sup>23,39</sup>.

66 In light of these observations, the stability of two nanoplastic models was studied. The first model  
67 is a monodisperse polystyrene latex (PSL) sphere. The second model is produced from the mechanically  
68 degraded primary microplastic (PS pellets) and, as such, is more environmentally relevant due to its  
69 irregular, asymmetrical shape and polydisperse size. NPs' aqueous stability was assessed at different  
70 ionic strengths (5 to 770 mmol L<sup>-1</sup> NaCl) and in the presence of varying concentrations (0.005 to  
71 140 mg L<sup>-1</sup>) of two NOMs which have different properties: humic acid (HA) and sodium alginate (SA).  
72 HA has a relatively compact structure and amphiphilic properties, whereas SA has a more linear  
73 structure with hydrophilic properties. HA represents terrestrial organic matter, whereas SA represents  
74 marine organic matter and is a significant component of EPS produced by microbial communities<sup>46,47</sup>.  
75 It was demonstrated that both NOMs stabilize the environmentally relevant NP model at high ionic  
76 strength. However, due to their different physico-chemical properties, the NOMs have different  
77 stabilizing mechanisms. These were characterized by asymmetrical flow field flow fractionation  
78 coupled to static light scattering (A4F-SLS) and confirmed by dynamic dynamic light scattering (DLS).  
79 The present work discusses these mechanisms and their possible implication for the fate of nanoplastics  
80 in both terrestrial and marine environments.

81

## 82 **EXPERIMENTAL**

### 83 **Sample preparation**

84 All aqueous solutions and dispersions were prepared with analytical grade deionized (DI) water  
85 (Millipore, 18.2 MΩ). A stock solution of NaCl (solid, LabKem ExtraPure) at 1.80 mol L<sup>-1</sup> was prepared.  
86 The pH of all solutions was fixed at pH of 5, 6.5, or 8 using NaOH (Fisher Scientific, Analytical Grade)  
87 and HCl (70%, Sigma Aldrich, ACS Grade). All solutions and dispersions were stored at 4°C in the dark

88 before use. Two nanoplastic (NPs) models were used in this study and are described in Table 1 and  
 89 illustrated in Figure S1. Carboxylated polystyrene latex spheres of 200 nm (*PSL COOH*) are purchased  
 90 from Polysciences© (Polybead® Carboxylate Orange Dyed Microspheres 0.20 µm, Warrington USA).  
 91 A stock dispersion at a concentration of 100 mg L<sup>-1</sup> was prepared. A NP model with irregular and  
 92 polymorphic shapes (*NPT-P*) was produced by the mechanical abrasion of industrial-grade polystyrene  
 93 (PS) pellets (Total, Paris, France) as described by El Hadri et al. (2020)<sup>48</sup>. The pellets are composed of  
 94 primary (-P) PS, which contains no additives and has not been aged. Due to the less stable nature of the  
 95 *NPT-P* compared to *PSL COOH*, the experiments presented here used different batches of *NPT-P* to  
 96 avoid a bias brought about by the aging of the stock dispersion. Each batch was produced using PS from  
 97 the same degradation round. Before each experiment, the size of the nanoplastic dispersions was verified  
 98 with DLS measurements. Concentration of the stock *NPT-P* solution was measured with a Total Carbon  
 99 Analyzer (Shimadzu TOC-V CSH) and varied between 22 and 35 mg L<sup>-1</sup>. According to the molecular  
 100 composition of PS, 1 mg L<sup>-1</sup> of organic carbon was converted to 1.08 mg L<sup>-1</sup> *NPT-P*.

101

102 *Table 1: Characteristics of the two nanoplastic (NP) models. The polydispersity index (PDI) is defined as the variance of the*  
 103 *Gaussian-fitted size distribution. The aspect ratio is defined as the ratio of the length of the major axis and minor axis as*  
 104 *determined by TEM images (Figures S1 and S2).*

Nanoplastic model	z-average diameter (nm)	Polydispersity Index (PDI)	Aspect ratio*	Zeta potential in 5 mmol L <sup>-1</sup> NaCl (mV)		
				pH 5	pH 6.5	pH 8
<i>PSL COOH</i>	197 ± 2	0.03 ± 0.01	1.02 ± 0.05	-37.69 ± 1.91	-38.65 ± 2.23	-42.80 ± 2.98
<i>NPT-P</i>	339 ± 7	0.18 ± 0.03	1.70 ± 0.57	-31.67 ± 1.01	-33.54 ± 2.72	-35.14 ± 2.13

105 \* Figure S2 illustrates the aspect ratio of *NPT-P* particles

106

107 Sodium alginate (SA) was prepared by introducing 60 mg of SA powder (solid, Acros Organics)  
 108 into 0.1 L DI water and mixing at 350 rpm in a square bottle overnight. The humic acid (HA) used in  
 109 this work was Leonardite purchased from the International Humic Substance Society (IHSS). The stock  
 110 solution of HA was prepared by adding 50 mg of Leonardite powder to 0.1 L of DI water. To solubilize

111 the stock solution, pH was adjusted to 11 (with NaOH at 0.1 mol L<sup>-1</sup>) under continual agitation with a  
112 magnetic stirrer. Then, the solution was mixed at 350 rpm for 24h. pH was then fixed to either 5, 6.5, or  
113 8 using 0.1 mol L<sup>-1</sup> HCl. The concentrations of the NOM stock solutions were determined with a Total  
114 Carbon Analyzer (Shimadzu TOC-V CSH). According to the NOM's molecular composition, 1 mg L<sup>-1</sup>  
115 of organic carbon was converted to 1.6 mg L<sup>-1</sup> HA and 2.8 mg L<sup>-1</sup> SA.

116

### 117 **Size characterization**

118 Hydrodynamic diameters ( $d_H$ ) were determined by dynamic light scattering (DLS) probe  
119 (Vasco-Flex, Cordouan Technologies, Pessac, France). The measured  $d_H$  of an agglomerating  
120 suspension is the average of the  $d_H$  of the individual particles and aggregates, weighted by their scattered  
121 light intensities<sup>49</sup>. The backscattered light is collected at a geometric angle of 170° with respect to the  
122 incident beam direction. For time-resolved DLS, each correlation function was accumulated for 60  
123 seconds and were spaced 30 seconds apart. DLS measurements of stock solutions are composed of an  
124 average of six measurements of 60 seconds. The z-average hydrodynamic diameter ( $d_{zH}$ ) was determined  
125 by fitting a normal distribution to the raw data using the cumulant algorithm. To analyze the different  
126 populations in size present in a dispersion, the Sparse Bayesian learning (SBL) algorithm was used. The  
127 distribution of the NPs' gyration radii was measured by static light scattering (DAWN HELEOS 18  
128 Angles, Wyatt Technology) with prior size fractionation using an asymmetrical flow field flow  
129 fractionation (A4F, Eclipse 3+, Wyatt Technology, Dernbach, Germany) and a UV-vis absorbance  
130 detector (1200 series, Agilent Technologies, France) as a concentration detector at 254 nm. The global  
131 method of A4F separation was used. It was previously optimized and described by Gigault et al. (2017)<sup>50</sup>  
132 (see Supplemental Information, S1).

133

### 134 **Kinetics of Colloidal Aggregation**

135 The kinetics of nanoplastic aggregation were determined by measuring the z-average  
136 hydrodynamic diameters ( $d_{zH}$ ) of the dispersions over one hour. A total volume of 3 mL was prepared  
137 by adding NaCl and DI water to the vial, followed by NOM (when it was studied), and vigorously

138 mixing the solution. Finally, the nanoplastic dispersion was added to the vial, marking the beginning of  
 139 the kinetic study. All kinetic studies were performed in triplicate. The aggregation rate ( $k$ ) was  
 140 determined from the slope of the one-hour-long kinetic study, according to equation (1):

$$141 \quad \left( \frac{dd_{zH}(t)}{dt} \right)_{t \rightarrow 0} \propto kN_0 \quad (1)$$

142 where  $d_{zH}(t)$  is the hydrodynamic diameter of aggregates as a function of time  $t$  and  $N_0$  is the initial  
 143 number-based particle concentration. Statistical analyses were operated using one-way ANOVA.  
 144 Pairwise comparisons of aggregation rates were made using Tukey's method.

145 At low ionic strengths, electrostatic repulsion between particles is high due to a thick electrical double  
 146 layer (EDL): the colloidal dispersion is said to be in the reaction-limited aggregation (RLA) regime. As  
 147 ionic strength increases, electrostatic repulsion decreases, and the aggregation rate increases. At an ionic  
 148 strength corresponding to the critical coagulation concentration (CCC), the interparticle energy barrier  
 149 is eliminated, aggregation rate is maximal ( $k_{fast}$ ), and the diffusion-limited aggregation (DLA) regime is  
 150 reached. The attachment efficiency  $\alpha$  describes aggregation kinetics by normalizing aggregation rates  
 151 under RLA regime ( $k$ ) by the DLA regime ( $k_{fast}$ ):

$$152 \quad \alpha = \frac{k}{k_{fast}} = \frac{\left( \frac{dD_{zH}(t)}{dt} \right)_{t \rightarrow 0}}{\left( \frac{dD_{zH}(t)}{dt} \right)_{t \rightarrow 0, fast}} \quad (2)$$

153

#### 154 **Derjaguin Landau Verwey Overbeek (XDLVO) theory of colloidal stability**

155 The total interaction energy as a function of the distance separating the particles,  $G^{tot}(h)$ , is  
 156 calculated as the sum of the Lifshitz-van der Waals attraction,  $G^{LW}(h)$ , the electrical double layer (EDL)  
 157 repulsion,  $G^{EDL}(h)$ , and the Lewis acid-base energy of interaction  $G^{AB}(h)$ . The surface interaction energy  
 158 was calculated at an ionic strength of 5 mmol L<sup>-1</sup>. Particle diameters and zeta-potential are presented in  
 159 Table 1.



160 The Lifshitz-van der Waals component,  $G^{LW}(h)$ , was calculated using the expression of the  
 161 retarded van der Waals interactions between two identical approaching spheres proposed by Gregory  
 162 (1981)<sup>51</sup>:

$$163 \quad G^{LW} = - \frac{Hr_{p1}r_{p2}}{6(r_{p1}+r_{p2})h} \left[ 1 - \frac{bh}{\lambda} \ln \left( 1 + \frac{\lambda}{bh} \right) \right] \quad (3)$$

164 where H is the Hamaker constant of polystyrene particles interacting through water, equal to  $1.23 \cdot 10^{-20}$   
 165 J;  $r_{p1}$  and  $r_{p2}$  are the radii of particles 1 and 2, respectively; b is an empirically defined constant,  $b = 5.32$ ;  
 166 and  $\lambda$  is the characteristic wavelength of the interaction with a value of  $\sim 100 \text{ nm}$ <sup>52</sup>.

167 The electrical double layer repulsion  $G^{EDL}(h)$  was calculated using the expression proposed by  
 168 Hogg et al. (1966)<sup>53</sup>:

$$169 \quad G^{EDL} = \pi\epsilon \frac{r_{p1}r_{p2}}{(r_{p1}+r_{p2})} \left[ 2\xi_{p1}\xi_{p2} \ln \left( \frac{1+e^{-\kappa h}}{1-e^{-\kappa h}} \right) + (\xi_{p1}^2 + \xi_{p2}^2) \ln (1 - e^{-2\kappa h}) \right] \quad (4)$$

170 where  $\epsilon$  is the permittivity of the medium, equal to  $6.95 \cdot 10^{-10} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$ ,  $\zeta_{p1}$ , and  $\zeta_{p2}$  are the surface charges  
 171 of particles 1 and 2, respectively, approximated by the zeta potential; and  $\kappa$  is the inverse of the EDL  
 172 thickness (Debye Huckel length reciprocal length), determined by the following equation:

$$173 \quad \kappa = \left[ \frac{e^2}{\epsilon k_B T} \sum i z_i n_i \right]^2 \quad (5)$$

174 where e is the charge of the electron;  $k_B$  the Boltzmann constant, T the temperature,  $z_i$  the valency of the  
 175 ions i, and  $n_i$  the number of ions i per unit volume.

176 The Lewis acid-base energy of interaction  $G^{AB}(h)$  of our system is the expression proposed by  
 177 van Oss (1993)<sup>54</sup>:

$$178 \quad G^{AB}(h) = 2\pi \frac{r_{p1}r_{p2}}{(r_{p1}+r_{p2})} \lambda_{AB} \Delta G_{(h=h_0)}^{AB} e^{\left( \frac{h_0-h}{\lambda_{AB}} \right)} \quad (6)$$

179 where  $\lambda_{AB}$  is the correlation length, chosen as 1.65 nm, according to Valsesia et al. (2018), and  $h_0$  is the  
 180 minimum distance of separation between the particle and the surface, taken as  $0.158 \text{ nm}$ <sup>55</sup>. The acid-  
 181 base potential  $\Delta G_{h=h_0}^{AB}$  is expressed as:

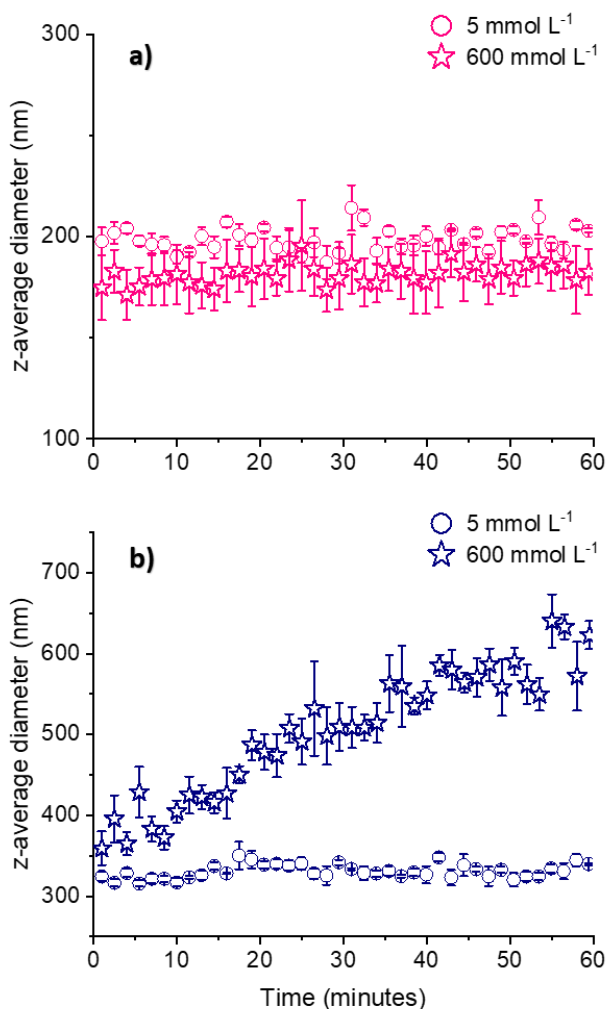
182 
$$\Delta G_{(h=h_0)}^{AB} = -2 \left( \gamma_{p1}^{AB} + \gamma_{p2}^{AB} - 2 \sqrt{\gamma_{p1}^{AB} \gamma_{p2}^{AB}} \right) \quad (7)$$

183 With  $\gamma_{p1}^{AB}$  and  $\gamma_{p2}^{AB}$  the polar component of the surface free energy for particles 1 and 2, respectively.

184  $\gamma_p^{AB}$  was directly quantified using the method by Valsesia et al. (2018) and found to be equal to 33.91

185 and 31.82 mJ.m<sup>-2</sup> for *PSL COOH* and *NPT-P*, respectively<sup>55</sup>.

186



189

190 *Figure 1: Aggregation kinetics of 4 mg L<sup>-1</sup> a) PSL COOH and b) NPT-P in either 5 mmol L<sup>-1</sup> or 600 mmol L<sup>-1</sup> NaCl at pH 6.5*

191

*(Error bar = standard deviation)*

192 Figure 1 shows that both particles are stable and low ionic strengths (5 mmol L<sup>-1</sup>). However, as ionic  
 193 strength increases, the particles show differences in stability: *PSL COOH* is stable at high ionic strength  
 194 (600 mmol L<sup>-1</sup>), while *NPT-P* aggregates, with  $d_{zH}$  increasing from 359 to 623 nm in one hour. While  
 195 the aggregation kinetics presented in Figure 1 took place at a pH of 6.5, the trends in stability were the  
 196 same at pH 5 and 8, representing the pH range of natural waters (Figure S3). Based on these kinetics of  
 197 aggregation, the *NPT-P*'s critical coagulation concentration (CCC) in NaCl was determined to be 59 and  
 198 67 mmol L<sup>-1</sup> NaCl at pH 6.5 and 8, respectively (Fig. S4). These values are lower than the CCC of 260

199 mmol L<sup>-1</sup> (NaCl, unadjusted pH) previously determined by El Hadri et al. (2020) and show no significant  
200 increase in stability with pH<sup>48</sup>. This suggests that the *NPT-P* studied here has lower surface oxidation  
201 than those studied by El Hadri et al. (2020), as confirmed by a lower zeta (-33 vs. -44 mV). For *NPT-P*,  
202 the concentration of -COOH on the surface is lower, inhomogeneous, and uncontrolled. The mechanical  
203 degradation method used to produce *NPT-P* cannot control the -COOH functionalization of their surface,  
204 which induces possible variability on the CCC. The CCC value of *PSL COOH* was not assessed since  
205 these particles were stable up to 1 M NaCl, which is above environmentally relevant concentrations.  
206 The CCC of *NPT-P* was lower than that of *PSL* models, as illustrated in Table 2. The reasons behind  
207 differences in stability between our *PSL* and *NPT-P* models are discussed below. Differences in stability  
208 between *PSL* particles and environmentally relevant nanoplastic models are commonly observed.  
209 Indeed, Yu et al. (2019) determined that non-functionalized and carboxylated *PSL* spheres have a CCC  
210 of 310 and 308 mmol L<sup>-1</sup> NaCl, respectively<sup>39</sup>. Mao et al. (2020) found an even greater CCC of 591  
211 mmol L<sup>-1</sup> NaCl for non-functionalized *PSL* spheres<sup>37</sup>. The aging of these particles by UV-irradiation  
212 strongly oxidized their surface. This caused stronger electrostatic repulsion, and consequently, the CCC  
213 increased up to 1108 mmol L<sup>-1</sup>. Singh et al. (2019) found a lower CCC of 140 mmol L<sup>-1</sup> NaCl for non-  
214 functionalized *PSL* and attributed this difference to the removal of surfactants<sup>31</sup>. The CCC calculated  
215 for *NPT-P* was coherent with observations made on other non-spherical, non-emulsified and surfactant-  
216 free, nanoplastic models. For example, NPs produced by laser ablation of PS show strong aggregation  
217 in 300 mmol L<sup>-1</sup> NaCl<sup>39</sup>. NPs produced from mechanical fragmentation polyethylene glycol  
218 terephthalate (PET-G) had a CCC of 54 mmol L<sup>-1</sup> NaCl at pH 6, and 110 mmol L<sup>-1</sup> NaCl at pH 10<sup>43</sup>.  
219 These recent observations confirm that particles' surface functionalization and morphology, as well as  
220 the presence of surfactants play key roles in the kinetics of aggregation.

221

222

Table 2: Summary of different critical coagulation concentrations (CCC) of NaCl for various NP models

<b>NPs models studied</b> Nomenclature : Composition Type of particle <i>Surface functionalization</i> * Nominal size (Charge)	<b>CCC (mmol L<sup>-1</sup>)</b>	<b>Reference</b>
PS Latex sphere <i>NF</i> 100nm (-)	310 in NaCl at pH 7.4	Yu et al., 2019 (39)
PS Latex sphere <i>COOH</i> 100nm (-)	308 in NaCl at pH 7.4	
PS Laser ablation 60 nm (-)	Not determined. Strong aggregation in 300 mmol L <sup>-1</sup> NaCl pH 7.4	
PS Latex sphere <i>NF</i> 100 nm (-)	591 in NaCl pH 7.5	Mao et al., 2020 (37)
PS Latex sphere aged by UV-irradiation during 60 hours <i>NF</i> 100 nm (-) **	957 in NaCl pH 7.5	
PS Latex sphere aged by UV-irradiation during 120 hours <i>NF</i> 100 nm (-) **	1108 in NaCl pH 7.5	
PS Latex sphere <i>NF</i> 240(-)	140 in NaCl pH 6	Singh et al., 2019 (31)
PET-G Mechanical degradation 500 nm (-)	54 in NaCl pH 6 110 in NaCl pH 10	Dong et al., 2020 (43)
PS Mechanical degradation 350 nm (-)	260 in NaCl pH unadjusted	El Hadri et al., 2020 (48)
PS Mechanical degradation 350 nm (-)	59 in NaCl pH 6.5	<i>NPT-P</i> particles studied here
PS Mechanical degradation 350 nm (-)	67 in NaCl pH 8	

223 \**NF* = Non-functionalized, *COOH* = carboxylated224 \*\* Initial particles were non-functionalized. Aging produced an increasing amount of carbonyl functional groups on the  
225 surface.

226

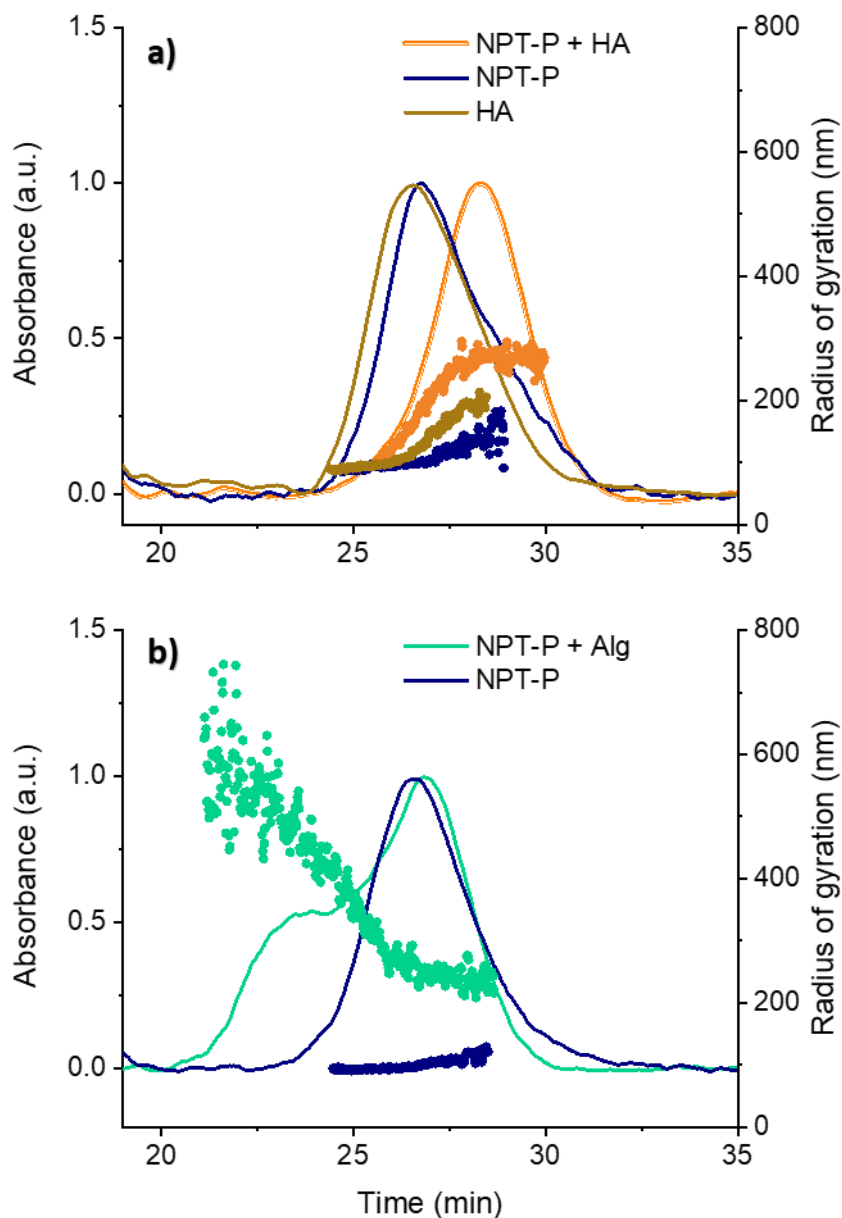
227 To characterize the effect of the particles' properties (size, surface potential, etc.) on their  
228 stability, the level of repulsion (energy barrier) between particles can be modeled by the extended  
229 Derjaguin Landau Verwey Overbeek (XDLVO) theory. According to the XDLVO theory, the  
230 interaction energies between *NPT-P* and *PSL COOH* are not significantly different (Table S1 and Figure  
231 S5). This demonstrates that size, surface charge, and hydrophobicity (Table 1), which are used to  
232 calculate interaction energy profiles, do not explain differences in stability. Instead, it suggests that *NPT-*  
233 *P*'s morphologies and polydispersity (Table 1 and Figure S1), as well as the lack of surfactants in the  
234 dispersion, are responsible for the aggregation rates observed. Indeed, particle morphology will affect  
235 their attachment efficiency. *NPT-P* has an aspect ratio of  $1.70 \pm 0.57$  and asperities on their surface,  
236 whereas *PSL COOH* has an aspect ratio of  $1.02 \pm 0.05$  and a smooth surface. At close approach, particles  
237 with elongated shapes (high aspect ratios) have larger van der Waals attraction when their major axii  
238 face each other<sup>56</sup>. While this has been difficult to demonstrate experimentally<sup>57</sup>, a few aggregation  
239 experiments support this theory<sup>43,58</sup>. Also, the collision of irregular and rough particles is likely to occur  
240 between particle protrusions and edges<sup>59</sup>.

241 For this reason, it is more accurate to model the interaction energy between *NPT-P* and  
242 asperities, using the smallest radius of curvature as the asperity radius<sup>60</sup>. This significantly reduces the  
243 level of repulsion (Fig. S5) since the final volume of interaction is reduced and repulsive forces  
244 (electrostatic and acid-base) decay more quickly with distance than attractive forces (Lifshitz-van der  
245 Waals)<sup>61,62</sup>. Secondly, particle collision rate during perikinetic aggregation (i.e., induced by collisions  
246 driven by the Brownian motion) is always more significant for dispersions containing different particle  
247 sizes<sup>63</sup>. Finally, *NPT-P* particles are free of surfactants, which have a stabilizing effect<sup>63,64</sup>. Since the  
248 more environmentally relevant nanoplastic model, *NPT-P*, is not stable at high ionic strengths, the  
249 stabilizing effect of natural organic matters (NOMs) was studied.

### 250 **Stabilization of *NPT-P* by natural organic matters**

251 Two different NOMs were chosen to represent the wide variety of physico-chemical properties  
252 of naturally occurring organic matters. The interaction of the *NPT-P* with the natural organic matter was  
253 described by characterizing the size of *NPT-P* with NOM at high ionic strength. Asymmetrical flow  
254 field-flow fractionation coupled to static light scattering (A4F-SLS) was used to characterize the  
255 assembly of *NPT-P* with NOM as this technique can discriminate different size populations and changes  
256 in polydispersity. Figure 2 illustrates the fractograms obtained for *NPT-P* in the presence of HA (Fig  
257 2a) and SA (Fig. 2b). *NPT-P* and HA alone have similar times of elution and variation of their radii of  
258 gyration ( $R_g$ ) over time. For *NPT-P* with HA, the peak's elution time range is identical, suggesting that  
259 *NPT-P* and HA stay dispersed and retain their initial sizes. However, the maximum of the peak increases  
260 from 26 to 28 minutes, with the corresponding  $R_g$  increasing from 100 nm up to 270 nm. This shift  
261 suggests that a specific size fraction of HA is associated with *NPT-P* and formed larger hetero-  
262 aggregates. Concerning the mixture of *NPT-P* with SA (Figure 3b), no fractograms were obtained for  
263 SA in these fractionation conditions due to its low scattering properties at this concentration  
264 ( $57 \text{ mg L}^{-1}$ ). In the presence of SA, two peaks are observed: one eluted around 23 minutes and another  
265 around 26 minutes. The first peak corresponds to a  $R_g > 400 \text{ nm}$ , while the second corresponds to a  
266 smaller  $R_g$ , around 250 nm. In A4F, the normal elution mode occurs when the relative diffusion between  
267 the different populations through the channel's height allows their separation according to the parabolic

268 profile of the main velocity flow. However, an earlier peak with a high  $R_g$  is indicative of steric elution  
 269 mode<sup>65</sup>. In this mode, the particles become too large to be separated based on diffusion coefficient and  
 270 are instead eluted by dragging forces. This first peak, in steric mode, corresponds to SA bridging  
 271 separate *NPT-P* particles and sorbing onto small aggregates of *NPT-P*. The second peak overlaps with  
 272 that of *NPT-P* alone and can be explained by the association of SA with single *NPT-P* or smaller  
 273 aggregates.

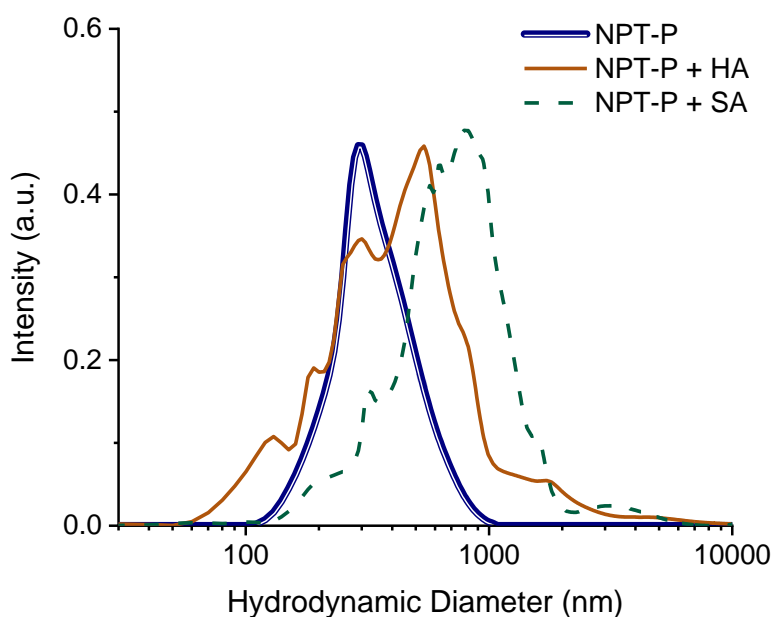


274

275 *Figure 2: Fractograms showing absorbance (line) and radius of gyration ( $R_g$ ) (points) of a) NPT-P in 5 mmol L<sup>-1</sup> NaCl,*  
 276 *NPT-P with 30 mg L<sup>-1</sup> HA in 600 mmol L<sup>-1</sup> NaCl, and 30 mg L<sup>-1</sup> HA in 600 mmol L<sup>-1</sup> NaCl at pH 6.5 and b) NPT-P in*  
 277 *5 mmol L<sup>-1</sup> NaCl and NPT-P with 57 mg L<sup>-1</sup> SA in 600 mmol L<sup>-1</sup> NaCl at pH 8, as a function of retention time*

278

279 To validate the variations in size populations and distributions, Figure 3 shows the size  
280 distributions of *NPT-P* with HA and with SA at high ionic strength based on the Sparse Bayesian  
281 Learning (SBL) algorithm. This algorithm allows investigating differences in size population within the  
282 limits of the DLS resolution. With HA, the *NPT-P* size distribution is large but still covering the size  
283 range of the initial *NPT-P*. However, HA induces a shift towards a higher  $d_H$  of 530 nm compared to the  
284 initial  $d_H$  of 320 nm for *NPT-P* alone. This shift may be due to the non-covalent adsorption of larger HA  
285 molecules onto the *NPT-P* surface. In the presence of SA, the size distribution is less polydisperse but  
286 with a maximum  $d_H$  around 820 nm. This larger size population can be explained by the physical  
287 association of SA with several ( $n > 2$ ) *NPT-P* particles.



288

289 *Figure 3: Average of intensity-based size distributions according to SBL algorithm of NPT-P with 30 mg L<sup>-1</sup> humic acid (HA)*  
290 *at pH 6.5 or 57 mg L<sup>-1</sup> sodium alginate (SA) at pH 8, in 600 mmol L<sup>-1</sup> NaCl measured between 45 and 60 minutes (n ≥ 18).*  
291 *The SBL algorithm reveals the most probable continuous size distribution among a set of 25 solutions.*

292 The A4F-SLS fractograms and DLS size distributions (Figures 2 and 3) suggest that HA and SA have  
293 different stabilization mechanisms. On the one hand, the HA molecules that are free in solution stabilize  
294 *NPT-P* by providing electrostatic repulsion. Some low molecular weight HA molecules are also  
295 adsorbing onto the *NPT-P* surface and providing steric repulsion. The co-occurrence of these two  
296 mechanisms is supported by the fact that leonardite humic acid is one of the more large and polydisperse



297 humic acids<sup>66</sup>. Indeed, electrostatic repulsion is attributed to the smaller size fraction of humic and fulvic  
298 acids<sup>38,40</sup>, while surface adsorption of the larger size fraction of HAs may occur via  $\pi$ - $\pi$  interactions  
299 (with the aromatic structures of HA) and result in steric hindrance<sup>22,31,39,67</sup>. Saavedra et al. (2019) noted  
300 that both HA and SA<sup>41</sup> stabilized negatively charged particles. Due to HA's compact structure,  
301 adsorption of HA onto colloids did not increase their size. However, SA's high molecular weight (282  
302 kDa, Fig. S6) and semi-rigid chains can lead to the formation of larger aggregates<sup>17</sup>. Indeed, SA chains  
303 stabilize *NPT-P* particles by wrapping around single particles and small aggregates and bridging  
304 separate particles. These hetero-aggregates are then prevented from further aggregating by steric  
305 hindrance. Since SA is highly hydrophilic, its adsorption onto nanoplastics can be attributed to hydrogen  
306 bonds and van der Waals interactions<sup>42,46,68,69</sup>. Indeed, Bhattacharya et al. (2010) demonstrated a  
307 significant affinity between negatively charged carboxylated PSL and negatively charged algae<sup>70</sup>. This  
308 affinity has been attributed to hydrogen bonds forming between the cellulosic component of algae and  
309 the PSL. Finally, using TEM, it appears that *NPT-P* is embedded in SA, while HA does not seem to  
310 have such a strong affinity with the *NPT-P* surface (Fig. S7).

311

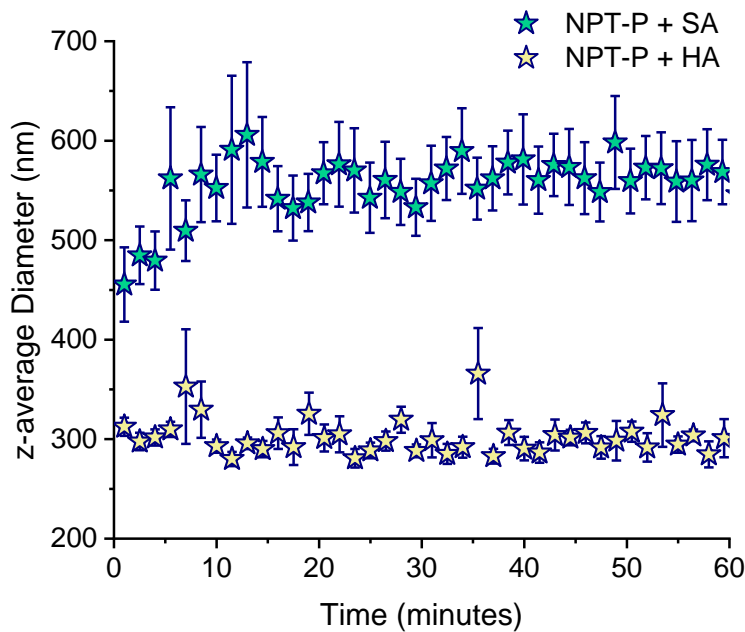
### 312 **Colloidal stability of NPT-P according to the nature and concentrations of NOM**

313 These two mechanisms of stabilization will have distinct impacts on nanoplastics' colloidal stability  
314 in aqueous media. Figure 4 illustrates the size variation of *NPT-P* in 600 mmol L<sup>-1</sup> NaCl with either HA  
315 or SA. At 600 mmol L<sup>-1</sup> NaCl, the size of *NPT-P* increases in the absence of NOM (Fig. 1). Figure 4  
316 shows that HA can stabilize *NPT-P* immediately, while SA stabilizes *NPT-P* within 10 minutes. The  
317 final sizes obtained (i.e., 300 nm for HA and 560 nm for SA) corroborate that different interactions  
318 occur between *NPT-P* and the two NOMs. In the presence of HA, the  $d_{zH}$  of *NPT-P* remains constant  
319 around 300 nm. HA is highly polydisperse with a colloidal fraction centered around 230 nm. So, for  
320 kinetics of *NPT-P* with HA, the  $d_{zH}$  presented in Figure 4 is a combination of both the  $d_{zH}$  of *NPT-P*  
321 (339 nm) and the  $d_{zH}$  of HA (230 nm). Despite this significant contribution of HA to the DLS signal,  
322 DLS will rapidly detect if aggregation occurs since scattering is highly sensitive to increases in size<sup>71</sup>.

323 In the presence of SA, the size of *NPT-P* increases within the first 10 minutes and stabilizes around 560  
324 nm. Without NOM, such an increase in size takes more than 30 minutes (Fig. 1).

325 Contrary to HA, 57 mg L<sup>-1</sup> SA does not contribute to the DLS signal. Therefore this increase in size  
326 followed by a stabilization is explained by a rapid hetero-association between *NPT-P* (particles and/or  
327 aggregates) and SA. Instead of keeping all particles separate as HA does, the SA biopolymer wraps  
328 separate or slightly aggregated plastic nanoparticles. Alginate molecules have been observed to form a  
329 layer with an approximate thickness of 20 nm around positively charged PSLs<sup>23</sup>. Also, when studying  
330 the aggregation of NPs with the dissolved (< 0.22 μm) fraction of organic matter that is naturally present  
331 in seawater, Chen et al. (2018) obtained similar kinetics of hetero-aggregation, with a rapid increase in  
332 size followed by a plateau around micrometric sizes<sup>68</sup>.

333 The relative quantity of particles and aggregates present in the dispersions over time was estimated  
334 based on the hydrodynamic diameter ( $d_{zH}$ ), the intensity of scattered light ( $I_{\theta}$ ), and a spherical form  
335 factor ( $P_{\theta}$ ), as described in Supplemental Information (S7). At high ionic strength, results show that the  
336 relative concentration of *NPT-P* plummets without NOM (Fig. S8). The relative *NPT-P* particle  
337 concentration does not decrease in the presence of HA, indicating colloidal stabilization induced by  
338 electrostatic repulsion. On the contrary, with SA, the relative *NPT-P* particle concentration decreases  
339 significantly and then stabilizes. Such behavior can be explained by the hetero-association of SA with  
340 *NPT-P* leading to a final state where all the *NPT-P* are associated with SA. Consequently, the rate of  
341 collision is reduced because of (i) the low rate of diffusion of large aggregates, (ii) the reduced number  
342 of separate particles and aggregates, and (iii) the effective repulsion between SA-coated surfaces.



343

344 Figure 4: Aggregation kinetics of  $4.0 \text{ mg L}^{-1}$  NPT-P, in  $600 \text{ mmol L}^{-1}$  NaCl, with  $57 \text{ mg L}^{-1}$  sodium alginate (SA) at pH 8  
 345 and  $30 \text{ mg L}^{-1}$  humic acid (HA) at pH 6.5 (Error bar = standard deviation)

346

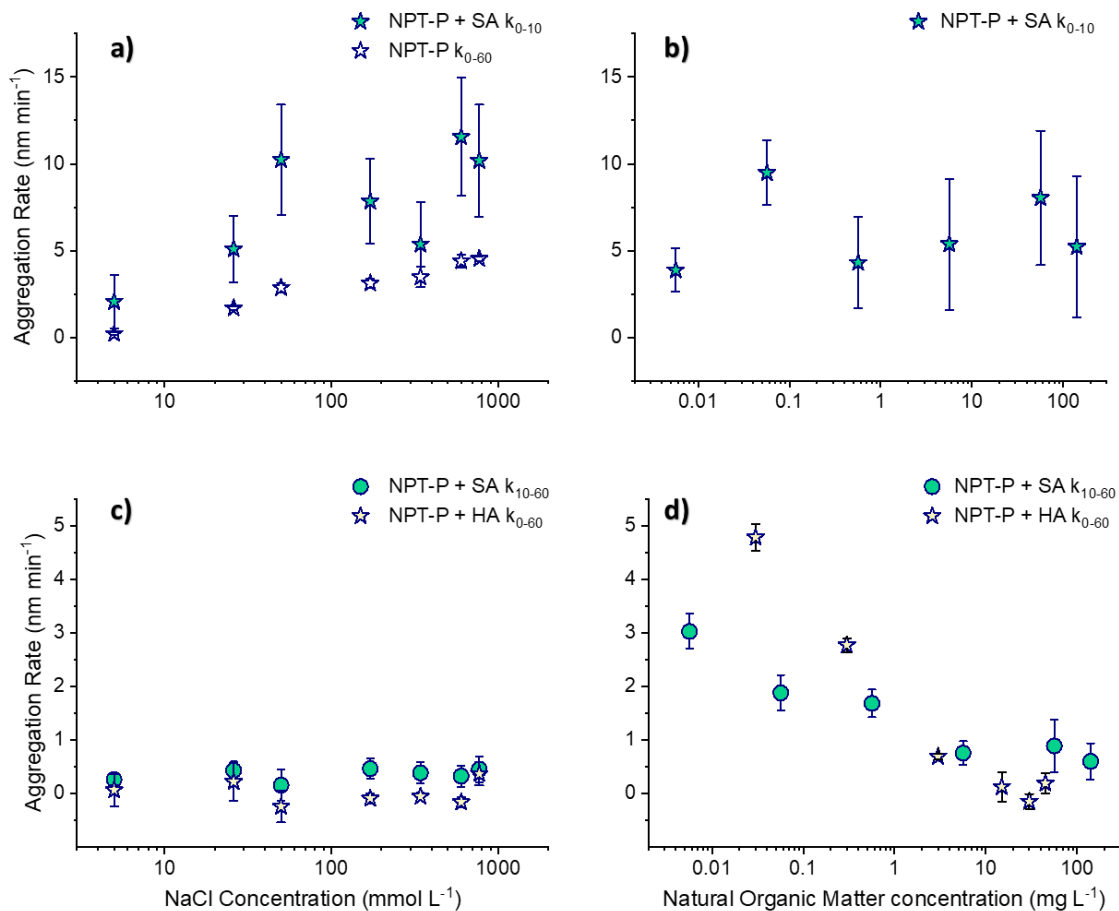
347 To validate this hypothesis, Figure 5 illustrates the different kinetics of association according to  
 348 NaCl and NOM concentration. Due to the nature of the kinetics of aggregation of *NPT-P/SA* in the  
 349 presence of SA, two different slopes were compared:  $k_{0-10}$ , which represents the fast rate of aggregation  
 350 from 0 to 10 minutes, and  $k_{10-60}$  representing the plateau, observed from 10 to 60 minutes. Figure 5a  
 351 shows that NPT-P and SA's association is always faster than the homo-aggregation of *NPT-P* for the  
 352 whole range of the ionic strength investigated ( $5$  to  $770 \text{ mmol L}^{-1}$ , pH 8). So, the aggregation kinetics  
 353 are initially accelerated by SA, which sorbs onto and bridges *NPT-P* particles. Figure 5b shows no  
 354 significant increase in the rate of the initial, fast aggregation rate ( $k_{10-60}$ ) as a function of SA  
 355 concentration. This suggests that small SA concentrations are sufficient to cover and stabilize *NPT-P*.  
 356 The SA that remains free in the solution (non-adsorbed) may have a stabilizing effect by increasing the  
 357 solution's electrostatic repulsion. This agrees with Summers et al. (2018), who observed that a low  
 358 concentration ( $\leq 1 \text{ mg L}^{-1}$ ) of EPS in a nanoplastic dispersion could play a dispersant effect<sup>42</sup>.

359 Figure 5c presents the aggregation rate of *NPT-P* with NOM as a function of ionic strength  
 360 during the stable section of aggregation's kinetics. In the presence of NOM, all aggregation rates were

361 lower than without NOM, except at 5 mmol L<sup>-1</sup> NaCl, where there was no significant difference (Fig.  
362 5c and S3). In the presence of HA, *NPT-P's* aggregation rate is not significantly different from 0 nm  
363 min<sup>-1</sup> except at 26 and 770 mmol L<sup>-1</sup> (p < 0.05). At 770 mmol L<sup>-1</sup>, the aggregation rate increases,  
364 suggesting that HA is losing its stabilizing effect due to a strong electrostatic screening by this high  
365 ionic strength. In the presence of SA, the aggregation rate hovers around 0.4 nm min<sup>-1</sup>, especially at  
366 higher ionic strengths. This suggests that HA may have a stronger stabilizing effect than SA. The NOM  
367 concentration in Fig. 5c was the minimum concentration required best stabilize the nanoplastic models  
368 at 600 mmol L<sup>-1</sup> NaCl (cf: Fig. 5d). Figure 5d shows that at high ionic strength HA rapidly reduces  
369 *NPT-P's* attachment efficiency. This is supported by the observations made by Singh et al. (2019),  
370 indicating that low concentrations of HA increased the CCC of negatively charged PSL spheres almost  
371 4-fold<sup>31</sup>. However, even high SA concentrations do not reduce  $k_{10-60}$  under 0.6 nm min<sup>-1</sup>. This agrees  
372 with Summers et al. (2018), who show that high alginate concentrations can have a flocculant effect<sup>42</sup>.

373 Furthermore, Lodeiro et al. (2016) noted that SA only slightly increased the stability of silver  
374 nanoparticles<sup>72</sup>. Saleh et al. (2010) also noted that HA was more effective than SA at stabilizing carbon  
375 nanotubes in NaCl<sup>73</sup>. The slightly more effective stabilizing capacity of HA compared to SA can be  
376 attributed to the fact that SA sorbs onto particles while HA causes repulsion between them. Indeed, the  
377 first mechanism is more likely to form flocs that are large enough to be affected by gravity.

378



379

380 *Figure 5: a) Aggregation rate of NPT-P and fast aggregation rate ( $k_{0-10}$ ) of NPT-P with 57 mg L<sup>-1</sup> SA, at pH 8 as a function of*  
 381 *NaCl concentration b) fast aggregation rate ( $k_{0-10}$ ) of NPT-P with varying concentrations of SA at 600 mmol L<sup>-1</sup> NaCl and pH*  
 382 *8. Aggregation rates of NPT-P with c) 57 mg L<sup>-1</sup> SA ( $k_{10-60}$ ) at pH 8 and with 30 mg L<sup>-1</sup> HA ( $k_{0-60}$ ) at pH 6.5 as a function of*  
 383 *NaCl and d) in 600 mmol L<sup>-1</sup> NaCl, with varying concentrations of HA at pH 6.5 and different concentrations of SA at pH 8.*

384

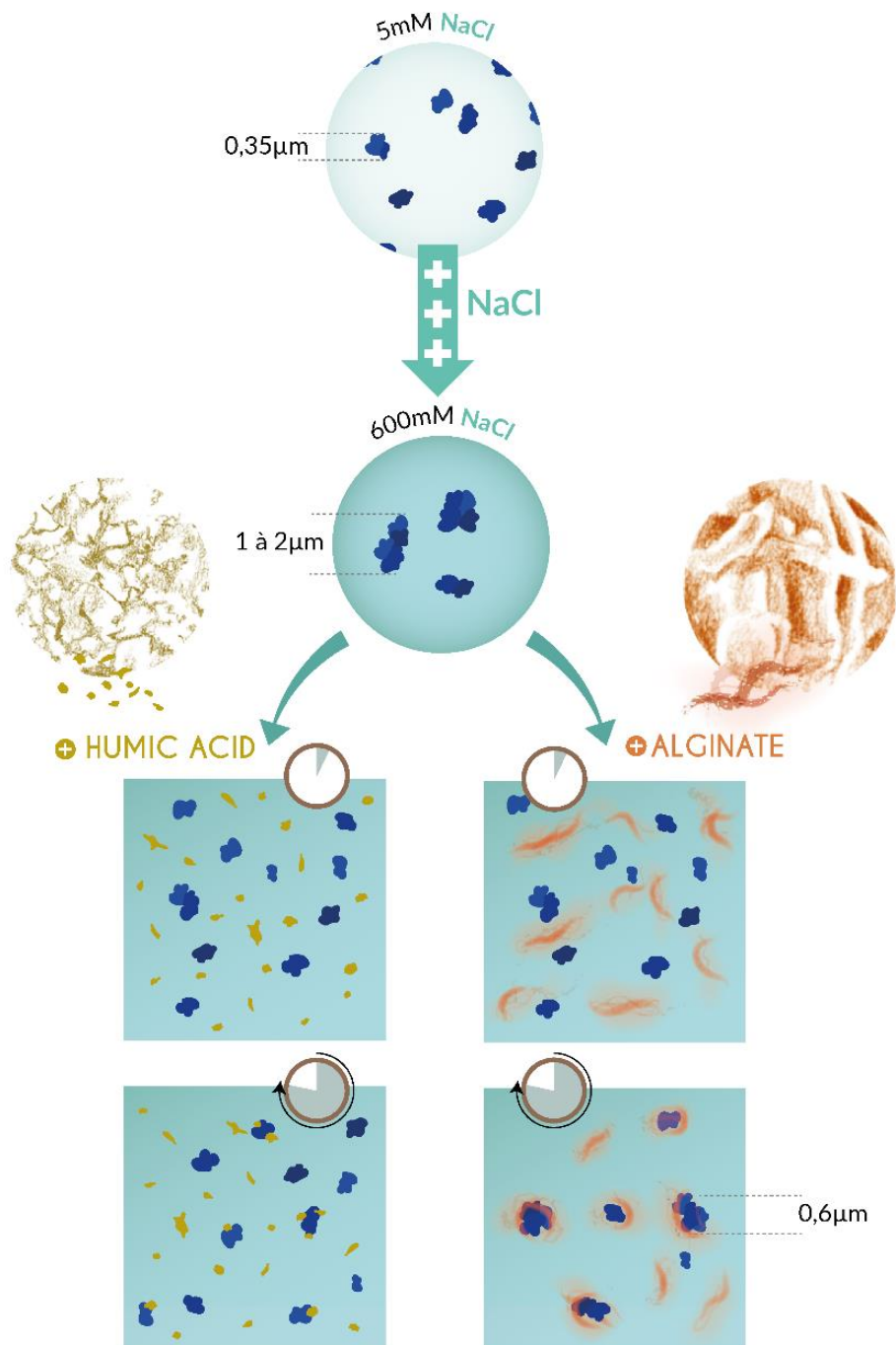
### 385 Environmental Implications of NOM-NP interactions

386 The aggregation rates presented in Figure 5 were determined at pH 6.5 for HA and pH 8 for SA,  
 387 as these pHs are representative of terrestrial and marine aquatic systems, respectively. Kinetic studies  
 388 performed at pH 5, 6.5, and 8 for both NOMs show that the same stabilizing mechanisms operate in the  
 389 pH range of natural waters (Fig. S9). At a given ionic strength, aggregation rates did not significantly  
 390 differ with pH ( $p < 0.05$ ). This minimal pH-dependency is to be expected since (i) *NPT-P's* stability is  
 391 not pH-dependent, (ii) HA stabilizes these particles by electrostatic and steric repulsion, which only  
 392 requires the NOM to be significantly negatively charged and unfolded, (iii) SA stabilizes *NPT-P* by  
 393 sorption via hydrogen bonds and van der Waals attraction, which are operational in this range of pH.

394 The different stabilizing mechanisms are summarized in Figure 6. These mechanisms have been shown  
395 to stabilize natural colloids<sup>17</sup> as well as engineered nanomaterials<sup>73-77</sup>. When studying the stability of  
396 fullerene, Espinasse et al. (2007) also noted the different mechanisms of stabilization of HA and SA<sup>74</sup>.  
397 Fullerene were more water-soluble in the presence of HA. HA's combination of hydrophobic regions  
398 and ionizable functional groups allows the former to sorb to hydrophobic particles and the latter to  
399 increase the particle's hydrophilicity. The amount of HA sorption onto carbon nanotubes was  
400 proportional to the HA aromaticity<sup>75</sup>. So, HA increases particles' stability by steric and charge  
401 stabilization. However, SA's large size promoted the aggregation of stable, polar fullerenes by bridging  
402 and encapsulating them<sup>74</sup>. Indeed, in NaCl, SA coats positively charged titanium dioxide and hematite  
403 nanoparticles which then confers electrostatic stability<sup>76,77</sup>. SA also coats and stabilizes negatively  
404 charged, carbonaceous nanomaterials, such as single-walled carbon nanotubes<sup>73</sup>.

405 In aqueous media, we might expect that SA will stabilize NPs and increase their dispersal. At  
406 the same time, it will induce retention when it is attached to a solid interface (i.e., soils, sediments,  
407 etc.)<sup>69,74</sup>. Furthermore, Cunha et al. (2020) showed that nanoplastics and microplastics' presence  
408 enhanced the production of EPS carbohydrates by freshwater *Cyanothece sp.*, suggesting a feedback-  
409 loop may occur<sup>78</sup>. The presence of NOM will impact nanoplastics environmental fate and affect the  
410 potential for co-transport of contaminants<sup>79,80</sup>. For example, compared to a matrix containing only a  
411 nanoplastic model and hydrophobic organic compounds (HOCs), the addition of HA to the matrix  
412 increased *Daphnia magna's* rate of uptake of the HOCs by ingestion<sup>81</sup>.

413



414

415 *Figure 6: Summary of the mechanisms of stabilization of NPT-P by humic acid (HA) and sodium alginate (SA) in NaCl*

416

417

418 **CONCLUSION**

419 This study investigated the mechanisms of stabilization of nanoplastics by natural organic matter (NOM)  
420 according to the media's ionic strength. The interaction of the nanoplastics with NOMs was determined  
421 by characterizing the size distributions and shapes using asymmetrical flow field-flow fractionation  
422 coupled to static light scattering (A4F-SLS) and confirmed by dynamic light scattering (DLS).  
423 According to their origin, the different NOM models, i.e., sodium alginate (SA) for marine environments  
424 and humic acid (HA) for terrestrial ones, present different stabilization mechanisms. Humic acid  
425 stabilizes the nanoplastic dispersion by electrostatic repulsion between particles, while larger molecules  
426 may sorb onto nanoplastics and provide a steric hindrance. However, sodium alginate adsorbs onto the  
427 nanoplastics' surface and bridges particles to form small aggregates that remain stable by steric  
428 hindrance against the increase in ionic strength. This study highlights the need to consider NOM's  
429 physico-chemical properties when assessing nanoplastics behavior in the aqueous environment.



430 **SUPPORTING INFORMATION.**

431 Images and size description of the nanoplastics models (Figure S1 and S2, pages S2-S3); Description of  
432 the asymmetrical field flow fractionation method (Section S1, page S4); Aggregation rates and Critical  
433 Coagulation Concentrations of the nanoplastics in NaCl (Figure S3 and S4); Results of the Extended  
434 Derjaguin Landau Verwey Overbeek (XDLVO) model (Table S1 and Figure S5, page S7,);  
435 Characterization of the sodium alginate (Figure S6, text page S8); Images of nanoplastics in the presence  
436 of natural organic matter (Figure S7 and text page S9); Evolution of nanoplastics concentration  
437 according to time calculated from static light scattering (Figure S8, text page S10 and S11); Aggregation  
438 kinetics of nanoplastics models in the presence of natural organic matter (Figure S9, page S12). This  
439 material is available free of charge via the internet at <http://pubs.acs.org>.

440

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443

444

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## Supporting Information for:

### Stabilization of fragmental polystyrene nanoplastic by natural organic matter:

#### Insight into mechanisms

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**The Supporting Information contains 9 figures, 1 table, 2 sections of text (SI1 and SI2), 9 references, 13 pages.**

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Supplemental Information 1: Method for Asymmetrical Flow Field Flow Fractionation (A4F) coupled to Static Light Scattering (SLS)

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Supplemental Information 2: Extended Derjaguin Landau Verwey Overbeek (XDLVO) theory of colloidal stability

Table S1: Energy barrier between particles according to DLVO and XDLVO theories, scaled to  $k_B T$

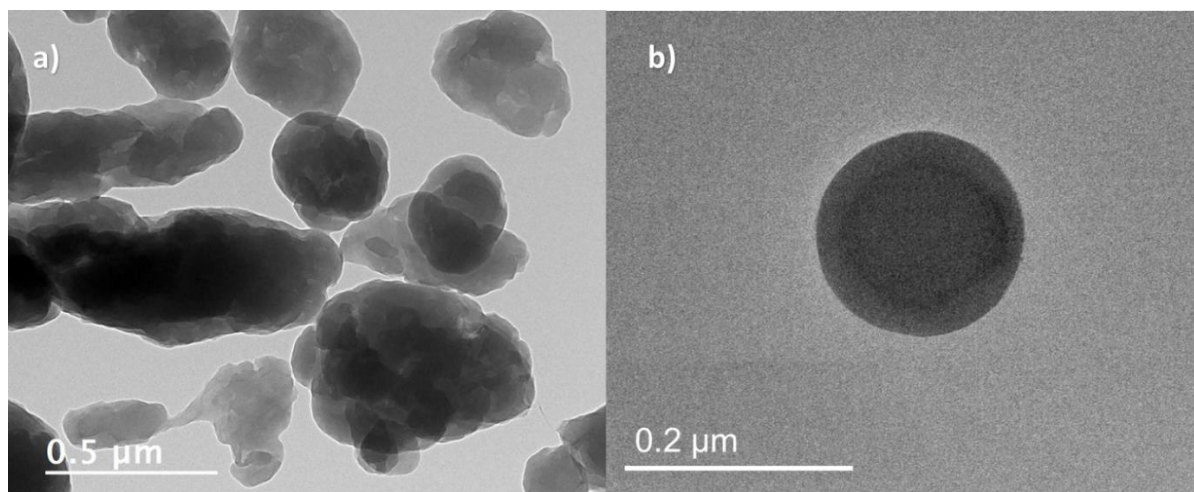
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Figure S7: Transmission Electron Microscopy Images of a) b) NPT-P without organic matter c) d) NPT-P with humic acid (HA) and e) f) NPT-P with sodium alginate (SA)

Figure S8: Relative particle concentration of NPT-P at 5 and 600 mmol L<sup>-1</sup> NaCl at a) pH 6.5, b) pH 8, c) with 30 mg L<sup>-1</sup> humic acid (HA) at pH 6.5 and d) with 57 mg L<sup>-1</sup> sodium alginate (SA) at pH 8.

Figure S9: Aggregation rate of NPT-P with a) 30 mg L<sup>-1</sup> humic acid b) 57 mg L<sup>-1</sup> sodium alginate, as a function of ionic strength and pH (Error bars = standard deviation)



*Figure S1: Transmission Electron Microscopy Images of a) NPT-P and b) PSL COOH*

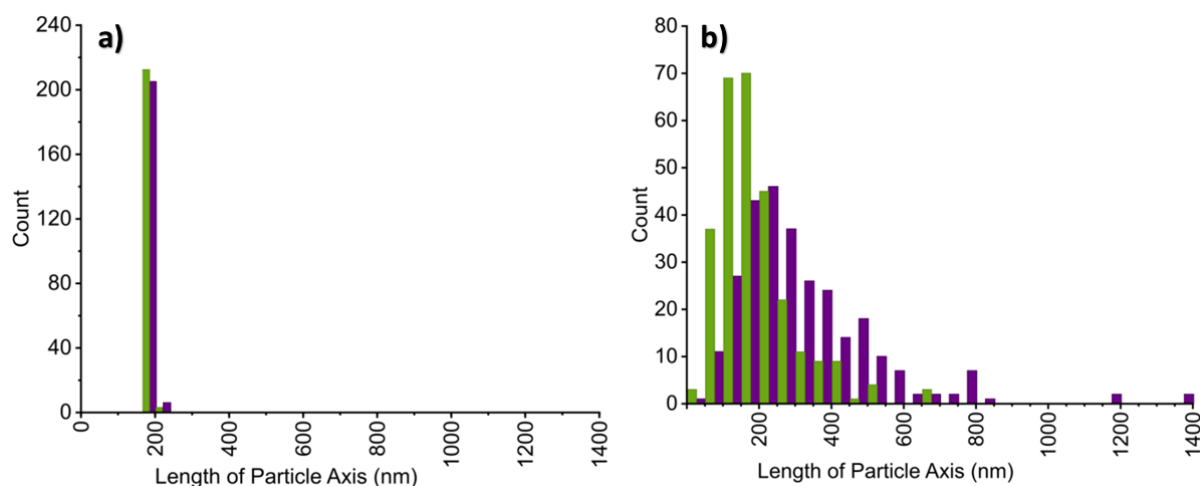


Figure S2: Histogram of short axis (green) and long axis (purple), as determined by TEM images of a) PSL COOH and b) NPT-P nanoplastic models in linear distribution (PSL COOH:  $n = 212$  and NPT-P:  $n = 283$ )

TEM images were obtained by a Jeol JEM 2100 HR (200kV) with an LaB<sub>6</sub> filament. The camera was a Gatan Orius SC 200 D. A 4  $\mu\text{L}$  drop was deposited on a full carbon grid and allowed to air dry. Data was analyzed with ImageJ software and the NanoDefine plugin, using the watershed fitting mode (Verleysen et al., 2019). The length of the major axis and minor axis were the longest and shortest lengths of the minimum bounding rectangle. Based on these images and assuming the NPT-P particles is either a sphere or an ellipsoid, the specific surface area was determined to be  $30.2 \pm 16.4$  and  $34.2 \pm 18.9$   $\text{m}^2 \text{g}^{-1}$ , respectively. The specific surface area was determined to be  $29.6 \pm 0.6$   $\text{m}^2 \text{g}^{-1}$  for PSL COOH.

The NPT-P minor and major axis followed a log-normal distribution, as determined with the orthogonal distance regression method. Equation (S1) was used to fit the data, with  $\mu$  the average of distribution and  $\sigma$  the standard deviation of distribution.

$$y = \frac{A}{\sigma x \sqrt{2\pi}} \exp \frac{-\ln(\frac{x}{\mu})^2}{2\sigma^2} \quad (\text{S1})$$

The following parameters were determined:

- For the NPT-P major axis:
  - $\mu = 395.70 \pm 30.65$
  - $\sigma = 380.52 \pm 48.34$
  - $A = 20734.02 \pm 6774.76$
  - $R^2$  (COD) = 0.99994
- For the NPT-P minor axis :
  - $\mu = 213.54 \pm 3.93$
  - $\sigma = 461.88 \pm 13.53$
  - $A = 9986.26 \pm 260.98$
  - $R^2$  (COD) = 0.98101

### Supplemental Information 1:

#### Method for Asymmetrical Flow Field Flow Fractionation (A4F) coupled to Static Light Scattering (SLS)

The mobile phase flow was generated by a 1200 series high-performance liquid chromatography (HPLC) pump (Agilent Technologies, Les Ulis, France). The Asymmetrical Flow Field Flow Fractionation (A4F) system was an Eclipse 3+ (Wyatt Technology, Dernbach, Germany). Injections were performed with an Agilent Technologies 1200 series autosampler. At the outlet, the detectors were a 1200 series UV-vis absorbance detector (Agilent Technologies, Les Ulis, France) and a DAWN HELEOS multi-angle laser, static light scattering (SLS) detector (Wyatt Technology). For UV-Vis detection, the selected wavelength was 254nm.

The A4F channel height was established using a spacer (Mylar film) of 250  $\mu\text{m}$ . The dimensions of the spacer were 26.5 cm length and narrowing width from 2.1 to 0.6 cm. The accumulation wall was composed of Polyethersulfone (PES) 10 kDa membranes (Wyatt Technology). The A4F method was based on the general (fast) method O described by Gigault et al. (2017). The elution flow rate was fixed at 0.5  $\text{mL min}^{-1}$ . The injection flow rate was fixed at 0.2  $\text{mL min}^{-1}$ . The focus-flow during the relaxation was 0.5  $\text{mL}\cdot\text{min}^{-1}$  and the cross-flow rate during elution ( $V_c$ ), was a function of time (t)  $V_c = 2e^{-0.27t}$ .

The mobile phase was composed of 0.5  $\text{mmol L}^{-1}$   $\text{NaNO}_3$  (>99% purity Reagent Plus, Sigma Aldrich), which was filtered on polyethersulfone (PES) filters (0.1  $\mu\text{m}$ , Pall®), purchased from VWR (Fontenay-sous-Bois, France). The injection volume was 100  $\mu\text{L}$ . First, the effects of the duration of the focus period and the ionic strength of the injected dispersion, on the quality of detection were studied. Subsequently, a focus time of 5 minutes and an ionic strength of 600  $\text{mmol L}^{-1}$  was selected. The injected dispersion was prepared in the same way as for the aggregation kinetic study, described below.

Data from a minimum of 14 out of 18 SLS detectors were collected and processed using Astra software, version 6 (Wyatt Technology). The radius of gyration ( $R_g$ ) was determined using the Berry formalism using SLS signal at different angles.

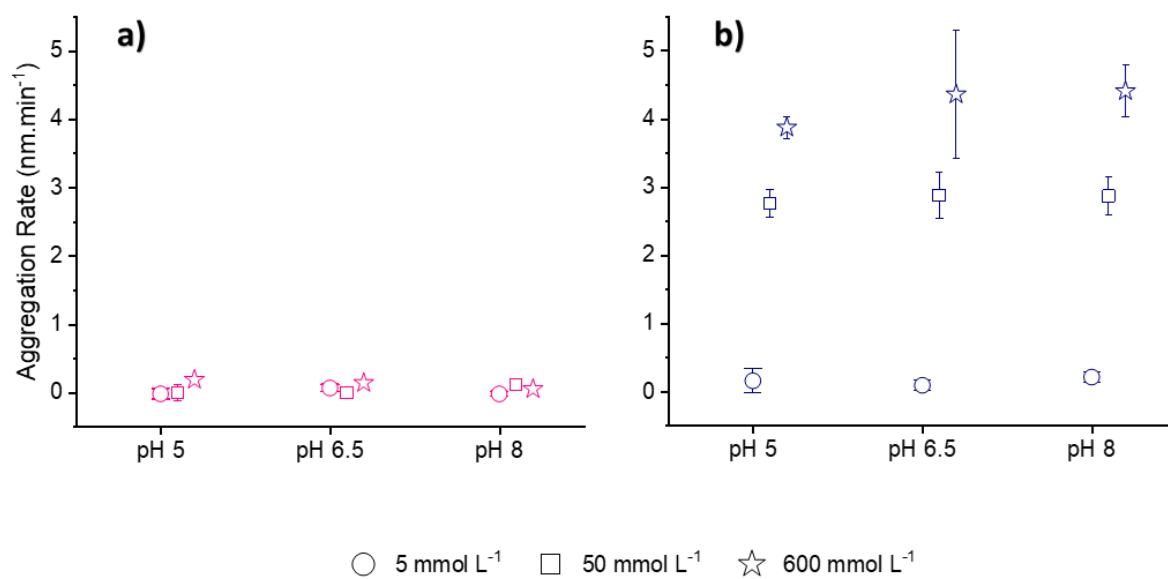


Figure S3: Aggregation rate of a) PSL COOH and b) NPT-P models, as a function of NaCl concentration and pH (Error bars = standard deviation)

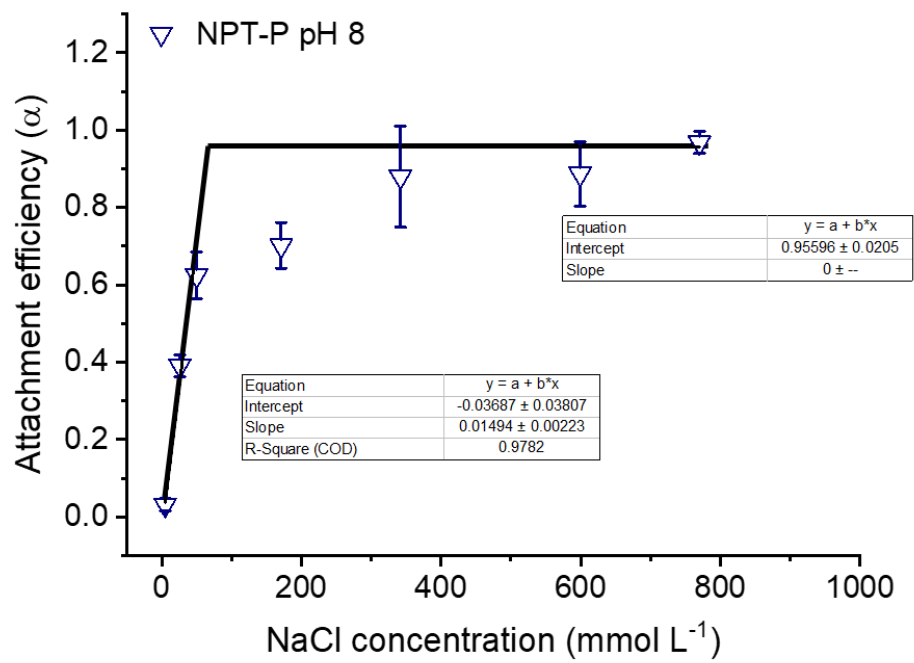
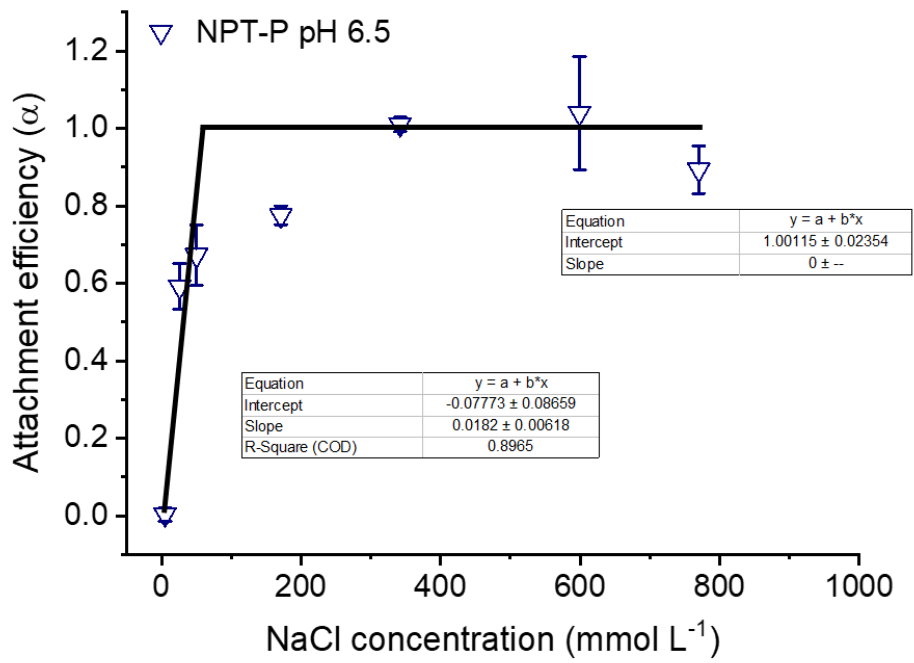


Figure S4: Determination of the Critical Coagulation Concentration (CCC) of NPT-P particles in NaCl at pH 6.5 and pH 8

Table S1: Energy barrier between particles according to DLVO and XDLVO theories, scaled to  $k_B T$

Particle 1	PSL COOH	NPT-P		
Particle 2	PSL COOH	NPT-P	small (50 nm) NPT-P asperity*	large (100 nm) NPT-P asperity*
DLVO theory	70	76	21	38
XDLVO theory	28	24	7	12

\* Assuming the NPT-P particles are ellipsoids, the smallest radius of curvature, defined as the square of the short axis divided by the long axis, is on average 64nm.

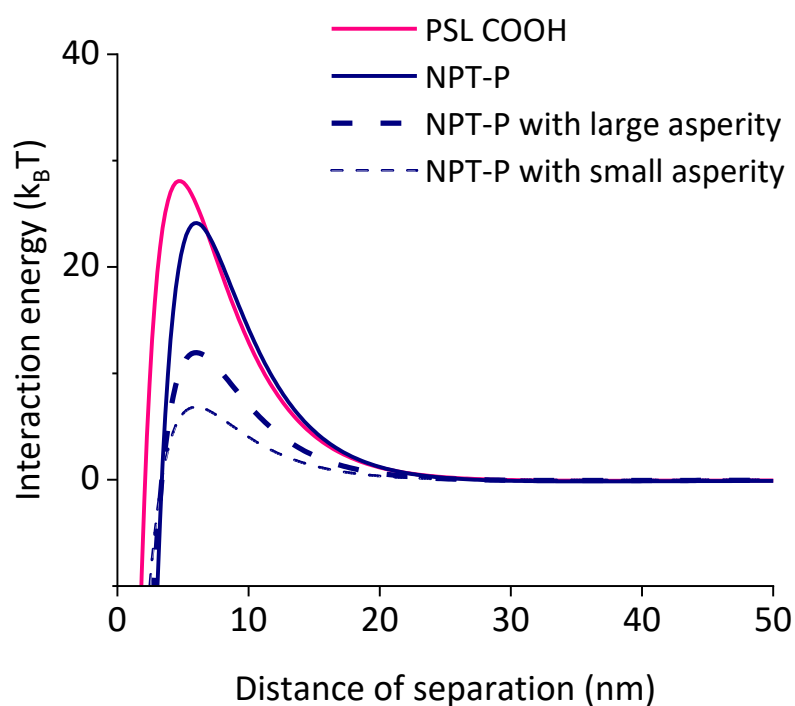


Figure S5: Interaction energy, scaled to  $k_B T$ , between different nanoplastic models, according to XDLVO theory

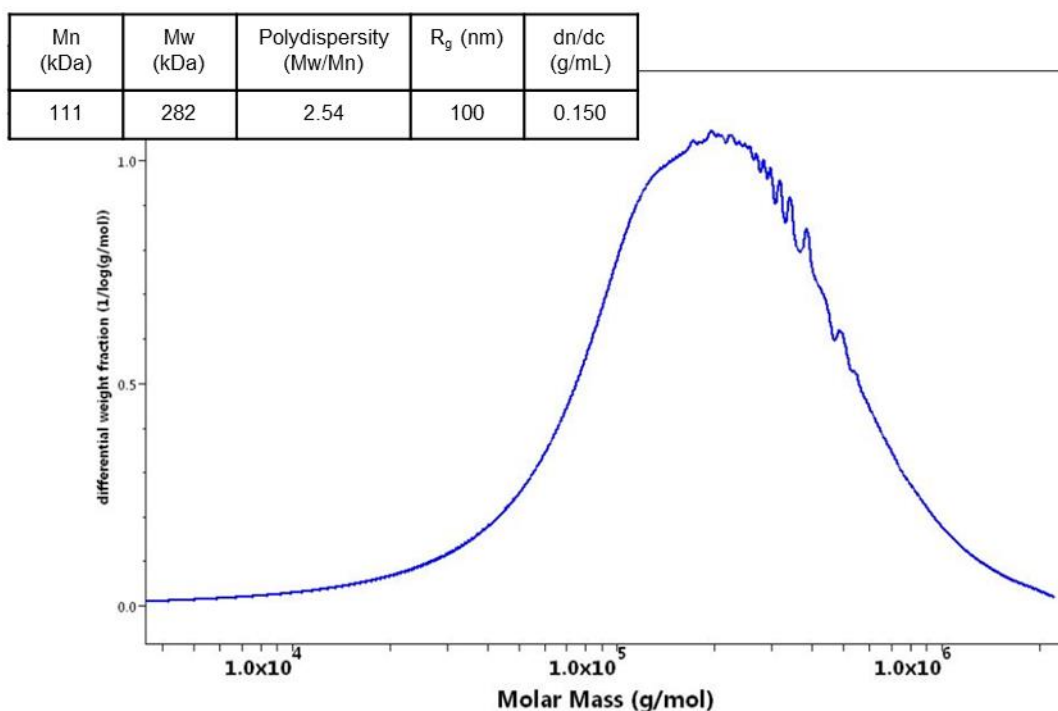


Figure S6: Molar mass distribution of sodium alginate, as determined by SEC coupled to SLS and RI

The source and extraction method of sodium alginate are not standardized, which results in wide variations in molar mass (Masuelli and Illanes, 2014). So, the weight-averaged molar mass of this macromolecule was measured by SEC coupled to SLS and refractive index (RI) measurement. On-line purified mobile phase ( $0.1 \text{ mmol L}^{-1} \text{ NaNO}_3$ ) was delivered with an 1200 series HPLC pump (Agilent Technologies) at a flow rate of  $5 \text{ mL min}^{-1}$  to a chromatographic pre-column SB-807G, followed by four columns, SB-805HQ, SB-807HQ, SB-802HQ and SB-803HQ (Shodex, Munich, Germany). The temperature was kept at  $30^\circ\text{C}$ . Sodium alginate was injected at a concentration of  $500 \text{ mg L}^{-1}$  in  $600 \text{ mmol L}^{-1} \text{ NaCl}$ . At the outlet, sodium alginate was characterized by the DAWN HELEOS SLS detector (Wyatt Technology) and RI was measured by an Optilab T-rEX (Wyatt Technology).



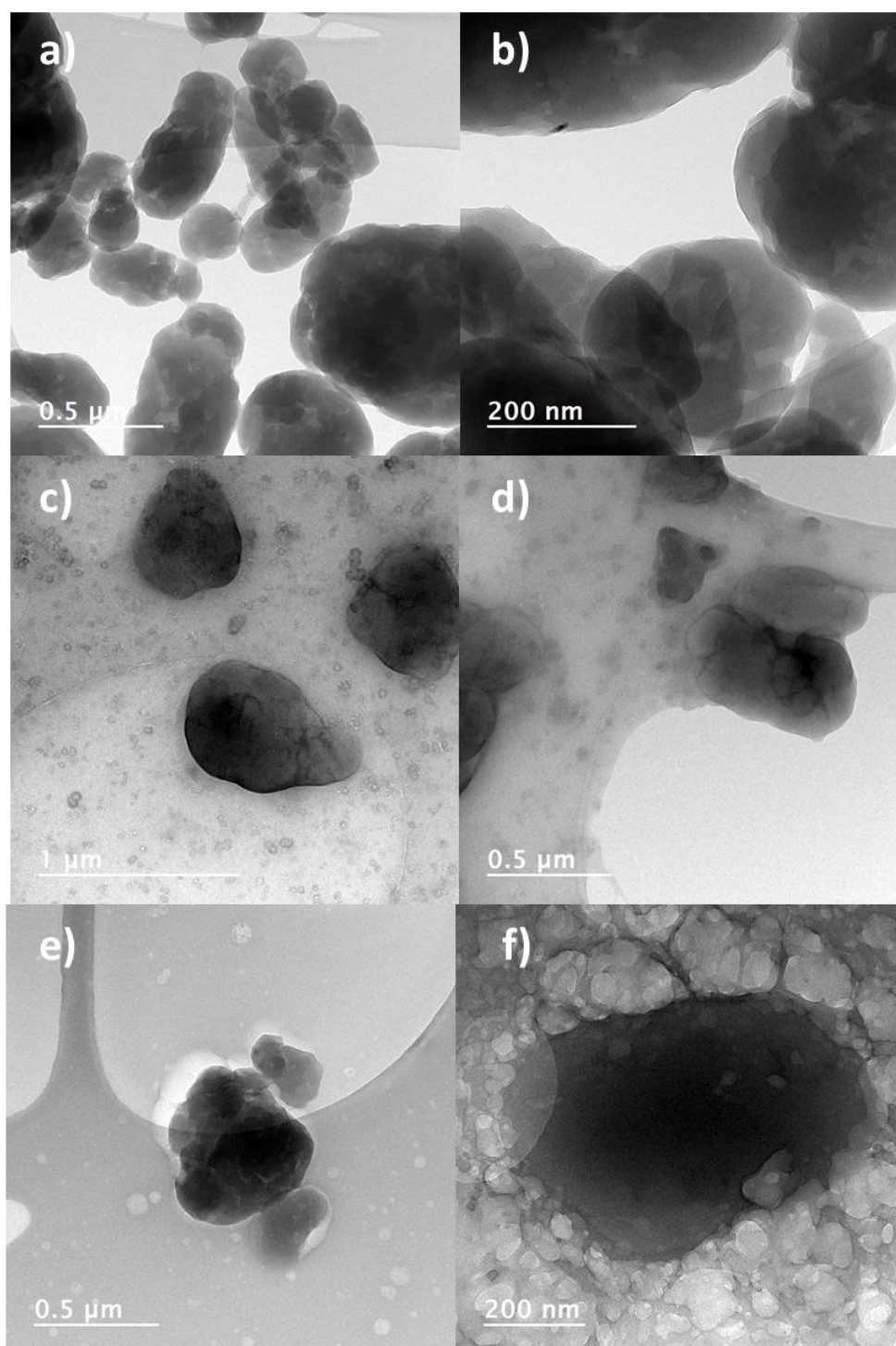


Figure S7: Transmission Electron Microscopy Images of a) b) NPT-P without organic matter c) d) NPT-P with humic acid (HA) and e) f) NPT-P with sodium alginate (SA)

Images a, c and e, show NPT-P at a lower magnification, to illustrate the matrix of NOM (c and e) or lack thereof. Images b, d, and f were taken at a higher magnification to observe the interface between NOM and NPT-P. The particles appear to be embedded in SA (e and f). In image e, the lighter halo around the particle is probably caused by the displacement of the. Figures c and d show that while NPT-P is also embedded in HA (c), at closer magnification, they seem less closely associated (d).

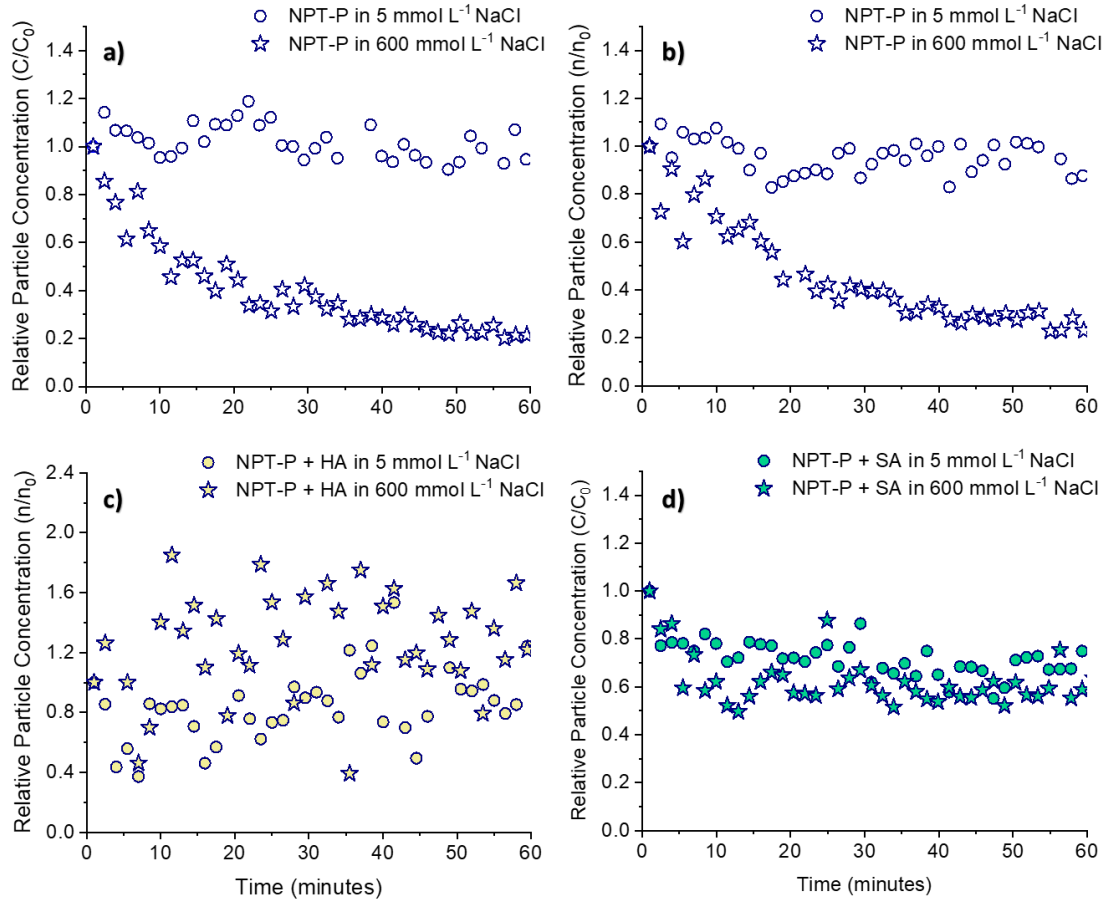


Figure S8: Relative particle concentration of NPT-P at 5 and 600 mmol L<sup>-1</sup> NaCl at a) pH 6.5, b) pH 8, c) with 30 mg L<sup>-1</sup> humic acid (HA) at pH 6.5 and d) with 50 mg L<sup>-1</sup> sodium alginate (SA) at pH 8

The relative particle concentration ( $n/n_0$ ) was determined according to the relation that links the intensity of scattered light and the particle size. This relationship is only valid assuming that all particles are spherical (Wyatt, 1993). The intensity of scattered light, at a give scattering angle and particle concentration  $I_{(\theta,c)}$ , is given by the following equation:

$$I_{(\theta,c)} = KcM_W P_{(\theta)} \quad (S7)$$

with  $\theta$ , the angle at which light is scattered, which is equal to 170 degrees and  $c$  the concentration in g L<sup>-1</sup>,  $K$  the instrument constant,  $M_W$  the molar mass in g mol<sup>-1</sup> and  $P_{\theta}$  the form factor. For a sphere, the form factor  $P_{\theta}$  is given by:

$$P_{(\theta)} = \left[ \frac{3}{u^3} (\sin(u) - u \cos(u)) \right]^2 \quad (S8)$$

For a sphere,  $u$  is defined as:

$$u = q * r_p \quad (S9)$$

with  $r_p$  the sphere's radius and  $q$  the wave vector, defined as:

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (\text{S10})$$

with  $\lambda$  the wavelength of scattered light, which is 658 nm. So we have:

$$u = \frac{2\pi D_{zH} \sin\left(\frac{\theta}{2}\right)}{\lambda} \quad (\text{S11})$$

For a sphere the  $M_w$  is proportional to the sphere volume:

$$M_w \propto \left(\frac{D_{zH}}{2}\right)^3 \quad (\text{S12})$$

So, equation S7 can be written as:

$$I_{(\theta,c)} \propto Kc \left(\frac{D_{zH}}{2}\right)^3 \left[\frac{3}{u^3} (\sin(u) - u\cos(u))\right]^2 \quad (\text{S13})$$

Since,  $c$  is proportional to the particle concentration  $n$  and  $K$  and  $\Theta$  are held constant, so:

$$n \propto \frac{I_{(\theta,c)}}{\left(\frac{D_{zH}}{2}\right)^3 \left[\frac{3}{u^3} (\sin(u) - u\cos(u))\right]^2} \quad (\text{S14})$$

Equation S14 can be simplified to:

$$n \propto \frac{I_{(\theta,c)}}{\left(\frac{9}{q^6 r_p^3}\right) (\sin(u) - u\cos(u))^2} \quad (\text{S15})$$

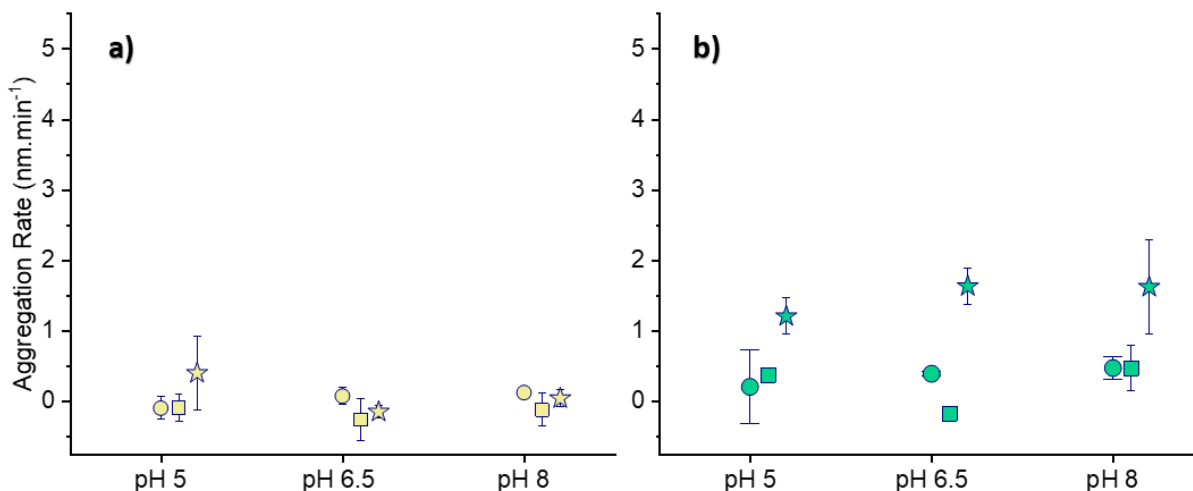


Figure S9: Aggregation rate of NPT-P with a) 30 mg L<sup>-1</sup> humic acid b) 57 mg L<sup>-1</sup> sodium alginate, as a function of ionic strength and pH (Error bars = standard deviation)

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